

SOLID STATE PHOTOELECTROCHEMICAL CELL BASED ON DYE SENSITIZED TiO₂ AND POLYMER ELECTROLYTE COMPLEXED WITH I₃⁻/I⁻

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ABSTRACT: A solid state photoelectrochemical solar energy conversion device based on nanocrystalline-TiO₂ sensitized with Di-Tetrabutylammoniumcis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II) (N719) dye has been constructed and characterized. The current density-voltage characteristics in the dark and under white light illumination and action spectra under monochromatic illuminations have been studied. The following device parameters were obtained when the potential is scanned: an open circuit voltage of 762 mV and a short circuit current density of 33 μAcm^{-2} at light intensity of 100 mWcm^{-2} ; the IPCE percentage obtained was 1.7% at 330 nm. The dependence of the short-circuit current density and an open circuit voltage on the incident light intensity and illumination time have also been studied. The results of time dependence study show that the steady state J_{sc} and V_{oc} values are consistent with those obtained from the J-V curve.

Key words/phrases: I₃⁻/I⁻ redox couple, nanocrystalline-TiO₂, polymer electrolyte, solid state photoelectrochemical cell

INTRODUCTION

Extensive use of non-renewable fossil fuels for conventional energy production is depleting global reserves rapidly. Moreover, greenhouse gas emissions and increasing production costs of non-renewable fossil fuels have underscored the need to develop alternate energy sources. One area that is continuing to attract a lot of interest is the possibility of energy generation from the sun. The focus of solar energy utilization has mainly been toward electricity. The conversion of solar energy into electricity is a clean, abundant and renewable energy source. Conventional solar cells made from inorganic materials use very expensive materials of high purity and energy intensive processing techniques. New ways of manufacturing solar cells that can extend to large volumes and low cost are required. A very wide range of solar cell technologies are currently being developed, including dye-sensitized nanocrystalline photoelectrochemical solar cells, polymer/fullerene bulk heterojunctions, small molecule thin films and organic-inorganic hybrid devices.

In contrast with the conventional single crystal silicon-based or compound-semiconductor thin-film solar cells, dye sensitized solar cells (DSSCs)

are thought to be advantageous as a solar energy conversion device possessing both practicable high efficiency and cost effectiveness. So far, the most successful DSSC was obtained on nanocrystalline-TiO₂ film combined with a ruthenium-polypyridine complex dye, as first reported by O'Regan and Grätzel (1991). Overall conversion efficiency of 10.4% was achieved on a TiO₂-RuL'(NCS)₃ (black dye) system, in which the spectral response of the complex dye was extended into the near-infrared region so as to absorb far more of the incident light (Nazeeruddin *et al.*, 2001; Grätzel, 2003; 2007). The porous nature of nanocrystalline-TiO₂ films drives their use in DSSCs due to the large surface area available for dye-molecule adsorption. Moreover, the suitable relative energy levels at the semiconductor-sensitizer interface (*i.e.*, the position of the conduction-band edge of TiO₂ being lower than the excited-state energy level of the dye) allow for the effective injection of electrons from the dye molecules to the semiconductor (Nelson and Chandler, 2004).

From the time of the first report on DSSCs (O'Regan and Grätzel, 1991), the basis for energy conversion of which is the injection of electrons from a photoexcited state of the dye sensitizer into the conduction band of the TiO₂ semi-

conductor upon absorption of light, DSSCs have received considerable attention over the past decade because of their attractive features such as high energy conversion efficiency and relatively low production costs. Even though the light-to-electrical energy conversion efficiencies of DSSCs based on liquid electrolytes have reached over 10% under AM 1.5 (100 mWcm^{-2}) (Nazeeruddin *et al.*, 1993), there are some problems such as leakage of the electrolytes, evaporation of the solvent and high temperature instability, which cause difficulties in sealing and performance degradation of DSSCs (Smestad, 2003).

Enormous efforts have been devoted to solve these problems by employing solid or quasi solid state electrolytes that substituted the conventional volatile organic solvent-based electrolytes to fabricate DSSCs (Cao *et al.*, 1995; Bach *et al.*, 1998; Nogueira *et al.*, 2001; O'Regan *et al.*, 2002). The polymer electrolyte is an important class of the solid or quasi solid state electrolytes for DSSCs because it has the advantages of relatively high ionic conductivity and easy solidification (Li *et al.*, 2006).

Previously Assefa Sergawie *et al.* (2007) reported a work on regenerative type PEC based on emeraldine base form of polyaniline as a sensitizer. In this work we report the studies made on an all-solid-state PEC constructed with nanocrystalline-TiO₂ coated onto indium tin-oxide (ITO), covered N719 dye and used as a photoactive electrode, the ion conducting polymer poly[oxymethylene-oligo(oxyethylene)], POMOE, complexed with redox couple as a solid polymer electrolyte, and a PEDOT coated on ITO as counter electrode. The polymer electrolyte POMOE, having a repeating unit of $\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_9$, was used since it is a good ionic conductor at room temperature (Craven *et al.*, 1986; Nicholas *et al.*, 1988; Linden and Owen, 1988; Nekoomanesh *et al.*, 1992). When iodide/triiodide was used as a redox couple in the all-solid-state PEC, oxidised poly-3,4-ethylenedioxythiophene, PEDOT, coated onto ITO was used as a counter electrode. Oxidised PEDOT improves the charge transfer between ITO and the iodide/triiodide redox couple (Teketel Yohannes and Inganäs, 1998). The basic structure of the device is shown in Figure 1.

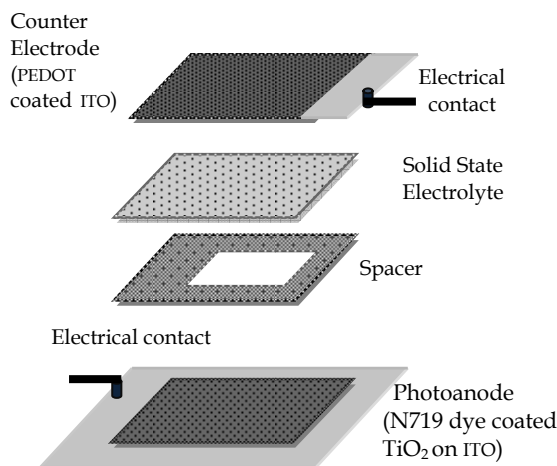


Fig. 1. The device structure of the solid state PEC.

MATERIALS AND METHODS

ITO-coated glass having transmittance above 80% in the visible region of the solar spectrum was employed as a substrate for the photoactive materials and counter electrodes. It was cleaned in ultrasonic bath successively with acetone (Aldrich), 2-propanol (Riedel-de Haen), and ethanol (BDH) and dried with an air gun.

Preparation of mesoporous TiO₂ film was done with the method described elsewhere (Nazeeruddin *et al.*, 1993). Nanocrystalline-TiO₂ films were prepared by spreading a viscous dispersion of colloidal TiO₂ particles on ITO with heating under air for 30 min at 450°C. The method for preparation of nanocrystalline films employed commercial TiO₂ (P25, Degussa). 3 g of TiO₂ powder was ground in a porcelain mortar with 1 mL water containing 0.1 mL acetylacetone to prevent reaggregation of the particles. After the powder had been dispersed by the high shear forces in the viscous paste, it was diluted by slow addition of 4 mL water under continued grinding. Finally, a detergent 0.05 mL Triton X-100 (Aldrich), was added to facilitate the spreading of the colloid on the substrate. The ITO was covered on two parallel edges with adhesive tape to control the thickness of the TiO₂ film and to provide noncoated areas for electrical contact. The colloid was applied to one of the free edges of the conducting glass and distributed with a glass rod sliding over the tape-covered edges. After air drying, the electrode was fired for 30 min at 450°C in a furnace (Carbolite Model ELF 11/14B).

Coating of the TiO₂ surface with dye was carried out by soaking the film for 2 h in a 0.3 mM solution of N719 dye (Aldrich) in dry ethanol. The dye coating was done immediately after the high temperature annealing while still hot in order to avoid rehydration of the TiO₂ surface or capillary condensation of water vapor from ambient air inside the nanopores of the film (Nazeeruddin *et al.*, 1993). The presence of water in the pores decreases the injection efficiency of the dye. After completion of the dye adsorption (Nazeeruddin *et al.*, 1993), the electrode was withdrawn from the solution under a stream of dry air. It was stored in dry ethanol or immediately wetted with redox electrolyte solution for testing.

The polymer film for the counter electrode was formed by electrochemical polymerization of 3,4-ethylenedioxythiophene (EDOT) (Aldrich), in a three electrode one-compartment electrochemical cell. The electrochemical cell consisted of a pre-cleaned ITO-coated glass working electrode, platinum foil counter electrode and quasi-Ag/AgCl reference electrode. The solution used for the polymerization contained 0.2 M EDOT and 0.1 M (C₂H₅)₄NBF₄ (Aldrich) in acetonitrile (Aldrich). The monomer was used as received. The polymerization was carried out potentiostatically at +1.8 V for 2 seconds. At this potential, the electrode surface becomes covered with blue-doped PEDOT film. The PEDOT covered ITO glass was then rinsed with acetonitrile and dried in air. The polymer electrolyte was prepared by dissolving 311 mg of POMOE in 25 ml of methanol. The redox couple I₃⁻/I⁻ was prepared by dissolving 48.47 mg KI 25 ml of methanol and 7.41 mg I₂ in 25 ml of methanol. Finally, 1ml of each of the above three solutions were mixed to produce the polymer electrolyte complexed with a redox couple. The mole ratio of oxygen to potassium as calculated by taking into account both the oxymethylene and oxyethylene oxygen atoms was 25 and the mole ratio of KI to I₂ was 10. The conductivity of POMOE is known to be high at room temperature when the oxygen to cation (potassium) mole ratio is 25 (Nagae *et al.*, 1992) and E_{redox}(I₃⁻/I⁻) = -4.9 eV at mole ratio of KI to I₂ of 10 making dye regeneration effective (Hagfeldt and Grätzel, 2000; Teketel Yohannes *et al.*, 1996).

Finally, the polymer electrolyte complexed with I₃⁻/I⁻ was deposited in the form of thin film by solvent casting on top of the dye coated TiO₂

electrode and allowed to dry in a laboratory atmosphere. The PEC was completed by pressing against PEDOT-coated ITO glass counter electrode. The PEC was then mounted in a sample holder inside a metal box with 1 cm² opening to allow light from the source. All experiments were carried out at room temperature.

The photoelectrochemical measurements of the cell were performed using a computer controlled CHI630A Electrochemical Analyzer. A 250-W tungsten-halogen lamp regulated by an Oriol power supply (Model 68830) was used to illuminate the PEC. A grating monochromator (Model 77250) placed into the light path was used to select a wavelength between 300 and 800 nm. The measured photocurrent spectra were corrected for the spectral response of the lamp and the monochromator by normalization to the response of a calibrated silicon photodiode (Hamamatsu, Model S1336-8BK) whose sensitivity spectrum was known. No correction was made for the reflection from the surface of the sample. The white light intensity was measured in the position of the sample cell with Gigahertz-Optik X₁ Optometer. A series of neutral density filters were used to vary the light intensity incident on the sample.

RESULTS AND DISCUSSION

Current density-voltage characteristics

When an external field is applied to a solar energy conversion device, it acts to diminish the effects of the internal barrier field. Carriers can acquire sufficient energy to cross the barrier, and at high enough external voltages a large current will flow. On the other hand, if the bias is reversed, the external field enhances the barrier potential and only small current flows. Thus, the junction acts as a rectifier since the current flowing for a given positive external voltage is quite different from the current flowing at the same negative voltage. Such a current density-voltage characteristic is described mathematically as (Sze, 2003):

$$I = I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \dots\dots\dots(1)$$

where I₀ is the saturation current, q the electron charge, k the Boltzmann constant, T the absolute temperature, v the applied voltage, and n the ideality factor.

The current density–voltage characteristics of the ITO | PEDOT | POMOE: I₃/I | TiO₂: dye | ITO PEC in the dark and under illumination are shown in Figure 2(a) and (b), respectively. The device was illuminated through the ITO|TiO₂: Dye side using white light the intensity of which is 100 mW/cm². The current density–voltage characteristic of the polymer electrolyte|TiO₂: dye interface in the dark obeys the diode equation as depicted in Figure 2(a). The forward current corresponds to a positive bias where the barrier height is lowered, whereas in reverse polarization the increased barrier prevents the passage of a current.

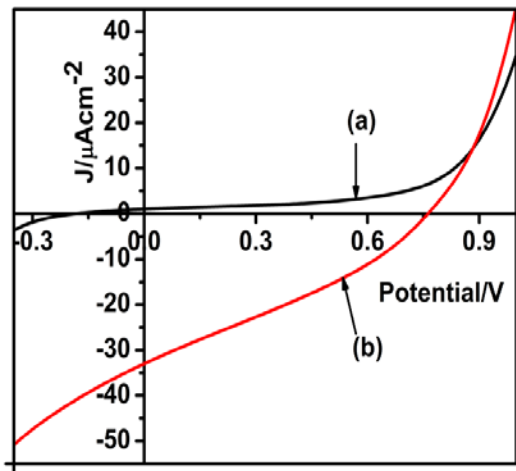


Fig. 2. Current density–voltage characteristics of ITO | PEDOT | POMOE: I₃/I | TiO₂:N719 | ITO cell (a) in the dark and (b) under illumination through front side with light intensity of 100 mWcm⁻².

Under illumination, absorption of photons initially creates excitons, and later both the majority and the minority carriers. The concentration of photogenerated majority carriers is usually small. This implies that illumination does not significantly perturb the majority carrier. Because the majority carrier concentrations are essentially unchanged, the majority charge flow is also unchanged. Majority carriers should thus exhibit the J–V characteristic that is well described by the diode equation, regardless of whether it is in the dark or under illumination. The current under illumination can generally be described by adding the current from photogenerated carriers to the dark current. From Equation 1 the J–V characteristic under illumination is given by:

$$I = I_{ph} - I_0 \left[\exp\left(\frac{qV}{nkT}\right) - 1 \right] \dots\dots\dots (2)$$

The TiO₂ used in this work is lightly n-doped wide bandgap semiconductor. These large bandgap semiconductor oxide films are insulating in the dark; however, a single electron injected in a 20 nm sized particle produces an electron concentration of $2.4 \times 10^{17} \text{ cm}^{-3}$. This corresponds to a specific conductivity of $1.6 \times 10^{-4} \text{ Scm}^{-1}$ if a value of $10^{-4} \text{ cm}^2 \text{ s}^{-1}$ is used for the electron diffusion coefficient (Grätzel, 2005).

As it is depicted in Figure 2, the short circuit current density (J_{sc}) and the open circuit voltage (V_{oc}) were measured to be $33 \mu\text{Acm}^{-2}$ and 762 mV, respectively. The fill factor which is the measure of the squareness of the output characteristics, was calculated using Equation 3 and was 0.32 which is very low value.

$$FF = \frac{V_{mp} J_{mp}}{V_{oc} J_{sc}} \dots\dots\dots (3)$$

where V_{mp} and J_{mp} are the voltage and current density at the maximum power point, respectively whereas V_{oc} and J_{sc} are open circuit voltage and short circuit current density, respectively and FF is the fill factor.

The dependence of J_{sc} and V_{oc} on illumination time

Time dependence of short circuit current density (J_{sc}) and open circuit voltage (V_{oc}) was studied for the hybrid PEC through illumination with a white light intensity of 100 mWcm⁻². The short circuit current density and open circuit voltage were induced by periodically blocking the light path to the sample and are depicted in Figures 3 and 4, respectively. When the light is switched on, the photocurrent density rises to a steady-state value of about $35 \mu\text{Acm}^{-2}$ and decays at approximately the same rate to zero current when the light is switched off.

As can be seen from changes in photocurrent with time of illumination, the photoactive material seems stable towards light. Open circuit voltage obtained from the transient measurements was 771 mV. The results of time dependence study show that the steady state J_{sc}

and V_{oc} values are consistent with those obtained from the J-V curve.

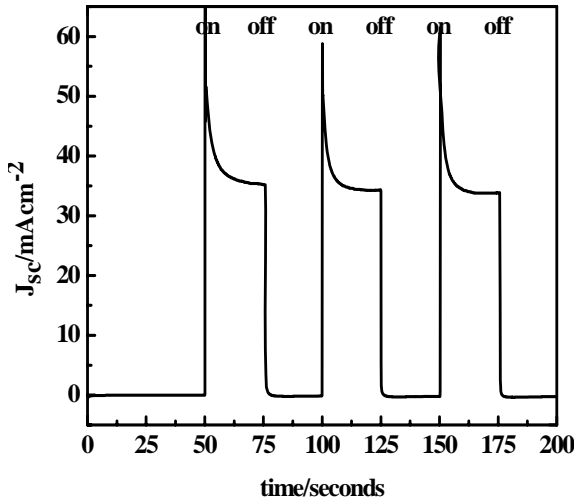


Fig. 3. Photocurrent density response to transient illumination with light intensity of 100 mWcm⁻² for the ITO|PEDOT|POMOE: I₃/I|TiO₂:N719|ITO solid state PEC from the front side.

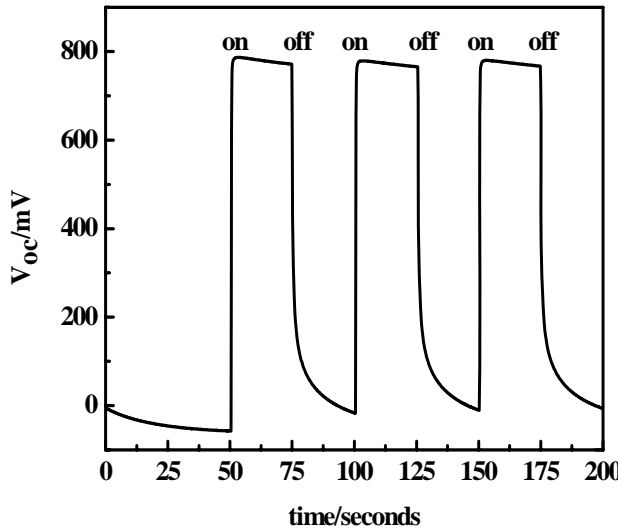


Fig. 4. Photovoltage response to switching illumination on and off from the front side of ITO|PEDOT|POMOE: I₃/I|TiO₂:N719|ITO solid state PEC with light intensity of 100 mWcm⁻².

Photocurrent action spectra

The incident monochromatic photon-to-current conversion efficiency (IPCE), defined as the number of electrons generated by light in the external circuit divided by the number of

incident photons, is plotted as a function of excitation wavelength in Figure 5. This was obtained from the photocurrents by means of the following equation:

$$IPCE\% = \frac{1240 \times J_{sc} [\mu A.cm^{-2}]}{\lambda[nm] \times I_{in} [W.m^{-2}]} \dots\dots\dots (4)$$

The maximum IPCE percentage obtained for the hybrid PEC was 1.7% at 330 nm.

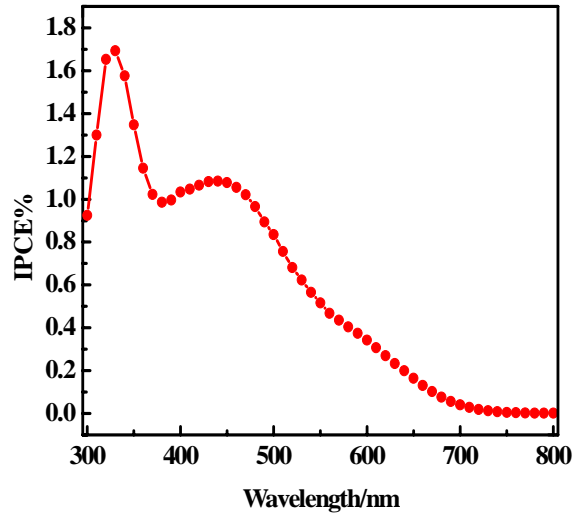


Fig. 5. Photocurrent action spectra for ITO|PEDOT|-POMOE:I₃/I|TiO₂:N719|ITO solid state PEC.

The dependence of J_{sc} and V_{oc} on light intensity

The maximum open circuit photovoltage attainable in the dye-sensitized solar cell is the difference between the Fermi level of the solid under illumination and the Nernst potential of the redox couple in the electrolyte. However, for these devices this limitation has not been realized and V_{oc} is in general much smaller. It appears that V_{oc} is kinetically limited and for an n-type semiconductor in a regenerative cell the diode equation (Equation 5) can be applied (Kumar *et al.*, 1992),

$$V_{oc} = \left(\frac{kT}{q} \right) \ln \left(\frac{I_{inj}}{n_{cb} k_{ct} [I_3^-]} \right) \dots\dots\dots (5)$$

where I_{inj} is the flux of charge resulting from sensitized injection and n_{cb} is the concentration of electrons at the TiO₂ surface.

For organic and some inorganic solar cells, the J_{sc} increases with increasing incident light intensity (I_{in}) and is proportional to I_{in}^α (Meier, 1974). Thus, a plot of $\log J_{sc}$ versus $\log I_{in}$ yields a straight line whose slope is characteristic of the photoactive material. The plot of $\log J_{sc}$ versus $\log I_{in}$ of the ITO | PEDOT | POMOE: I_3^-/Γ^- | TiO₂: Dye | ITO PEC is shown in Figure 6. The illumination intensity was varied from 0.01 mWcm⁻² to 100 mWcm⁻². The J_{sc} increases with illumination intensity and is proportional to I_{in}^α , where α is the power factor (Meier, 1974). The plot of $\log J_{sc}$ versus $\log I_{in}$ yielded a straight line with $\alpha = 0.98$ which is very close to 1 indicating that recombination traps are absent (Meier, 1974). For Schottky junction solar cells under open circuit conditions, no net current will flow through the junction. The gain in open circuit voltage can be calculated from the equation (Grätzel, 2009):

$$V_{oc} = \left(\frac{nRT}{F} \right) \ln \left[\frac{I_{sc}}{I_0} - 1 \right] \dots\dots\dots (6)$$

where n is the ideality factor whose value is between 1 and 2 for the DSSC and I_0 is the reverse saturation current.

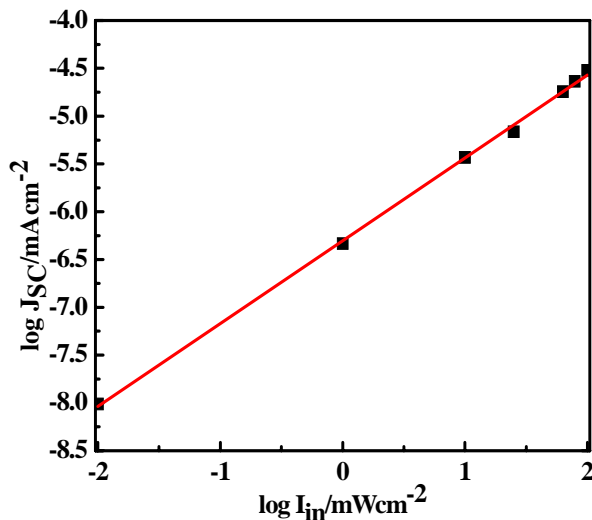


Fig. 6. Plot of $\log J_{sc}$ versus $\log I_{in}$ of ITO | PEDOT | POMOE: I_3^-/Γ^- | TiO₂:N719 | ITO solid state PEC.

As can be seen from Equation 6, V_{oc} increases logarithmically with the light intensity because J_{sc} is linearly proportional to the incident light

intensity. The plot of V_{oc} versus $\log I_{in}$ of the ITO | PEDOT | POMOE: I_3^-/Γ^- | TiO₂:Dye | ITO PEC is shown in Figure 7. V_{oc} increases logarithmically with the light intensity, in agreement with the projected behavior for semiconductor based solar cell devices (Sze, 2003).

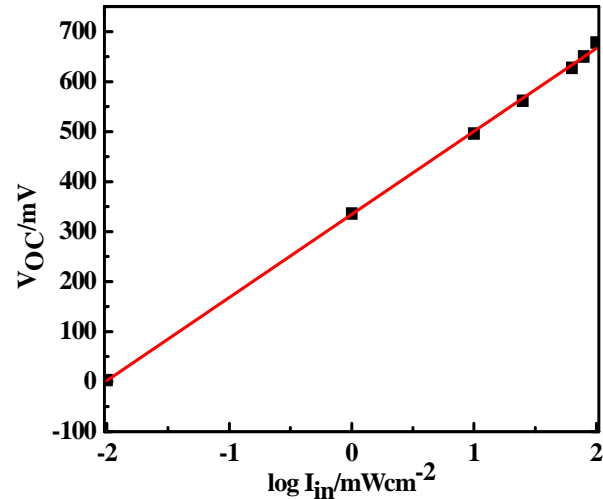


Fig. 7. Plot of V_{oc} versus $\log I_{in}$ of ITO | PEDOT | POMOE: I_3^-/Γ^- | TiO₂:N719 | ITO solid state PEC.

CONCLUSIONS

In this study, all solid state dye sensitized PEC was constructed using nc-TiO₂ and N719 dye as a sensitizer and was used as a photoactive electrode. The ion-conducting polymer POMOE complexed with redox couple was used as a solid polymer electrolyte and a PEDOT coated ITO was used as a counter electrode. Photoelectrochemical properties of this device was studied using current density-voltage characteristics together with the dependence of J_{sc} and V_{oc} on illumination intensity. The dependence of J_{sc} on intensity indicated that there are no traps. An open circuit voltage of 762 mV and a short circuit current density of 33 $\mu\text{A}/\text{cm}^2$ at light intensity of 100 mW/cm² maximum IPCE percentage of 1.7% for front side illumination at a wavelength of 330 nm were obtained. The results of time dependence study on the steady state J_{sc} and V_{oc} show that the steady state J_{sc} and V_{oc} values are consistent with those obtained from the current density-voltage curve. Though the performances of the PECs under the present experimental conditions are low, the results indicate that we can make use of the polymer based solid state

electrolyte system for dye sensitized solar cell application.

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