

Non-steady state operation of polymer/TiO₂ photovoltaic devices

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ABSTRACT

We present data on the initial period of operation of Gilch-route MEH-PPV/TiO₂ composite solar cells (CSCs) which show that during this period the CSCs operate in a non-steady state regime. The behavior is complex and may include a gradual rise of the open circuit voltage (V_{oc}) and of the short-circuit current density (J_{sc}) with time, a passage through a maximum of either or both parameters, and even a sign reversal. The mechanisms most probably contributing to the transient processes are: i) diffusion driven redistribution of charges resulting in the build up of a quasi steady state charge density profile across the device; ii) photo-doping resulting in a relatively slow increase of the average charge carrier concentration and consequently of the conductivity of the device. The latter is responsible for a strong decrease in V_{oc} , and is evidenced by the significant increase in dark current after device illumination.

Keywords: MEH-PPV/titanium dioxide solar cells, time dependent performance, photo-doping

1. INTRODUCTION

Conjugated polymer/TiO₂ photovoltaic (PV) cells are currently being investigated by academic research groups and industrial companies as a solid-state alternative to dye sensitized solar cells. The highest reported power conversion efficiency η for this type of device is 0.5%¹. Typically, reports on the performance of CSCs quote single values for the device parameters: V_{oc} , J_{sc} , fill factor (FF) and η ¹⁻⁴. Theoretical models applied to describe the operation of polymer/TiO₂ and of organic PV cells in general consider their steady state characteristics and therefore also utilize a single set of performance parameters^{3,5}. In our experience however, polymer/TiO₂ devices operate in a non-steady state regime at the start of illumination. All PV parameters vary with time and the variation is strongest during the first 10-20 minutes of operation. Surprisingly, this transient behavior seems not to have been described in the scientific literature. In this paper we present examples of the non-steady state operation of Gilch-route poly[2-(2-ethylhexyloxy)-5-methoxy-1,4-phenylenevinylene] (MEH-PPV) based solar cells and discuss the origin of the observed time dependence.

2. EXPERIMENTAL

Photovoltaic devices were formed on pre-patterned ITO/glass in a single layer (ITO/MEH-PPV/Au) and bi-layer (ITO/TiO₂/MEH-PPV/Au) configuration. The ITO glass substrates were cleaned using a Decon 90 solution, followed by sequential ultrasonication in deionised water, and hot acetone and 2-propanol baths. The TiO₂ layers were prepared by doctor blading a paste (Solaronix, SA Switzerland). The doctor bladed layers were allowed to dry at 100°C for a few minutes before annealing in a furnace for 10 hours at 450°C. TiO₂ films were also prepared by a sol-gel method. The details of this process have been described elsewhere⁶.

MEH-PPV was synthesized via the Gilch route⁷. Polymer films, of the order of 30 to 60 nm thick, were formed on top of the ITO/glass or onto the TiO₂ layers by spin coating from chlorobenzene solutions at a spin speed of 2000 rpm. The thickness of the polymer films on ITO/glass was determined using AFM (CP model, Park Scientific) in contact mode. The PV devices were completed by evaporation of a gold electrode (45 nm thick) at a rate of 20 Å/min in vacuum of the order of 10⁻⁶ mbar. The active area of each device was 0.063 cm².

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The I - V measurements of the photovoltaic devices were carried out using a Keithley 2400 source meter in the dark and under simulated AM1.5 illumination. The light illumination experiments were performed using a KH Steuernegel 1200 Solar Simulator. The illumination power at the sample position was 80 and 86 $\text{mW}\cdot\text{cm}^{-2}$ for experiments performed with a 490 and 420 nm long-pass filter, respectively and 100 $\text{mW}\cdot\text{cm}^{-2}$ in measurements performed without a filter. All I - V experiments were performed in a vacuum of $\sim 1.5 \times 10^{-2}$ mbar.

3. RESULTS AND DISCUSSION

The experimentally observed variation with time of V_{oc} and J_{sc} in the CSC follows two main patterns that can be schematically represented using the generalized curves in Figure 1.

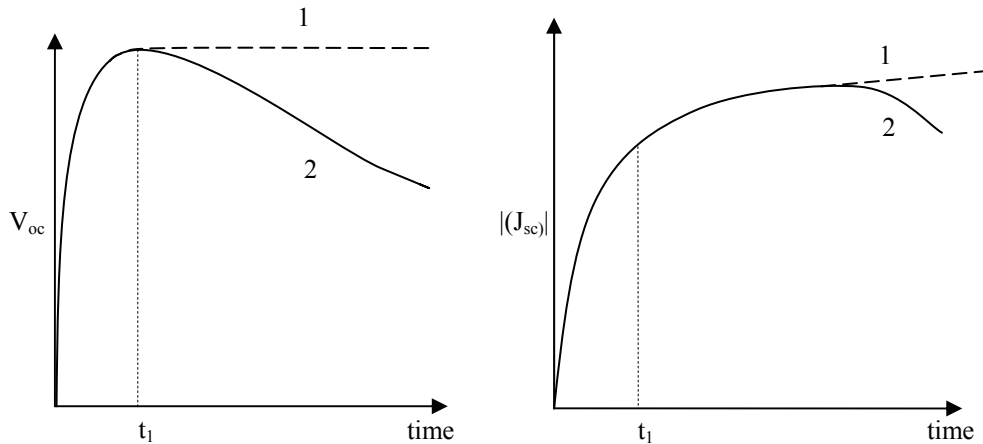


Figure 1. Generalized curves showing the time dependence of V_{oc} and J_{sc} of polymer based CSCs.

In the first pattern of time dependence, customarily denoted here as Type 1 (dashed line in Figure 1), both V_{oc} and J_{sc} increase initially rapidly with time, but the rate of increase gradually slows down and the two parameters assume values which tend towards a quasi-equilibrium level. In the second pattern of time dependence, the open circuit voltage passes through a maximum at time t_1 and subsequently decreases. The short circuit current density typically continues increasing well after t_1 , although as indicated in the figure in some instances (usually when UV light is present) it also begins to decline. We denote this kind of time dependence as Type 2 (solid line in Figure 1). The kinetics and the magnitude of change in the PV parameters are affected by the materials employed in the bi-layer cells, the architecture of the cell as well as by the spectral range and the intensity of the incident light.

We present two sets of experimental results which illustrate the characteristic patterns of time dependence. Figure 2 shows the transient behavior of a bi-layer device (ITO/TiO₂(Solaronix)/MEH-PPV/Au) upon illumination with light of two different spectral compositions. In the experiment where light wavelengths shorter than 490 nm have been filtered out, V_{oc} rapidly reaches a value of 0.73 V and maintains a level of 0.74-0.75 V within the duration of the measurement. In contrast when the spectral range has been extended (420 nm long-pass filter in place) V_{oc} passes through a maximum of not less than 0.82 V after approximately two minutes of illumination and subsequently decreases to 0.62 V after 43 minutes of illumination. In both cases the short circuit current of the PV cell increases continuously within the duration of the experiment, the increase being greatest during the initial 10-20 minutes of light exposure. The higher J_{sc} level obtained in the 420 nm filter measurement can be explained by better matching of the incident light spectrum with the absorption spectrum of MEH-PPV (absorption maximum \sim 490 nm) and by the increase by 6 $\text{mW}\cdot\text{cm}^{-2}$ of the incident light intensity.

The PV performance of the CSC in the initial stages of operation can be even more complex than indicated in the schematic of Figure 1. In Figure 3, the PV parameters of a bi-layer device containing a TiO₂ layer prepared from a sol-gel exhibit a reversal in polarity with time upon illumination with light filtered using a 490 nm filter. In addition, V_{oc}

approaches a steady state value within a period much longer (~ 30 minutes) than in the example shown in Figure 2. Interestingly, no reversal in polarity is observed upon illumination with light incorporating shorter wavelengths (420 nm filter measurement). The data of Figure 3 do not represent an isolated case. Similar reversals in polarity (depending on the spectral composition of the incident light) were also observed for PV devices incorporating TiO_2 films prepared via other routes and for cells with a more complex architecture.

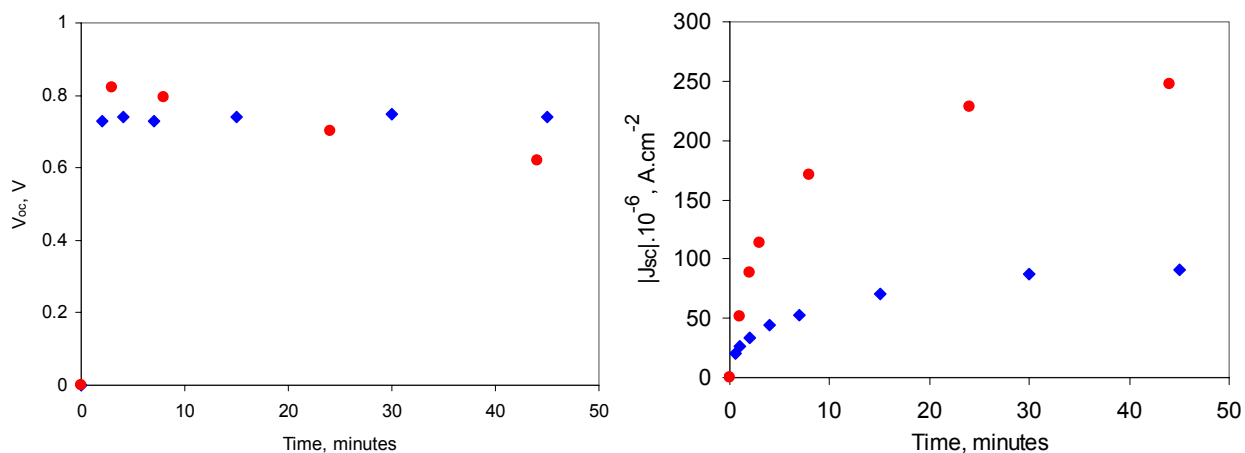


Figure 2. The time dependence of V_{oc} and J_{sc} of a bi-layer solar cell incorporating a TiO_2 layer prepared from the Solaronix paste upon illumination with light filtered using a 490 nm (diamonds) and a 420 nm (circles) long-pass filter.

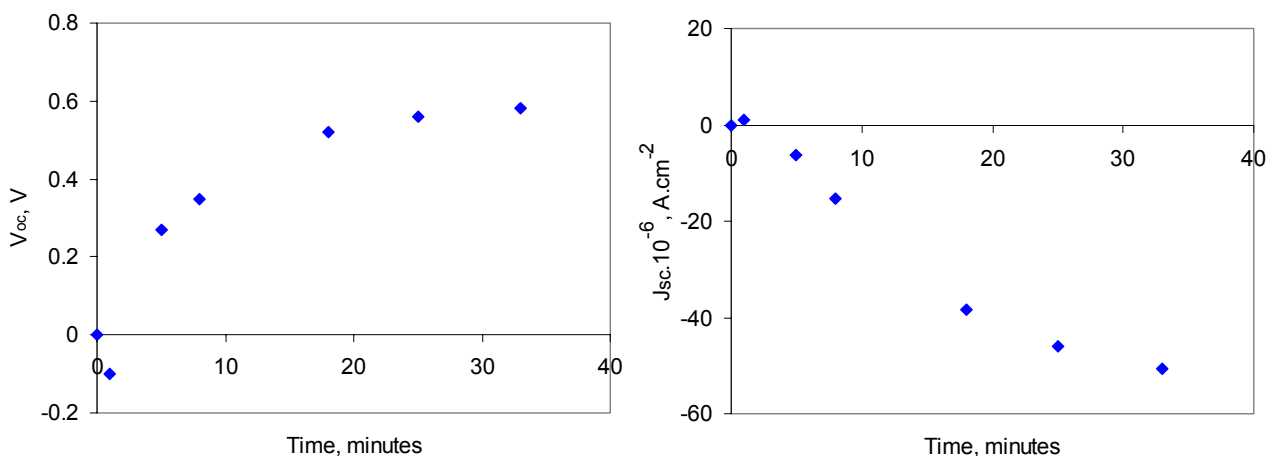


Figure 3. The transient behavior of V_{oc} and J_{sc} of a bi-layer solar cell incorporating a TiO_2 layer from a sol-gel upon illumination with light filtered using a 490 nm long-pass filter.

The slow kinetics of operation of the bi-layer devices is probably related to the charge transport properties of the constituent materials of the CSC. We have investigated the photovoltaic performance of single layer polymer devices in order to determine whether it shows similar transient behavior. Our data confirm that in single layer cells the open circuit voltage and short circuit current density do not settle to stable values instantly upon illumination. In an experiment carried out using a 390 nm long-pass filter, V_{oc} and J_{sc} increased rapidly in the first ten minutes, then continued to rise slowly and did not reach a constant value even after 115 minutes of illumination.

The time-dependence data can provide further insight into the principles of operation of organic photovoltaic cells and is pertinent to recent publications on the subject. It has been shown⁸⁻¹¹ that in excitonic solar cells the open circuit voltage has two main contributions – the electrical potential difference of the metal electrodes (\mathcal{O}_{bi}) and the photo-induced chemical potential gradient ($\nabla\mu_{hv}$) created by the interfacial exciton dissociation process. The latter is predominant in organic photovoltaic cells^{8,9}. As illustrated by the experimental examples above, initially the CSC works in a non-steady

state regime in which both V_{oc} and J_{sc} increase with time. We currently believe that the presented results manifest the diffusion driven operation of MEH-PPV based devices.

Briefly, qualitative understanding of the transient phenomena can be gained from the following consideration. The open circuit voltage V_{oc} is determined by the distribution of charges at the polymer/TiO₂ interface. The latter is a result of a balance between the processes of charge separation and charge recombination. As charge recombination is of bimolecular character it depends on the product of electron and hole densities on both sides of the interface. It can therefore be influenced by the rate of diffusion of charges across the electron donor and electron acceptor phase towards the cathode and the anode, respectively.

The initial rise in V_{oc} upon illumination is due to charge separation at the polymer/TiO₂ interface. For the ITO/TiO₂(Solaronix)/MEH-PPV/Au cell of Figure 2 (blue symbols), the steady state is reached relatively quickly indicating a rapid stabilization of the interfacial charge distribution due to slow recombination. For the bi-layer device with sol-gel TiO₂ (Figure 3) the change in V_{oc} occurs over a much longer period of time, most likely due to poor charge separation and/or a higher recombination rate of charge carriers at the polymer/TiO₂ interface. In this case the process of charge distribution at the interface is strongly influenced by the rate of charge transport away from the interface, and the steady state values of V_{oc} and J_{sc} are reached over a similar time scale. The reversal in polarity is likely to be due to imperfections in the cell. For example, the presence of areas where TiO₂ is in direct contact with the gold electrode could lead to a net flow of electrons through the external circuit towards the ITO electrode at the very start of illumination. However, since over the majority of the cell area $V_{\mu_{hv}}$ drives the electrons and holes generated at the MEH-PPV/TiO₂ interface towards ITO and Au, respectively, the net current running through the device would eventually reverse its direction.

We have considered the possible contribution of thermal heating of the sample upon illumination to the observed time dependence. An increase in temperature could lead to an improvement in charge mobility via thermally activated charge hopping, hence to an increase of the short circuit current density. The open circuit voltage can also be affected by the change in transport properties of TiO₂ and MEH-PPV. The comparison of I - V testing results obtained under varied spectral conditions for a wide range of cells, has lead us to conclude that while heating upon illumination is a contributory factor to the observed time dependence, it is not the main cause of the transient behavior. If heating was the dominant factor we would expect to see the same type of transient behavior for all bi-layer devices tested under identical conditions. In fact the time dependence of V_{oc} and J_{sc} appears to be more dependent on the way the polymer was synthesized.

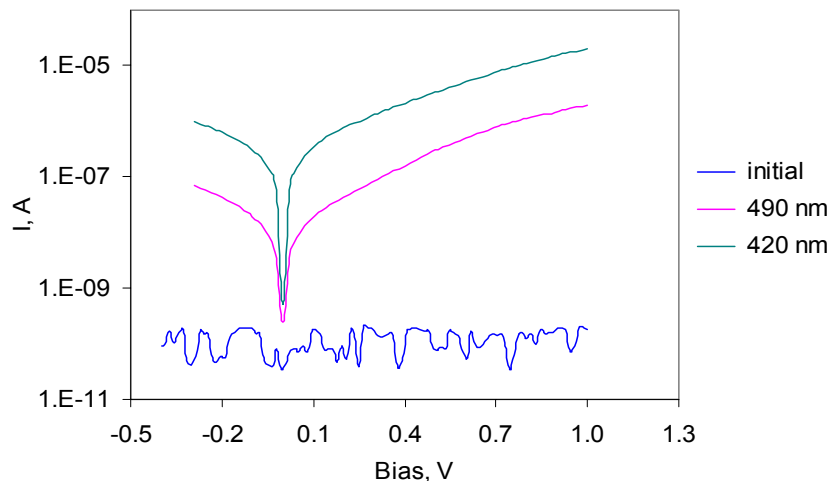


Figure 4. Dark current curves of the ITO/TiO₂(Solaronix)/MEH-PPV/Au bi-layer device before (bottom curve) and after illumination with light filtered using a 490 nm (middle curve) and a 420 nm long-pass filter (top curve). The time of illumination is 48 and 43 minutes, respectively.

After the initial period of illumination an ideal device should reach a (quasi) steady state of operation in which V_{oc} and J_{sc} are constant. As discussed above however, we frequently observe a passage through a maximum in V_{oc} followed by a gradual decrease. Our experimental results suggest that the latter is caused by charge accumulation in the CSC upon illumination. Figure 4 shows the I - V curves of the ITO/TiO₂(Solaronix)/MEH-PPV/Au bi-layer device measured in the dark before and after illumination. The dark current prior to illumination is very low, $\sim 10^{-10}$ A, which is at the sensitivity limit of the measuring instrument. After illumination for approximately 50 minutes the dark current has increased by several orders of magnitude, the increase being greater in the presence of light of shorter wavelengths. The latter correlates well with the notable drop of V_{oc} in Figure 2 for the 420 nm long-pass filter measurement. It is worth noting that the increase in dark current is reversible, but its return to the original level takes place over a matter of several days when the PV device is maintained in vacuum¹³. The fact that the dark current returns to its original level and that there is no deterioration in photovoltaic performance when the device is illuminated again indicates that the observed changes in V_{oc} and dark current and are not due to chemical degradation of the polymer.

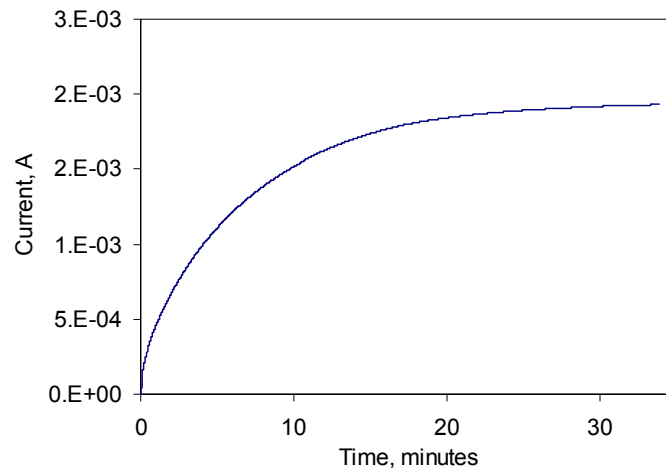


Figure 5. Current (at 0.5 V bias applied to the Au electrode) running through ITO/TiO₂/Au as a function of time of illumination with light filtered using a 420 nm long-pass filter. Note: The measurement was done in vacuum (1.5×10^{-2} mbar). The TiO₂ layer was formed by performing the doctor-blading procedure twice.

In principle, the process of charge accumulation upon illumination with light can occur in either layer (TiO₂ or MEH-PPV) of the bi-layer device. In order to elucidate which layer is the major contributor to the increase in dark current we carried out I - V measurements on ITO/TiO₂/Au and ITO/MEH-PPV/Au structures. Figure 5 demonstrates that there is a strong increase (by a factor of 10^3 - 10^4) in current running through ITO/TiO₂/Au upon illumination in vacuum when the incident light has been filtered using a 420 nm long-pass filter. The photo-generation of free charge carriers in the TiO₂ film follows its absorption profile and the increase in dark current even when a 420 nm filter is present can be related to the fact that the film has an absorption tail extending well into the visible light range. The UV-Vis spectrum of the TiO₂ layer has been presented previously¹² and the mechanism of photoconductivity and charge trapping in TiO₂ has been recently discussed¹³.

The operation of the ITO/MEH-PPV/Au device upon excitation by AM 1.5 light is presented in Figure 6. Notably, the open circuit voltage reaches a high maximum ($V_{oc} = 0.31$ V) after five minutes of illumination, but subsequently decreases dramatically and stabilizes at around 0.04 V. The short circuit current density rises for the first 40 minutes of operation, after which it declines in a manner similar to that shown in Figure 1. As in the case of Figure 4 the current after illumination is several orders of magnitude greater than the original dark current.

These results show that a build-up of charge density can occur in both the TiO₂ and MEH-PPV layers. In bi-layer devices these effects appear to be cumulative and here the changes in V_{oc} and J_{sc} are much more rapid. The influence of light on the composite materials (both MEH-PPV and TiO₂) can be considered as photo doping, e.g. electron-hole pairs which are not bound are generated upon illumination with light of a particular wavelength.

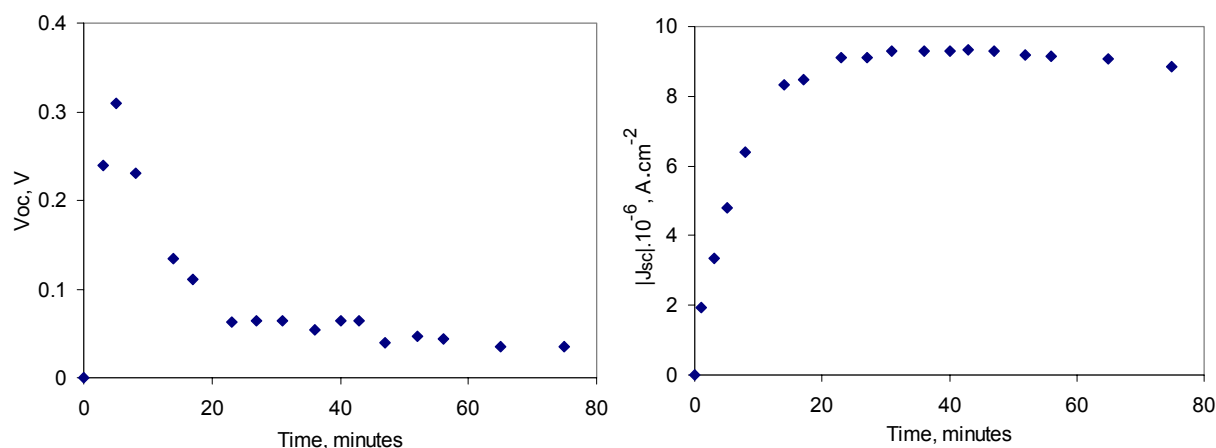


Figure 6. Photovoltaic performance of ITO/MEH-PPV/Au (top row) and ITO/TiO₂(Solaronix)/MEH-PPV/Au (bottom row) as a function of time of illumination with simulated AM 1.5 light.

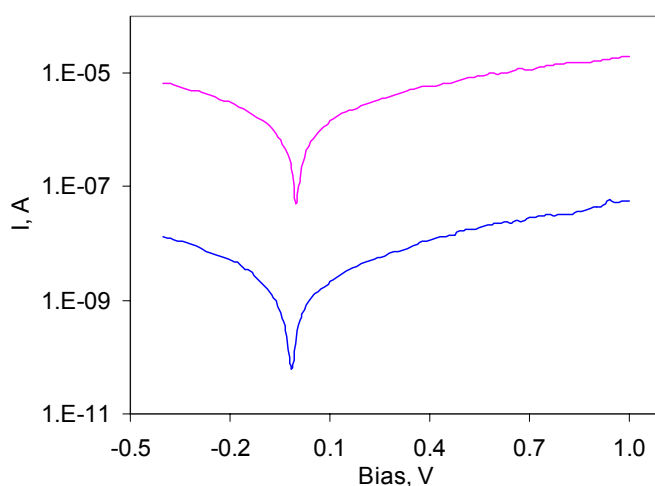


Figure 7. Dark current curves of the ITO/MEH-PPV/Au device of Figure 6 before (bottom curve) and after 75 minutes of illumination with simulated AM 1.5 light (top curve).

As discussed recently in the literature^{8,9}, the distinguishing characteristic of excitonic solar cells (including polymer/TiO₂ CSCs) in comparison with inorganic solar cells is that charges are simultaneously generated and separated across a hetero-interface. This creates a strong chemical potential gradient $\nabla\mu_{hv}$ which drives electrons and holes away from the interface and is the main contributor to the open circuit voltage of excitonic solar cells. However, photo-doping gives rise to free charges throughout the bulk of the TiO₂ and MEH-PPV layers, not just at their interface. This will therefore result in a loss of spatial specificity in the process of charge generation upon illumination and lead to a decrease (“flattening”) of $\nabla\mu_{hv}$, hence to a reduction of V_{oc} . The diminution of the force that drives electron and holes away from the TiO₂/polymer interface can lead to charge build up at the interface in which case the electric field induced by interfacial charge separation ∇U_{hv} will oppose further charge separation⁸. The net increase in charge concentration induced by photo-doping probably enhances the rate of charge recombination not just at the interface but also in the bulk of the electron/hole conducting layers and can therefore, as seen experimentally (Figure 6) result in a reduction of J_{sc} as well.

The observation on the time dependence of V_{oc} and J_{sc} values has implications for the reporting of device performance in the scientific literature. As already discussed above, the short circuit current density of the CSC increases continuously at the start of illumination. In the specific example of Figure 2 (red symbols) it rises five fold during the first thirty minutes, from $\sim 0.05 \text{ mA.cm}^{-2}$ to $\sim 0.25 \text{ mA.cm}^{-2}$. The period over which the change takes place is much longer than the typical duration of an $I-V$ sweep (3-4 minutes). When Type 1 of device operation is followed, the fill factor and consequently η also improve as a function of time. In the Type 2 scenario, the continuous rise of J_{sc} results only in a small improvement in efficiency due to the simultaneous decrease of V_{oc} and FF . When photo-doping occurs rapidly, η passes through a maximum and then decreases.

With this in mind it is clear that reporting values for photovoltaic parameters obtained using one $I-V$ sweep is not very informative, particularly if the measurement has been made at the very start of illumination when the polymer based CSCs operate in a non-steady state.

4. CONCLUSIONS

The photovoltaic performance of Gilch route MEH-PPV/TiO₂ based solar cells in the initial stages of operation is strongly time-dependent. Two main patterns can be distinguished in the time-dependence: i) an initial stage of rise in either or both V_{oc} and J_{sc} towards their quasi equilibrium values; ii) a passage of V_{oc} through a maximum followed by a gradual decline, which can be also accompanied by a drop in J_{sc} . We believe that the observed transient behavior is a manifestation of the diffusion driven operation of organic photovoltaic devices and is in line with recent publications which discuss the principles of operation of such devices^{5, 8-11}. Our results show a clear link between the decrease in open circuit voltage and the increase in dark conductivity of the cells after illumination. The latter is caused by charge build up (photo-doping) inside the CSCs and, as demonstrated, occurs (depending on the spectral composition of the incident light) in both TiO₂ and MEH-PPV. Since in the initial period of operation all photovoltaic parameters of the CSC vary with time, this has to be accounted for when reporting device performance in the scientific literature.

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