Transparent anodes for polymer photovoltaics: Oxygen permeability of PEDOT

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Abstract

The oxygen permeability of the transparent organic anode poly(3,4-ethylene dioxythiophene) with paratoluenesulphonate as the anion (PEDOT:pTS) was determined to be $2.5 \pm 0.7 \times 10^{-15}$ cm$^3$ (STP) cm$^{-2}$ s$^{-1}$ Pa$^{-1}$, and is thus comparable in magnitude to the oxygen permeability of polyethyleneterephthalate (PET). The oxygen diffusion through bilayers of polyethylene (PE) and PEDOT:pTS and bilayers of PET and PEDOT:pTS was established. The bilayer structures were applied as the carrier substrate and the transparent anode in polymer-based photovoltaic devices employing a mixture of poly(1-methoxy-4-(2-ethylhexyloxy)-p-phenylenevinylene) (MEH-PPV) and [6,6]-phenyl-C$_{61}$-butanoicacidmethylester (PCBM) as the active layer and aluminium as the cathode. The oxygen permeability of the layers and the aluminium cathode was correlated with the lifetime of the solar cell devices. It was found that the performance of the devices with PET as the carrier substrate degraded more slowly due to the lower oxygen and water permeability, whereas devices using PE as the carrier substrate gave devices with a very short lifetime. It was found that PEDOT:pTS on its own is a not a significant barrier for oxygen in the context of photovoltaic devices where long lifetimes are anticipated. It is concluded that the large oxygen permeability of the barrier layers contribute to the short device lifetimes while other permeates such as water also contribute to device degradation.

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1. Introduction

Organic and polymer photovoltaics \cite{1–6} have the potential to become a flexible low-cost alternative to inorganic semiconductor-based photovoltaics. In the past few years the technology of polymer photovoltaics has seen some drastic improvements. Most notably the power conversion efficiency has seen a steady increase in numerous reports \cite{6}. Power conversion efficiencies in the 5\% range have been reported \cite{7} and while this is not enough for on-grid electrical energy production it is sufficient for many small applications. The flexibility inherent to polymer solar cells gives them many potential advantages. The Achilles-heel of organic and polymer photovoltaics currently is, however, their short operational lifetime that has been linked to many degradation paths. To compete with inorganic semiconductor-based photovoltaics, lifetimes of 25 years or more under normal conditions with exposure to an outside environment must be achieved. The most important environmental parameters that influence the lifetime of polymer photovoltaics are diffusion of molecular oxygen and water into the active layer of the photovoltaic device and the reaction between the reactive metal electrodes and the constituents of the active layer. For this reason, the permeability of the electrodes towards small molecules like oxygen and water is an important parameter. Some of the possible solutions to the problem of oxygen and water diffusion into the cell include the use of barrier layers with low oxygen and water permeabilities. Also, “getter” materials that react with oxygen and water can be employed.

In this paper we describe the determination of the oxygen permeability of PEDOT:pTS which is the commonly
employed transparent organic anode in polymer photovoltaic cells. We further report initial studies on the stability of model photovoltaic devices using polyethylene-nitratephthalate (PET) and polyethylene (PE) as carrier substrate for polymer photovoltaics with a PEDOT:pTS anode, a MEH-PPV/PCBM bulk heterojunction as the active layer and aluminium as the cathode.

2. Experimental

2.1. Preparation of PEDOT:pTS

The PEDOT with paratoluene sulphonate (PEDOT:pTS) film was prepared by polymerisation of 3,4-ethylenedioxythiophene (EDT) using iron(III)tosylate as oxidant and pyridine as a basic inhibitor as reported earlier [8]. A volume of 6.5 ml of 40% iron(III)tosylate in butanol (Baytron C from H.C. Starck) was mixed with 0.15 ml pyridine and 0.22 ml EDT. The solution was spin coated onto polyester substrates and heated to 50°C to prevent the iron(III)tosylate from crystallising and to initiate the polymerisation. After ½ hour at 50°C the polymerisation was completed and the samples were washed twice in ethanol for 10 min in order to remove iron(II) and excess of tosylate and finally dried at 50°C for 1 h.

2.2. Oxygen diffusion measurements

The oxygen diffusion through the polymer films were measured with an OPT-5000 from PBI-dansensor. The diffusion was given in flux/bar [ml(m² day bar⁻¹)] where the difference in pressure is 1 bar. Measurements were performed with N2 (N50, 2 ppm O2) as the carrier gas and O2 (99.99%) as the test gas. The temperature was set to 38°C and the humidity to 0%. Before each measurement the oxygen diffusion through the film was stabilised for at least 30 min to obtain steady-state conditions.

After measuring the oxygen diffusion through PEDOT:pTS-coated PE films, the PEDOT:pTS layer was removed gently with an 1 M NaOH solution with a few drops of 99.9% ethanol. The cleaned PE films were measured to determine the permeability of PEDOT:pTS.

2.3. Photovoltaic characterisation

The solar cells were prepared on either PE or PET, with PEDOT:pTS as the cathode, aluminium as the anode and MEH-PPV/PCBM as the active layer. PEDOT:pTS on PE and PET was prepared as mentioned above. One-third of the PEDOT:pTS layer was removed with water to prevent contact with the aluminium anode. MEH-PPV with a molecular weight (Mw) of 375 000 g mol⁻¹ and a polydispersity (PD) of 14.3 was prepared according to the method described in the literature [9]. 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 purified product. PCBM was prepared according to the procedure described in the literature [10]. The active layer of the photovoltaic device was prepared by spincoating a hot microfiltered chlorobenzene solution of MEH-PPV (8 mg ml⁻¹) and PCBM (8 mg ml⁻¹) at an angular speed of 1500 rpm and a few millimetres were removed with chlorobenzene to establish contact with the PEDOT:pTS layer. The aluminium electrodes were applied by evaporation at a pressure of <1 × 10⁻⁵ mbar in a vacuum chamber. 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 60°C for 10 min. The active areas of the devices were approximately 3 cm². The devices were subjected to measurement directly after preparation. The solar cells were placed in a chamber with either nitrogen atmosphere (N50) or ambient atmosphere. The oxygen concentration in nitrogen atmosphere measured with a MAP Check 9000 using PBI-Dansensor was found to be <2 ppm. 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 were 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 lifetime of the devices was determined by monitoring the short circuit current, Isc, as a function of time. The electrical measurements were performed using Keithley 2400 sourcemeters. Comparison of solar cells in nitrogen and ambient atmosphere was performed on cells prepared in parallel so that the substrates from the same batch were used. The application of barrier layers and evaporation of the aluminium electrodes was as similar as experimentally possible. This was found necessary to minimise the effects of variation in the process-related parameters.

3. Results and discussion

3.1. Background

Studies on the lifetime of polymer photovoltaics have been reported in a few cases [11–18] and the major conclusion that can be drawn is that many degradation mechanisms are in play simultaneously during the operation of a polymer photovoltaic device. All the degradation mechanisms result in irreversible changes in the device that impairs the performance and lead to dysfunction of the device. The most significant degradation paths are reaction of the constituents of the active layer with oxygen and water. Also, the interface between the active layer and the electrodes has been shown to be important degradation
paths. Most notably when aluminium is employed as the cathode, it has been demonstrated that aluminium metal reacts with the organic material and gradually diffuses into the active layer giving rise to a poor electrical contact and rapid lowering of the short circuit current [18]. The use of materials that do not readily allow diffusion phenomena to take place has demonstrated significant improvements of the lifetime [19,20]. It is of paramount importance that light is shed on the possibilities for encapsulation of polymer photovoltaics and in particular that the available materials are characterised with respect to diffusion of oxygen and water. Here, we wish to report the oxygen permeability of the commonly employed transparent anode PEDOT.

3.2. Oxygen diffusion measurements on PE and PET carrier substrates

We chose to prepare the photovoltaic devices directly on the carrier substrates that were polyethylene (PE) and polyethyleneterephthalate (PET). In order to establish the contribution to the oxygen permeability by the carrier substrates, we determined the oxygen permeabilities of the carrier substrates. The oxygen flux per bar (J/P) through PE and PET films was measured by the instrument (OPT-5000) and the thickness (l) of the films was measured with a micrometer screw. From these values for the permeability, P, was calculated

\[
\frac{Jl}{\Delta p} \left[ \frac{\text{mL(STP)}}{\text{m}^2 \text{day bar}} \right] = \frac{P}{\Delta p} \left[ \frac{\text{cm}^3(\text{STP)}}{\text{m}^2 \text{day bar}} \right] \]

\[\Rightarrow P \left[ \frac{\text{cm}^3(\text{STP)}}{\text{m}^2 \text{day bar}} \right] = 1.16 \times 10^{-14} \left[ \frac{\text{cm}^3}{\text{s Pa}} \right] \]

In Table 1 our experimental permeabilities and typical values from literature are listed. It is shown that our values are in good agreement with the reported values. The deviation in the permeability may be ascribed to the differences in crystallinity and density.

3.3. Methodology for the determination of the oxygen permeability for PEDOT

Since PEDOT anodes are always applied as a thin layer, free-standing films of a thickness similar to the one employed in devices is difficult to obtain. As a solution to this we chose to use PE and PET carrier substrates during measurements. To calculate the permeability of the PEDOT:pTS layer on a carrier substrate like PE or PET, multi-laminate theory was used assuming that oxygen diffusion through polymers follows Fick’s 1. law

\[P_{\text{PEDOT-PS}} = \frac{l_{\text{PEDOT-PS}}}{I_{\text{total}}/P_{\text{total}} - l_{\text{PE}}/P_{\text{PE}}},\]

where

\[P_{\text{total}} = \frac{J_{\text{total}} \cdot l_{\text{total}}}{\Delta p_{\text{total}}} \cdot k \quad \text{and} \quad P_{\text{PE}} = \frac{J_{\text{PE}} \cdot l_{\text{PE}}}{\Delta p_{\text{PE}}} \cdot k \]

\[\Rightarrow P_{\text{PEDOT-PS}} = \frac{l_{\text{PEDOT-PS}}}{(1/J_{\text{total}}/\Delta p_{\text{total}} - 1/J_{\text{PE}}/\Delta p_{\text{PE}})} \cdot k,\]

where k is the conversion factor, \(k = 1.16 \times 10^{-14} \text{m}^2\text{day bar}/(\text{s Pa cm}^2),\) and \(\Delta p_{\text{total}} = \Delta p = 1\text{bar}.\)

We found that the oxygen permeability of PEDOT was similar to PET and therefore PET was not suitable as a carrier substrate for accurate measurements. PE was, however, well suited as a carrier substrate since oxygen diffusion in PE is much faster. The thickness of the PEDOT:pTS layer measured using AFM was found to be 250 nm.

3.4. The effect of the barrier layer on the performance of solar cells

All lifetimes curves of the solar cells were fitted with a double exponential function \(I_{\text{sc}}(t) = a \cdot e^{-bt} + c \cdot e^{-dt}\) as described earlier [17]. The first, \(T_{1},\) and the second, \(T_{2},\) half-life for the solar cells were found to be

\[T_{1} = \frac{\ln(2)}{b} \quad \text{and} \quad T_{2} = \frac{\ln(2)}{d}\]

They were used to describe the lifetime curves. By integrating the lifetime curves, from 0 to 30 000 s, the total amount of charge was found and is a good standard of reference for the solar cells, see Table 2. SC1PE and SC1PET,O2 were only integrated to 3000 s because the experiment was stopped because of a very low \(I_{\text{sc}}.\)

According to the half-life, \(T_{1}\) is generally 10 times shorter than \(T_{2}\) except for SC3PET,O2 and SC4PE,N2. The amount of charge produced for the first term is generally 10 times larger except for SC3PET,O2 and SC4PE,N2. This indicates that the curves have a steep decay in the beginning of the measurements followed by a more slow decay. The low values generally observed for \(I_{\text{sc}}\) is ascribed to sheet resistive losses i.e. there is no underlying layer with high conductivity.

3.5. The effect of PE and PET as a barrier

The degradation of solar cells on a PE substrate is faster than for solar cells on a PET substrate when operated in the atmosphere. We ascribe this in part to the faster transport of oxygen through PE as compared to PET. We cannot neglect the effect of water transport into the cell through the substrate where water transport in PE is known to be ~20 times faster than in PET [22,23]. From the experiments in a nitrogen atmosphere where the oxygen and water content is <2 ppm degradation still takes place but is slowed down by a factor of 10. Since the degradation in a nitrogen atmosphere is slower than degradation in air this confirms that the atmosphere (oxygen and water) has a damaging effect on the lifetime of the solar cells. Recent
The oxygen permeability obtained for PEDOT:pTS was determined on a PE carrier substrate at 38 °C. The permeabilities of PE and PET were measured at 38 °C and 50 °C and the permeabilities were successively calculated at 25 °C according to the Arrhenius equation. This was performed to verify the results obtained by the OPT-5000.

### Table 2

Half-lives for the solar cells measured under short circuit conditions. The total charge per area \(Q_I\), the total charge produced per area \(Q_{exp}\) and the total charge produced per area \(Q_{exp}\) at infinity \(Q_{inf}\), for the duration of the experiment \(Q_{exp}\) and \(I_{oc} \) max.

<table>
<thead>
<tr>
<th>Device</th>
<th>(T_1) (s)</th>
<th>(T_2) (s)</th>
<th>(Q_I) (μC/cm(^2))</th>
<th>(Q_{exp}) (μC/cm(^2))</th>
<th>(Q_{inf}) (μC/cm(^2))</th>
<th>(I_{oc} ) max (μA/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SC1PEDOT</td>
<td>1.4 \times 10^5</td>
<td>2.3 \times 10^1</td>
<td>7.7 \times 10^1</td>
<td>1.2 \times 10^3</td>
<td>1.3 \times 10^3</td>
<td>1.3 \times 10^3</td>
</tr>
<tr>
<td>SC1PETO</td>
<td>4.1 \times 10^4</td>
<td>8.5 \times 10^0</td>
<td>1.9 \times 10^2</td>
<td>1.4 \times 10^4</td>
<td>1.5 \times 10^4</td>
<td>1.5 \times 10^4</td>
</tr>
<tr>
<td>SC2PEDOT</td>
<td>1.7 \times 10^2</td>
<td>2.8 \times 10^0</td>
<td>4.5 \times 10^3</td>
<td>1.3 \times 10^5</td>
<td>1.7 \times 10^5</td>
<td>2.0 \times 10^5</td>
</tr>
<tr>
<td>SC2PETO</td>
<td>1.6 \times 10^2</td>
<td>1.0 \times 10^0</td>
<td>1.8 \times 10^3</td>
<td>1.2 \times 10^5</td>
<td>1.4 \times 10^5</td>
<td>1.5 \times 10^5</td>
</tr>
<tr>
<td>SC3PEDOT</td>
<td>1.2 \times 10^2</td>
<td>1.7 \times 10^0</td>
<td>3.9 \times 10^3</td>
<td>4.1 \times 10^5</td>
<td>4.1 \times 10^5</td>
<td>4.1 \times 10^5</td>
</tr>
<tr>
<td>SC3PETO</td>
<td>2.1 \times 10^2</td>
<td>2.1 \times 10^0</td>
<td>2.0 \times 10^3</td>
<td>1.9 \times 10^5</td>
<td>4.0 \times 10^5</td>
<td>3.8 \times 10^5</td>
</tr>
<tr>
<td>SC4PETO</td>
<td>1.6 \times 10^2</td>
<td>6.3 \times 10^0</td>
<td>1.3 \times 10^4</td>
<td>3.7 \times 10^5</td>
<td>3.9 \times 10^5</td>
<td>3.9 \times 10^5</td>
</tr>
<tr>
<td>SC4PETO</td>
<td>2.0 \times 10^3</td>
<td>2.1 \times 10^0</td>
<td>1.0 \times 10^5</td>
<td>9.3 \times 10^5</td>
<td>1.0 \times 10^6</td>
<td>1.0 \times 10^6</td>
</tr>
</tbody>
</table>

Work has shown that water is particularly soluble in PEDOT:PSS and is responsible for part of the degradation [24]. Water diffusion through the substrates in our case is also expected to be responsible for some of the degradation. While this was not established through the present work it will be the subject of future work.

### 4. Conclusion

The permeability of PEDOT:pTS was determined to be \(2.5 \pm 0.7 \times 10^{-15}\) cm\(^3\)/(STP) cm/cm\(^2\) s Pa using PE and PET carrier substrates and multi-laminate theory for the extraction of the value for the oxygen permeability of PEDOT:pTS. Solar cells were prepared on PE and PET carrier substrates and as expected the solar cells prepared on PE carrier substrates produced a smaller amount of charge than the solar cells prepared on PET carrier substrates. Thus, a greater oxygen (and water) diffusion through the barrier layer leads to a faster decrease of the short-circuit current and a reduction of the lifetime of polymer-based solar cells.

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