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Lifetimes of organic photovoltaics: photochemistry, atmosphere effects and barrier layers in ITO-MEHPPV: PCBM-aluminium devices

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Abstract

Large area polymer photovoltaic cells based on poly[(2-methoxy-5-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-PPV) and [6,6]-phenyl-C\textsubscript{61}-butyric acid methyl ester (PCBM) were prepared. The lifetimes of the photovoltaic cells were studied in terms of the atmosphere, handling, electrode treatment, mode of preparation and barrier layers by recording the short circuit current as a function of time. Two exponential fits to the decay curves allowed for the extraction of the time constants for different degradation processes. For the periods of time studied here (24–300 h), the decay curves could be fitted with two exponential functions. Common to the preparations were that the first half-life remained short and was independent of the presence of oxygen. When fullerenes were employed by sublimation of a layer of C\textsubscript{60} or as the soluble PCBM, the first half-life was an order of magnitude longer and depended on the presence of oxygen. By employing different barrier layers, we found the first half-life to be linked to the aluminium polymer interface and ascribe it to a photochemical reaction between the organic material and the reactive aluminium at the interface. The second and
longer half-life was found to depend on the presence of oxygen. We also discuss our findings of the short lifetimes for organic photovoltaics under AM1.5 illumination in the context of future applications.

Keywords: Organic photovoltaics; Polymer photovoltaics; Stability; Lifetimes; Lifetime decay profiles; Lifetime decay mechanisms; Lifetime improvement

1. Introduction

Organic photovoltaics [1,2] show great promise as a low cost alternative to inorganic semiconductor-based photovoltaics. Recently, efficiencies as high as 3.8% have been reported [3] and the possibility of up to 5% has been suggested [3,4] making polymer photovoltaics rival the inorganic semiconductor-based photovoltaics at a fraction of the price in terms of materials and production cost. While the major obstacle for the large-scale use of organic photovoltaics for on-grid electrical energy production is their low efficiency and short lifetime. There are many applications where efficiencies of 1% or less are more than sufficient (i.e. small calculators, clocks, price tags, thermometers etc.). In this case, the only obstacle is the lifetime of the devices and their shelf-life (or stability in the dark). Inorganic semiconductor based photovoltaics has typical operational lifetimes well in excess of 25 yrs under normal conditions with exposure to an outside environment. While the lifetime for organic and polymer solar cells has been reported in some instances [5–9], there has been very few reports with a detailed study of the lifetimes using decay curves obtained for the solar cells under various conditions. Most reports give indirect evidence for the degradation of the solar cells through for instance infrared (IR) measurements as a function of time and while it was proven possible to demonstrate a change of the IR spectrum with time the study was not coupled to the function of the solar cell (i.e. generation of an electrical current). A recent and excellent study by Jeranko et al. demonstrated decay processes by two-dimensional mapping of the photovoltaic response over the active area of the device [9]. The authors were able to conclude that a major degradation path was along the edges of the active area and variations in the photocurrent over the area of the cell linked to the process of the application of the electrodes. Literature reports are normally limited to the incident photon current efficiency (IPCE), the efficiency ($\eta$) and the spectral response with no mention of the stability of the photovoltaic device or at what point during the photovoltaic life the data were recorded. Mostly it can be assumed to be when the photovoltaic was freshly prepared and literature values should probably be taken as maximum values in terms of efficiency unless otherwise stated.

In this paper, we describe results obtained from a systematic study of the decay of polymer photovoltaics based on a MEH-PPV, MEH-PPV and with a sublimed layer of C$_{60}$, bulk heterojunctions formed with MEH-PPV and PCBM in a film sandwiched between ITO and aluminium electrodes. The short circuit of the
photovoltaic devices subject to different modes of preparation and conditions was recorded under illumination as a function of time. We isolate various degradation processes responsible for the decay and demonstrate that both the aluminium electrode and the atmosphere are responsible for the degradation in this system.

2. Experimental

MEH-PPV with a molecular weight, $M_w$ of 65,600 g mol$^{-1}$ and a polydispersity PD of 4.1 was prepared according to the method described in the literature [10]. It was found desirable to purify the polymer product by dissolution in THF (10 mg ml$^{-1}$), filtration from insoluble impurities and precipitation by slow dropwise addition of the THF solution to 10 volumes of vigorously stirred methanol. Filtration, washing with methanol and drying in a vacuum oven at 70 °C gave the pure product that was ready for use. PCBM was prepared according to the procedure described in the literature [11]. A solar simulator (Solar Constant 575) providing AM1.5 illumination conditions from Steuernagel Lichttechnik GmbH was employed for all lifetime measurements under simulated sunlight. The spectral distribution and quality of the solar simulator was monitored using an AvaSpec-2048 spectrometer from Avantes covering the wavelength range 180–1100 nm and a precision spectral pyranometer from Eppley Laboratory to monitor the total power. The electrical measurements were performed using Keithley 2400 sourcemeters. The influence of the atmosphere was established by illumination in the ambient atmosphere or in a vacuum chamber with a quartz window allowing for a control of the atmosphere [12]. The comparison of cells in vacuum and the atmosphere were performed on cells prepared in parallel such that the substrates from the same batch were used, ultrasonic cleaning in isopropanol, application of barrier layers and evaporation of the aluminium electrode was as similar as experimentally possible. This was found necessary to minimise effects of variation in the process related parameters. There were however big differences between the vacuum and the air experiment. The ITO substrates were $<10 \Omega$ square$^{-1}$ and cleaned by immersion in isopropanol and subjected to ultrasound for 10 min prior to use. PEDOT:PSS was applied by spincoating a 1% (w/w) aqueous solution containing 1% (w/w) sorbitol onto the ITO substrate with an angular speed of 3000 rpm. The PEDOT:PSS substrates were subsequently heated in an oven at 180 °C for 2 h. The active layer of the photovoltaic device was prepared by spincoating a chlorobenzene solution of MEH-PPV (8 mg ml$^{-1}$) and PCBM (8 mg ml$^{-1}$) at an angular speed of 1500 rpm. Lithium fluoride (LiF) layers were prepared by thermal evaporation in a vacuum chamber [13,14]. $C_{60}$ layers were thermally sublimed on top of the active layer in a vacuum chamber [15–18]. The aluminium electrodes were prepared by evaporation in a vacuum chamber. Both aluminium, LiF and $C_{60}$ were evaporated at a pressure of $<1 \times 10^{-5}$ mbar. The active area of the devices were $\sim 3$ cm$^2$. After electrode evaporation and cooling, the evaporator was purged with argon. When the devices were completed, electrical contacts were applied using silver epoxy. The thermosetting silver epoxy was allowed to set in the dark in an oven at 95 °C for 3 min. The
temperature was not found to degrade the performance of the devices as established by leaving a device in the oven for 24 h. While a 24 h heat treatment at 95°C did degrade the solar cell it was typically 30% making the assumption that the short thermosetting procedure does not affect the photovoltaic performance adversely reasonable. The devices were mounted and subjected to measurements immediately. The entire mounting procedure could be completed in ~10 min. The duration of time from removal from the evaporator through mounting and pumping to a pressure <10⁻⁴ mbar (for the samples measured in vacuum) until measurements could begin was <20 min.

3. Results and discussion

Polymer photovoltaics have been studied for the past 25 yrs starting with polyacetylene as the active material as reported by Weinberger et al. in 1982 [19]. Much of the initiative built on the work using small organic molecules such as porphyrins, phthalocyanines, and perylene dyes that started in the late 1950s by Kearns and Calvin [20] and perhaps culminated with the report by Tang in 1986 [21] where an efficiency of 1% was achieved. Polymer materials are believed to be easier to process into stable flexible films than small molecules when it comes to large-scale industrial production. In the past decade, the state of the art in polymer photovoltaics have changed from single layer devices with efficiencies well below 1% [22] through the invention of the bulk heterojunction [23,24] to an efficiency of 2.5%. Improvements following this strategy have given polymer photovoltaic devices with efficiencies of 3.3% [14], 3.8% [3] and a hinted 5% [3,4]. While the efficiency is an important research goal and often used as the ruling argument when comparing solar cell technologies an equally important and virtually neglected issue is the stability of the polymer photovoltaic in time both under illumination and in the dark. The current limitation to the industrial application of polymer photovoltaics is not the low efficiency but rather the short lifetime of these devices. While long lifetimes for polymer photovoltaics have been claimed, they have not been documented to an extent where independent workers can reproduce the result [8]. Another issue is the active area of the devices employed in the studies reporting the efficiencies. Most often the active area of the devices is well below 1 cm² and often measure only a few mm². It is important to evaluate the effects of large area on the polymer photovoltaic performance [25].

In this study, we employed an equal mixture of the conjugated polymer material MEH-PPV and PCBM as the active layers in the photovoltaic devices spincoated from chlorobenzene solution (see Fig. 1). In some devices, a sublimed layer of C₆₀ was also employed. The choice of chlorobenzene was based on the documented advantageous effect this solvent has on the film morphology, PCBM crystallite size and performance of the photovoltaic device [26]. Our primary aim was to study the degradation of the polymer photovoltaic devices and if possible extract information on the possible degradation mechanisms from the recordings of the decay. As a measure of the decay we chose to record the short circuit current ($I_{sc}$) as a function
of time during illumination since the efficiency of the device and \( I_{sc} \) are linked. There is a direct correlation between the incident light and the number of photons converted into electrons in the external circuit. The open circuit voltage (\( V_{oc} \)) is not as suited for this purpose because it is not directly related to the amount of incoming photons in the incident light but rather reflects the internal resistance of the device at any given time as described earlier [6]. While there are currently very little knowledge about the processes that take place at the interface between the electrodes and the active layer in terms of detailed chemical mechanism, our aim was to study the decay curves by fitting the normalised data with a series of exponential decay curves according to Eq. (1)

\[
\frac{I_{sc}(t)}{I_{sc}(0)} = Ae^{-bt} + Ce^{-dt} + \ldots. \tag{1}
\]

From the time constants \( (b,d, \ldots) \) and the weighting of the individual exponential functions \( (A, C, \ldots) \) we anticipated that information on the individual processes responsible for the performance decay of the polymer photovoltaics could be extracted by variation of the experimental parameters. From the parameters, the integrated charge when extrapolated to infinity could be obtained by summation of the charge contributed by each of the exponential functions as shown in Eq. (2)

\[
Q_{\text{total}} = \frac{A}{b} + \frac{C}{d} + \ldots. \tag{2}
\]

We thus chose to perform parallel experiments in ambient atmosphere and in vacuum and further to include barrier layers between the active layer and the electrodes. The experimental parameters are listed below:

1. The atmosphere (parallel experiments in the ambient atmosphere and in vacuum).
2. A barrier layer between the ITO electrode and the active layer (PEDOT:PSS).
(3) A barrier layer between the aluminium electrode and the active layer (LiF or C\textsubscript{60}).
(4) The light intensity.
(5) The temperature (during the experiment).
(6) Storage (in the dark at room temperature and at 95°C).

The list is by no means exhaustive and many more experiments will be needed for a complete understanding of the prevalent degradation mechanisms in polymer-based photovoltaics. The complexity of the problem stems from the fact that the degradation phenomenon is a result of chemical reactions in a system (device) that is difficult to study in terms of chemical detail with the additional difficulty that the preparation of the system (device) is subject to many technical issues such as cleaning procedures, impurities, different morphologies induced by different solvents etc. It is essentially an example of system analysis of a system with many coupled parameters and a good understanding will require a large amount of data. Based on such a firm basis, the crucial elements of the degradation paths can possibly be drawn.

3.1. Performance of the different device geometries

The devices were prepared on glass substrates covered with indium tin oxide (ITO). The active layers of the device were then applied and finally the aluminium counter electrode was applied. The devices were subjected to measurement directly after preparation. Two devices were prepared in each experiment and it was found possible to reproduce their performance in terms of \(I\text{sc}\), \(V\text{oc}\) and dark resistance, \(R_d\), to within 10% (using substrates from the same batch, the same freshly prepared solution, electrode evaporation at the same time etc.). One of the devices was placed in a vacuum chamber and pumped with a turbomolecular pump to a pressure \(<10^{-4}\) mbar and the other device was placed under ambient conditions (the vacuum experiment served to reduce the oxygen level by a factor of \(10^7\) compared to the ambient atmosphere). Both samples were placed under the sun simulator with an AM1.5 spectral distribution and a luminous intensity of 1000 W m\(^{-2}\). The recording of \(I\text{sc}\) was begun and light from the sun simulator was subsequently admitted to the devices. In Table 1, typical values for \(I\text{sc}\) and \(V\text{oc}\) are shown for the devices employed in the study. The values obtained are as expected when comparing qualitatively with literature data for systems of this type or for similar systems. The simple homopolymer device with just MEH-PPV sandwiched between ITO and aluminium electrodes (type 1) gave the lowest value typical for homopolymer devices [22]. The addition of a PEDOT:PSS barrier layer between the ITO and MEH-PPV (type 2) gave up to a two-fold increase in \(I\text{sc}\) and gave a marginal improvement on the fillfactor, \(FF = \frac{|I\text{maxpower}\ V\text{maxpower}|}{I\text{sc} \ V\text{oc}}\). The incorporation of an additional LiF layer (types 3 and 6) reduced \(I\text{sc}\), \(V\text{oc}\) and FF. The formation of a heterojunction by sublimation of a layer of C\textsubscript{60} (\(~200\) nm) (type 4) as described earlier [15,16,18] gave a 25-fold increase in the current density as compared to the simple system (type 1). The formation of a bulk heterojunction [23,24] by addition of
the soluble fullerene derivative PCBM (types 5 and 7) gave the highest values for $I_{sc}$ as expected.

It is interesting to notice that the addition of barrier layers between the active layer and the aluminium electrode gives rise to a better diode characteristic and a much higher fill factor. The above results confirm that the devices under study behave similarly to reported systems and follow the expected trend. We ascribe the lower values that we obtain for $I_{sc}$ in the bulk heterojunction as compared to the literature to in part the fact that we only employed a 1:1 (w/w) mixing ratio of MEH-PPV:PCBM and in part to the large device area employed here (~3 cm$^2$). The maximum value for $I_{sc}$ in bulk heterojunction devices has been shown to be when the mixing ratio is 1:4 (w/w) MEH-PPV:PCBM [27] and the efficiency has been shown to decrease with increasing device area [25]. We, however, chose to employ a 1:1 mixing ratio as it was easier to reproduce the device characteristics.

3.2. The effect of the atmosphere on the lifetime of the photovoltaics

When the devices were illuminated under AM1.5 (1000 W m$^{-2}$) $I_{sc}$ generally decayed as shown in Fig. 2 with a fast initial decay followed by a more slow decay. The general length of the experiments was 24–300 h of uninterrupted illumination with the cell shorted (by the sourcemeter) at all times.

The general trend observed for the homopolymer devices (types 1–3) was a fast initial decay that within experimental error was independent of whether the device was exposed to the atmosphere or in vacuum. This is an important finding and can have two possible explanations. Either it is a reaction between dissolved oxygen in the device or it is a reaction between one of the electrodes and the polymer. When considering the amount of charge generated during the fast initial decay, it is unlikely that it is due to dissolved oxygen from the simple reason of stoichiometry. Suppose that the oxygen reacts with electrons in the conduction band or aids exciton dissociation by quenching the excited state. In that situation, each dissolved oxygen

<table>
<thead>
<tr>
<th>Device type and geometry</th>
<th>$I_{sc}$ (μA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ITO/MEH-PPV/Al</td>
<td>-15</td>
<td>0.82</td>
<td>22.9</td>
</tr>
<tr>
<td>2 ITO/PEDOT:PSS/MEH-PPV/Al</td>
<td>-18</td>
<td>0.82</td>
<td>23.3</td>
</tr>
<tr>
<td>3 ITO/PEDOT:PSS/MEH-PPV/LiF/Al</td>
<td>-2</td>
<td>0.58</td>
<td>21.6</td>
</tr>
<tr>
<td>4 ITO/PEDOT:PSS/MEH-PPV/C$_{60}$/Al</td>
<td>-504</td>
<td>0.65</td>
<td>26.7</td>
</tr>
<tr>
<td>5 ITO/PEDOT:PSS/MEH-PPV/PCBM/Al</td>
<td>-1714</td>
<td>0.73</td>
<td>32.6</td>
</tr>
<tr>
<td>6 ITO/PEDOT:PSS/MEH-PPV/PCBM/LiF/Al</td>
<td>-101</td>
<td>0.80</td>
<td>19.3</td>
</tr>
<tr>
<td>7 ITO/PEDOT:PSS/MEH-PPV/PCBM/C$_{60}$/Al</td>
<td>-1058</td>
<td>0.70</td>
<td>32.8</td>
</tr>
</tbody>
</table>
molecule would require up to a maximum of four electrons for complete conversion from $O_2$ through superoxide and peroxide into $O^{2-}$ (another possibility is in the form of aldehyde or carboxylic acid groups formed by $[2+2]$ addition to the double bonds of the PPV skeleton). The decay would, however, be expected to stop as the oxygen has been consumed and should as such be independent of the device geometry. The reaction rates, however, need not be coupled to the overall current density of the device since very few photons in actual fact are converted into an electrical current. Dissolved oxygen would be expected to be present in a very small amount ($\sim$1–10 ppb or less) since the film is very thin ($<100$ nm) and the device is pumped to a low pressure before evaporation of the electrodes. The oxygen concentration in the film is thus assumed to be in equilibrium with the oxygen concentration in the evaporation chamber with a pressure $<10^{-5}$ mbar. In the case of reaction between the polymer material and the electrodes, the introduction of barrier layers would be expected to influence the decay curves. In Table 2, typical decay parameters are shown for all the device geometries employed here. Also the total charge extracted from the device during the run of the experiment and when extrapolated to infinity is tabulated. The decay parameters were normalised such that the sum of pre-exponential factors equal one. The pre-exponential factors also indicate the weight of each term to the total current produced by the device. The total charge extracted from the device during the run of the experiment, $Q_{\text{exp}}$, far exceed the number of atoms (assuming a density of 1) in the device thus excluding the simple possibility that the macroscopic photovoltaic response observed from the device simply stems from photochemistry between the constituents or the constituents and the electrodes (i.e. photo-induced battery action only).

The possibility of a certain amount of photochemistry/electrochemistry contributing towards the photovoltaic response cannot be excluded however. In an excellent

![Fig. 2. An example of a normalised decay curve for a cell of type 2 (see Table 1) in ambient atmosphere and under vacuum. Notice how the initial decay is fast in both cases.](image)
report, Aziz and Xu [28] report on the stability of electroluminescent devices based on PPV and ITO/aluminium electrodes and find that the current–time behaviour of the devices depended heavily on whether operated in the dark or under illumination. They also demonstrated that the electrode materials reacted with the PPV that essentially acted as a weak electrolyte. Their work agrees well with a theoretical study examining the possible complex formation/chemical reaction between the PPV and the aluminium at the interface [29]. The chemical reaction between the interface of PPV derivatives and sodium has also been reported and give firm experimental evidence of the reaction between the electrode and the polymer at the interface [30,31]. From the second decay parameter a distinct influence of the atmosphere is observed.

The devices operated in air have a much shorter second decay parameter than the devices operated in vacuum. This is ascribed to the effect of molecular oxygen that by slow diffusion from the edges of the device (and perhaps through defects in the aluminium electrode) gradually enters the device and participates efficiently in device degradation. A recent study [8] reported various models for degradation kinetics and while both a single exponential and a linear model was applied the linear decay model was preferred. This is contrary to our findings where a linear model only fitted the data well in a few instances. When using several exponentials however, it became evident that good fits could be obtained as shown in Fig. 3.

### Table 2

Typical normalised decay parameters according to the general Eq. (1) under AM1.5 illumination with an incident power density of 1000 W m\(^{-2}\) in air and in vacuum (in paranthesis)

<table>
<thead>
<tr>
<th>Device</th>
<th>(A) (%)</th>
<th>(b) (s(^{-1}))</th>
<th>(C) (%)</th>
<th>(d) (s(^{-1}))</th>
<th>(I_0) ((\mu A cm^{-2}))</th>
<th>(Q_{\text{exp}}) (C cm(^{-2}))</th>
<th>(Q_{\text{total}}) (C cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td>41.6</td>
<td>(2.57 \times 10^{-3})</td>
<td>58.4</td>
<td>(1.91 \times 10^{-4})</td>
<td>(-12.05)</td>
<td>0.0198</td>
<td>0.0411</td>
</tr>
<tr>
<td></td>
<td>(42.3)</td>
<td>(2.17 \times 10^{-3})</td>
<td>(57.7)</td>
<td>(9.21 \times 10^{-5})</td>
<td>(-6.36)</td>
<td>(0.0138)</td>
<td>(0.0388)</td>
</tr>
<tr>
<td>Type 2</td>
<td>78.1</td>
<td>(1.56 \times 10^{-3})</td>
<td>21.2</td>
<td>(1.36 \times 10^{-4})</td>
<td>(-19.2)</td>
<td>0.0381</td>
<td>0.0406</td>
</tr>
<tr>
<td></td>
<td>(62.4)</td>
<td>(1.94 \times 10^{-3})</td>
<td>(37.5)</td>
<td>(8.68 \times 10^{-5})</td>
<td>(-20.5)</td>
<td>(0.0541)</td>
<td>(0.0950)</td>
</tr>
<tr>
<td>Type 3</td>
<td>90.4</td>
<td>(1.07 \times 10^{-3})</td>
<td>9.6</td>
<td>(1.56 \times 10^{-4})</td>
<td>(-1.77)</td>
<td>0.00255</td>
<td>0.00259</td>
</tr>
<tr>
<td></td>
<td>(86.7)</td>
<td>(3.64 \times 10^{-4})</td>
<td>(13.3)</td>
<td>(2.46 \times 10^{-5})</td>
<td>(-9.16)</td>
<td>(0.0616)</td>
<td>(0.0713)</td>
</tr>
<tr>
<td>Type 4</td>
<td>99.3</td>
<td>(5.23 \times 10^{-4})</td>
<td>0.7</td>
<td>(1.04 \times 10^{-5})</td>
<td>(-453)</td>
<td>1.07</td>
<td>1.18</td>
</tr>
<tr>
<td></td>
<td>(45.8)</td>
<td>(5.53 \times 10^{-5})</td>
<td>(54.2)</td>
<td>(2.74 \times 10^{-6})</td>
<td>(-163)</td>
<td>(15.4)</td>
<td>(33.6)</td>
</tr>
<tr>
<td>Type 5</td>
<td>45.8</td>
<td>(1.39 \times 10^{-4})</td>
<td>54.2</td>
<td>(2.79 \times 10^{-5})</td>
<td>(-1841)</td>
<td>38.1</td>
<td>41.8</td>
</tr>
<tr>
<td></td>
<td>(65.3)</td>
<td>(3.90 \times 10^{-5})</td>
<td>(34.7)</td>
<td>(2.57 \times 10^{-6})</td>
<td>(-871)</td>
<td>(37.6)</td>
<td>(132)</td>
</tr>
<tr>
<td>Type 6</td>
<td>35.3</td>
<td>(1.12 \times 10^{-3})</td>
<td>64.7</td>
<td>(1.22 \times 10^{-4})</td>
<td>(-85)</td>
<td>0.414</td>
<td>0.477</td>
</tr>
<tr>
<td></td>
<td>(58.4)</td>
<td>(7.66 \times 10^{-5})</td>
<td>(41.6)</td>
<td>(1.13 \times 10^{-5})</td>
<td>(-1118)</td>
<td>(31.6)</td>
<td>(49.7)</td>
</tr>
<tr>
<td>Type 7</td>
<td>91.8</td>
<td>(6.60 \times 10^{-5})</td>
<td>8.2</td>
<td>(1.20 \times 10^{-5})</td>
<td>(-1054)</td>
<td>21.8</td>
<td>85.8</td>
</tr>
<tr>
<td></td>
<td>(51.9)</td>
<td>(3.38 \times 10^{-5})</td>
<td>(48.1)</td>
<td>(1.00 \times 10^{-5})</td>
<td>(-652)</td>
<td>(97.1)</td>
<td>(324)</td>
</tr>
</tbody>
</table>

The typical starting short circuit current, \(I_0\), is also shown. The device temperatures were \(72 \pm 2\) °C during measurements. The charge drawn from the device during the run of the experiment, \(Q_{\text{exp}}\), and the total charge possible according to Eq. (2), \(Q_{\text{total}}\).
3.3. The effect of a PEDOT:PSS barrier layer between ITO-electrode and the active layer on the lifetime of the photovoltaics

A layer of PEDOT:PSS between the transparent ITO electrode and the active layer acts as a hole conductor and a chemical barrier. It thus has two functions, to limit charge transport across the active layer-ITO interface to hole-only transport and to allow us to probe if there are any changes in the plot of $I_{sc}$ against time. We observed a small increase in the overall current density but no significant changes in the decay parameters as shown in Table 2. This implies that the interface between the active layer and ITO does not play a significant role in the degradation of the performance of the photovoltaic under illumination. It does, however, improve the overall performance of the device, as expected.

3.4. The effect of a sublimed layer of LiF or C$_{60}$ between the active layer and the aluminium electrode on the lifetime of the photovoltaics

The introduction of a thin layer of LiF between the active layer and the aluminium electrode has been reported to increase the stability and lower the injection barrier for electrons in light-emitting devices as shown experimentally for devices and by ultraviolet photoelectron spectroscopy (UPS) studies [13,14,32]. For photovoltaics, it has equally been shown to improve the performance of the photovoltaic cells. It essentially acts as a tunnel barrier allowing for the passage of electrons while allegedly preventing chemical reactions between the active layer and the reactive electrode metal to take place. The detailed mechanism for the success of applying LiF (or similar layers such as MgO [13] or Al$_2$O$_3$ [33]) remains a subject of some dispute. We were unable to observe any increase in the decay parameters when a LiF barrier layer between the aluminium electrode and the active layer was employed. There are some inherent problems associated with the application of a LiF barrier
layer since it is a very good insulator. The layer has to be very thin and it is probably difficult to get an even layer that is just 10 Å thick. Evaporation will invariably give rise to holes in the film and the protection offered by the LiF layer is thus questionable from a practical point of view. In our case, the first lifetime was improved an order of magnitude when measurements were performed in vacuum (type 3) indicating that the polymer–aluminium interface has an important influence on the magnitude of the first half for the homopolymer devices. Relatively long lifetimes for large area devices prepared by silk screen printing under industrial conditions were observed (operated in air) when a layer of C₆₀ was sublimed on top of the active layer [18]. The advantage of a layer of C₆₀ is that it is a very good electron conductor and it is possible to make a thick layer (hundreds of nanometers) and it has many stable redox states making it a good candidate for a barrier layer between the active layer and aluminium. Upon application of a sublimed layer of C₆₀ (~200 nm), we observed a significant improvement on the lifetime of the device especially on the first decay parameter that was increased by one order of magnitude in air and two orders of magnitude in vacuum. Our conclusion based on the experiments with sublimed layers of C₆₀ is thus that the interface between the active layer and the aluminium electrode is responsible for the first decay parameter. By employing a layer of C₆₀, we form an efficient barrier that conduct electrons well and aid the exciton dissociation as evidenced by the large increase in the current density (type 4) for the simple device (type 2) with only a PEDOT:PSS and a MEH-PPV layer. It should be mentioned that most of the devices exhibited a decay from the moment where light was admitted to the device. For devices of types 4 and 7, however $I_{sc}$ increased for quite a while before the decay set in as shown in Fig. 4. This is consistent with earlier findings in the case of type 4 [18].

A possible explanation for this could be an annealing effect where the heterojunction gradually improves until it is overtaken by the degradation mechanisms. In Table 2, the decay parameters were derived from the point where the decay was observed.

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**Fig. 4.** An example of decay curves for a cell of type 7 (see Tables 1 and 2) in air and vacuum where $I_{sc}$ increases for several hours before the decay sets in.
3.5. The effect of the light intensity on the lifetime of the photovoltaics

The degradation mechanism was expected to be dependent on the intensity of the incident light. The only issue that was difficult to eliminate from the experiments with different light intensities was the temperature of the devices studied in vacuum since it is difficult to have good thermal contact with the device without possibly altering the device (e.g. heat transfer grease on the back side). If this were to be done properly a cryostat with a circulating inert gas would have to be employed (e.g. helium due to its large coefficient of thermal conduction). Such a set-up was, however, not available to us (see Table 3).

It is interesting to note that the current density (the pre-exponents) for the devices were linear with the incident light intensity (as expected) whereas, the second half life was shorter at high luminous intensities. This could be indicative of a link between the current density and the degradation mechanisms of the devices. From the experiments on the influence of barrier layers on the decay parameters, it was shown that the interface between the active layer and the aluminium electrode plays an important role in the decay of the device performance. The interface between the aluminium and the active material is also active in the exciton separation process as evidenced by earlier studies employing illumination from the ITO and aluminium side of the device, respectively [34]. The authors also observed a long tail in the photoresponse when switching the light off after illumination from the aluminium side of the device. High current densities as a result of high luminous intensities could accelerate the degradation. It is also noticeable that the weight of the first exponential was small at low luminous intensity but increased at higher luminous intensity.

3.6. The effect of storage and temperature on the lifetime of the photovoltaics

The devices were found to degrade when they were stored in the dark. The rate of degradation was much slower in vacuum than under ambient conditions. Freshly

Table 3

<table>
<thead>
<tr>
<th>Power</th>
<th>A (%)</th>
<th>b (s(^{-1}))</th>
<th>C (%)</th>
<th>d (s(^{-1}))</th>
<th>(I_0) ((\mu A cm^{-2}))(^a)</th>
<th>(Q_{\text{exp}}) (C cm(^{-2}))</th>
<th>(Q_{\text{total}}) (C cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>450 W m(^{-2})</td>
<td>15.1</td>
<td>4.27 \times 10^{-5}</td>
<td>84.9</td>
<td>1.28 \times 10^{-6}</td>
<td>-270</td>
<td>45.0</td>
<td>179</td>
</tr>
<tr>
<td>1000 W m(^{-2})</td>
<td>51.9</td>
<td>3.38 \times 10^{-5}</td>
<td>48.8</td>
<td>1.00 \times 10^{-6}</td>
<td>-652</td>
<td>97.1</td>
<td>324</td>
</tr>
<tr>
<td>1400 W m(^{-2})</td>
<td>50.2</td>
<td>5.29 \times 10^{-5}</td>
<td>49.8</td>
<td>4.42 \times 10^{-6}</td>
<td>-753</td>
<td>32.4</td>
<td>92</td>
</tr>
</tbody>
</table>

The typical starting short circuit current, \(I_0\), is also shown. The device temperatures were 72 ± 2 °C. The charge drawn from the device during the run of the experiment, \(Q_{\text{exp}}\), and the total charge possible according to Eq. (2), \(Q_{\text{total}}\).

\(^a\)The short circuit current for the individual devices showed a linear dependence on the incident light intensity. The variation exhibited here is due to variation between the different devices that amounts to 30%.
prepared cells were stored in the dark under ambient conditions and in vacuum (in both cases, the devices were connected in open circuit). The initial current density was found to be reduced one order of magnitude when stored in air. When stored in vacuum, the degradation was barely detectable when stored for 5 days which underlines the need to encapsulate the devices efficiently (see Table 4).

In both cases, the weight of the first exponential was largest and the total charge that could be drawn from the devices decreased more than two orders of magnitude when stored in air and an order of magnitude when stored in vacuum. This implies that the devices do degrade upon storage. The degradation does, however, not manifest itself as a decrease in $I_{sc}$ when stored in vacuum. It is also clear that the total charge that the device can generate is severely affected.

The performance of the device as a function of temperature was difficult to establish under conditions in vacuum, as described above, and will require a generalised experimental set-up where the media employed for temperature (i.e. heat transfer) does not adversely affect the device function. While the effect of the temperature here is in accordance with recent findings [35], this report did not explain the detailed experimental procedure (i.e. type of cryostat, means of heat transfer) thus making it difficult to reproduce the exact experimental conditions. We propose that a method should be developed where a temperature controlled inert gaseous media is circulated ensuring a constant temperature of the device. In this manner, the effect of the atmosphere can be evaluated in situ. Also the use of elevated temperature has been suggested as a means of doing accelerated lifetime testing of devices [8]. Under ambient conditions it was possible to control the temperature of the device by means of a fan. Our results confirmed recent findings [8] that a higher temperature accelerates the degradation of the device performance. One possible link between the temperature of device and the lifetime could be the glass transition temperature, $T_g$, of the polymer component. If a highly crystalline polymer material is used or the device is operated far below $T_g$, then a higher stability is reasonable to assume. If on the other hand the device is operated close to $T_g$, then a faster degradation is to be expected due to the increased motion of the polymer chains and possible diffusion of electrode degradation products. While the temperature plays an important role in the degradation of the device it cannot fully account for the observed degradation. A high current density as a result of high

<table>
<thead>
<tr>
<th>Storage</th>
<th>$A$ (%)</th>
<th>$b$ (s$^{-1}$)</th>
<th>$C$ (%)</th>
<th>$d$ (s$^{-1}$)</th>
<th>$I_0$ ($\mu$A cm$^{-2}$)</th>
<th>$Q_{exp}$ (C cm$^{-2}$)</th>
<th>$Q_{total}$ (C cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>96.9</td>
<td>$6.51 \times 10^{-3}$</td>
<td>3.1</td>
<td>$3.72 \times 10^{-5}$</td>
<td>$-112$</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>Vacuum</td>
<td>90.8</td>
<td>$1.23 \times 10^{-4}$</td>
<td>9.2</td>
<td>$5.65 \times 10^{-6}$</td>
<td>$-1165$</td>
<td>22.4</td>
<td>27.5</td>
</tr>
</tbody>
</table>

The devices were prepared and stored for 5 days in the dark before the measurement. The device temperatures were $72 \pm 2^\circ C$ during measurements. The charge drawn from the device during the run of the experiment, $Q_{exp}$, and the total charge possible according to Eq. (2), $Q_{total}$. 

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*Table 4*  
Typical normalised decay parameters for a device of type 5 according to the general Eq. (1) under AM1.5 illumination with 1000W m$^{-2}$.
incident light intensity was shown to play an important role in the degradation mechanism. While the light intensities employed here are extreme in comparison to what one would expect for a device operating under “real life” conditions. Lifetimes of the devices reported here would be longer due to natural variation of the light intensity (northern hemisphere, day/night, cloudy/blue sky, inside/ outside).

3.7. A putative mechanism

While the experiments performed for this system by no means are exhaustive and only carried out for one particular system under one very limited set of conditions, our results do allow us to draw some general conclusions and suggest some possible mechanisms of chemical degradation in the photovoltaic devices.

Our results show that the rate of degradation was accelerated when the photovoltaic devices were subjected to elevated temperatures and most importantly when the incident light intensity was increased giving a high current density.

Since the performance of the photovoltaic devices reported here in terms of efficiency is quite low (~0.5%) the link between the degradation and $I_{sc}$ may be derived from the large incident light intensity rather than the current density itself. There are many possible views on the charge carrier generation and transport in polymer-based photovoltaics and most pictures are derived from the well understood semiconductor physics. In Fig. 5, the process is viewed in terms of the band picture and the molecular orbital (MO) picture. While perfectly explanatory of the overall process, they do not take the molecular structure of the constituents nor the mechanism of transport into account. Conjugated polymer materials have been shown to conduct a current without significant degradation when doped. It has been shown that chemical doping leads to spin less transport (i.e. conduction by cations and anions) when the concentration of the dopant is increased beyond a small threshold value. When however the concentration of the dopant is below the threshold transport is no longer spin less (i.e. by radical cations and radical anions) [36]. We have in Fig. 6 outlined one possible mechanism of the process in terms of the molecular structure. The exciton is charge neutral and spinless. Photophysical studies on $C_{60}$ and PPV/PCBM blends coupled with electron spin resonance (ESR) have shown the fast formation of a PPV radical cation and a PCBM radical cation upon photo excitation [37–39]. This could imply that transport in organic photovoltaics is dominated by radical cations and radical anions. Movement of the cation in a PPV-based structure requires (formally) the movement of electron pairs leading to a lattice distortion whereas radical movement (single electron) erases the lattice distortion. Whether the cation and the electron are coupled and follow each other during transport is beyond the scope of this work but in either case it points to the problematic (for organic materials) presence of a radical–ion. Upon recombination at electrodes, the spin of the electron may lead to a singlet (relaxed) state or a triplet state (reactive). The presence of radicals and formation of carbenes in the solid will inevitably lead to chemical reactions that will break conjugation and destroy the properties of the materials in terms of photovoltaic device function even in the absence of oxygen. Molecule–molecule radical reactions may be responsible
for the degradation observed for devices in vacuum employing two barrier layers and part of the degradation that is efficiently attenuated by a sublimed C\textsubscript{60} layer may be due to the fact that C\textsubscript{60} efficiently accommodates several redox states and does not easily form chemical bonds with aluminium as shown for PPV type materials in a theoretical study by Bredas et al. [29]. The radical species are likely to react with aluminium metal thus gradually dissolving the metal electrode in the organic material leading to disruption of the conjugation in the MEH-PPV system. Such a process would not contribute to the photovoltaic current but would lead to the eventual formation of an insulating organo-aluminium barrier layer (in the absence of oxygen and water) between the active layer and the metallic aluminium electrode. It must be borne in mind that aluminium is a highly reactive metal in the context of organic molecules and has been used in the past for the chemical reduction of organic materials (e.g. the Clemmensen reaction). The observation that a sublimed layer of C\textsubscript{60} or dissolved PCBM improves the lifetime may be rationalised by the fact that exciton dissociation to a large extent is removed from the polymer–aluminium interface. From this point of view the lifetime should be improved if the exciton
3.8. Directions for future studies

Good temperature control under high luminous intensity and controlled atmosphere conditions where isotopic labelling studies could provide insight into the dissociation process can be removed from the electrode interface (probably only for the electron accepting electrode) and possibly if charge transport could be made spinless.

Fig. 6. An example of a possible process in terms of the molecular structure as illustrated for a short PPV segment. Light is absorbed (g) giving an exciton with a concomitant quinoid lattice distortion (h) exciton dissociation at the aluminium electrode interface by single electron injection gives a radical cation that is free to move (i) to the ITO electrode where the hole is annihilated leaving a radical (j).

3.8. Directions for future studies

Good temperature control under high luminous intensity and controlled atmosphere conditions where isotopic labelling studies could provide insight into the
chemical reactions between oxygen in the atmosphere and the active constituents of
the device. Furthermore, chemical studies where degradation products can be
isolated and analysed would be highly desirable.

4. Conclusion

We have shown that the lifetime of polymer based photovoltaics employing ITO
and aluminium electrodes can be increased by sublimation of a layer of C60 between
the active layer and the aluminium electrode. We found that the decay curves could
be fitted with a two-term exponential function corresponding to an initial fast decay
and a second slower decay. The fast decay was independent on the atmospheric
conditions under which the device operated and by variation of barrier layers was
found to be linked to the interface formed between the active layer and the
aluminium electrode. The second decay was found to depend on the atmosphere and
is ascribed to reaction with atmospheric oxygen. We have further confirmed that
increased temperature accelerates device degradation and shown that the degrada-
tion is linked to the light intensity and the consequent high current density. The
higher the current density the faster the degradation of the devices. This observation
could possibly be ascribed to chemical reactions of the photo-generated radical
anions and radical cations at the aluminium electrode interface. As the current
density increases, the concentration of charge carriers at the electrode interface
increase and when the surface density reaches a critical level, the probability of a
chemical reaction leading to chemical degradation is increased. Possible chemical
reactions responsible for the degradation were outlined. Seen in the light of our
findings, the instability problem relating to organic photovoltaics has to be
understood and solved before any ‘real life’ application can be envisaged.

References

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