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Flexible, long-lived, large-area, organic solar cells

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Abstract

We report herein large area ($>10\,cm^2$), interconnected organic solar cell modules both on glass substrates as well as on flexible ultra-high barrier foils, reaching 1.5% and 0.5% overall power conversion efficiency under AM1.5 conditions. Series connection is described, as these modules consist of up to three cells. Using our flexible barrier material, a shelf lifetime of polythiophene-based solar cells of 6000 h could be realized. Furthermore, we compare the photovoltaic performance of efficient conjugated polymer:fullerene solar cell modules with established technologies. Under typical indoor-office lighting, our modules are competitive with these systems.

Keywords: Organic solar cells; Photovoltaics; Bulk heterojunction; Encapsulation; Stability; Shelf lifetime

1. Introduction

In order to meet the demand for renewable energy, the photovoltaic sector has experienced exponential growth over the last years. In 2004 alone, the worldwide photovoltaic (PV) market grew by 58.5% [1]. This positive development is expected to continue in the future: an increase of the market from 5.8 billion euros (2004) to 25 billion euros in 2010 seems realistic [1]. In 2004, 90% of this emerging market was dominated by wafer-based crystalline silicon technology [1]. Nevertheless, new technologies are being developed and forecast to enter the market in the near future. One of these promising alternative concepts is organic solar cells.

Though still lacking behind in conversion efficiency, they exhibit several advantages over established technologies. Among these are the potential of cheap processing on large areas, possible semi-transparency, mechanical flexibility and light weight.

In this contribution, we deal with issues regarding the process of upscaling organic solar cells from laboratory design to shape devices that deliver appreciable electrical power to actually drive electronic gadgets or that can charge up a battery. Series connection of solar cells is discussed as it is desirable to increase the output voltage of the module, and also allows the effective use of the surface area of solar cell modules. The influence of the electrode width on the photovoltaic performance of the device is demonstrated by numerical calculations. We furthermore demonstrate efficient large area modules consisting of up to three series connected solar cell units and directly compare their performance to other solar cell technologies under various illumination intensities. Moreover, we deal with the aspects of encapsulation necessary to realize long-lived, flexible organic solar cells. Thus, we present shelf lifetime studies showing the feasibility of lifetimes in the range beyond 6000 h, or more than 8 months, achieved with entirely flexible encapsulation technology.

2. Experimental

2.1. Sample preparation and characterization

The samples investigated herein were prepared on two different kinds of substrates: Flexible, ultra-high barrier foils from NOVA-PLASMA, Inc. (a detailed description can be found in Ref. [2]) and glass slides covered with

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indium tin oxide (ITO, purchased from Merck, Inc.). The ITO bottom electrode was structured by deposition through a shadow mask directly onto the ultra-high barrier in the case of the foils and by chemical wet etching in the case of ITO on glass. A sheet resistance of approximately 60 Ω/square could be reached in the first case, of 15 Ω/square in the second. The substrates were subsequently covered with a layer of poly(3,4-ethylenedioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS, BAYTRON-PH, purchased from H. C. Starck) using the doctor blade technique. The same technique was employed to deposit the active layer from a chloroform solution of poly(3-hexylthiophene)(P3HT)/1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C61 (PCBM), ratio 1:2 (w/w). P3HT was purchased from Rieke Metals, Inc., PCBM from Nano-C, Inc.

To connect adjoined solar cell units in series, the active layer was structured by etching as shown in Fig. 1. The devices were finished with a thermally evaporated Al top electrode, using a shadow mask. The samples underwent thermal treatment at 110 °C for several minutes [3] prior to recording the current–voltage (I–V) characteristics with a Keithley 236 source measure unit. For the characterization as well as the determination of the power conversion efficiency, simulated AM1.5 solar irradiation (Steuernagel Lichttechnik GmbH, 100 mW cm^{-2}) was used unless explicitely stated otherwise. To compare solar cells based on various technologies a white box containing two fluorescent tubes (Philips PL-L 18W/840/4P, 18 W), dimmed to obtain the corresponding light levels (measured with a TES-1334 lightmeter) was used.

2.2. Degradation studies

For the degradation studies, devices built on and sealed with ultra-high barrier foils were used. Unlike the conjugated polymer deposition procedures that were done in air, the encapsulation step was carried out in a glove box in pure, dry Ar atmosphere. A two-component epoxy resin was used to seal the device with a top cap made of the same barrier material as the substrate. After curing the epoxy, the overall structure kept an appreciable flexibility. The active area of the non-optimized P3HT:PCBM-based solar cells was roughly 60 mm^2 (20 × 3 mm), yielding an overall power conversion efficiency of ~0.25%. Their shelf lifetime was compared to solar cells based on blends of poly [2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylene-vinylene] (MDMO-PPV, Covion GmbH) with PCBM (mass ratio 1:4, cast from chlorobenzene). Besides the different solvent, the device preparation was carried out analogously to the P3HT:PCBM case. The MDMO-PPV-based cells showed quite low initial power conversion efficiency under AM 1.5 conditions of about 0.035% (fill factor (FF) = 0.26; open circuit voltage (V_{OC}) = 1100 mV; short circuit current (I_{SC}) = 0.12 mA cm^{-2}). This is caused by the very large surface area (30 × 57 mm) of the two non-optimized series connected cells and an ITO coating with a high sheet resistance. However, we believe that the photovoltaic performance, limited due to an overwhelming series resistance, does not influence our lifetime study.

The shelf lifetimes reported herein represent the time the devices keep more than 50% of their initial efficiency measured under simulated AM1.5 solar irradiation. Between successive measurements, the solar cells were stored in the dark in ambient conditions (20–25 °C, 35–50% relative humidity).

3. Results and discussion

3.1. Modeling module performance

In large area solar cell modules, the dimensions of the electrodes is of outmost importance to avoid unnecessary losses. Organic solar cells require at least one transparent electrode to allow light to enter the photoactive layer. Typical materials for this electrode are transparent conducting oxides (TCO), such as ITO or fluorinated tin oxide. Novel approaches also include layers of doped conducting polymers [4,5] or even films of carbon nanotubes [6]. The limited conductivity of these materials induces restrictions on the design of solar cell modules.

To model the performance of organic solar cells, we assume the transparent electrode to be resistive, while the evaporated metal top electrode is considered not to contribute to resistive losses of the converted incident radiation power. We justify this simplification by a significantly smaller sheet resistance of the Al electrodes (< 1 Ω/square) yielding negligible losses compared to the ITO. The I–V characteristics of a solar cell of width w with one resistive electrode can be calculated by solving the two

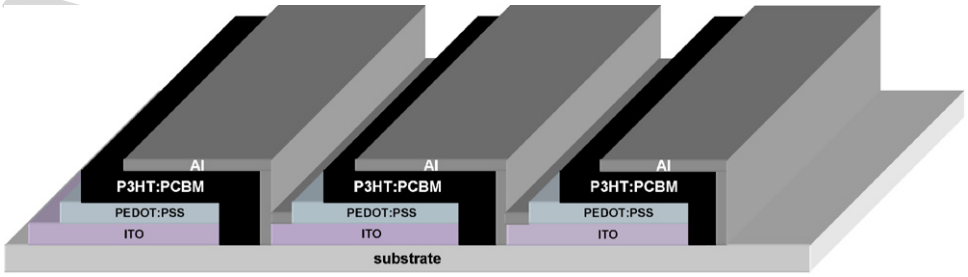

Fig. 1. Serial connection of organic solar cells.

coupled first-order differential equations for current $I(x)$ and voltage $V(x)$:

$$V'(x) = -\rho I(x) \quad (1)$$

and

$$I'(x) = j(V(x)) \quad (2)$$

with the boundary conditions:

$$V(0) = V_0 \text{ and } I(0) = 0.$$

In Eq. (1), ρ denotes the sheet resistance of the ITO, in Eq. (2), $I(x)$, is the lateral current flowing in the resistive electrode, while $j(V(x))$ is the current density delivered by the solar cell segments of infinitesimal size at position x (Fig. 2). The boundary condition $V(0) = V_0$ has to be chosen such that the electrical power of the device $P = V(w)\ I(w)$ is maximized, i.e., the solar cell works in the maximum power point. Calculations like this are typically used to help designing inorganic thin film solar cell modules, but rely on simplifications that are only valid close to the optimum electrode dimensions for certain light intensities. We chose a more general, direct numerical calculation of the efficiency as a function of the electrode dimension.

Starting point for the calculations is a typical organic solar cell with a width of 3 mm. The results are displayed in Fig. 3 and clearly show the rapid decay of the device efficiency upon increasing the width of the solar cell. Two cases are plotted in Fig. 3, the first displays results on a high-quality ITO on glass substrate, where 15 Ω/square can be reached, while the second case of 60 Ω/square is a typical value for ITO sputtered on flexible substrates.

In Table 1, the efficiencies of single devices with equal electrode area, but three different electrode shapes are compared. Only the width of the electrode is relevant for the device efficiency, nevertheless we have chosen different lengths to illustrate that the power output of a 10 cm^2 rectangular solar cell can deviate by more than a factor of six depending on the ratio of the side lengths. Within realistic ranges of substrate conductivities (15–60 Ω/square in our case), the overall device efficiency heavily depends on the width of the electrode. To keep the resistive losses in the electrode as small as possible, the width has to be narrow with the contacts taken on the long sides. This minimizes the distance the charge carriers extracted from the active layer have to travel in the resistive ITO electrode.

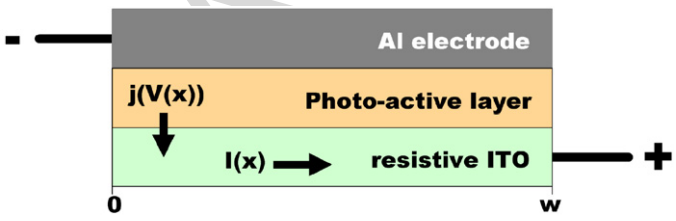

Fig. 2. Scheme showing the current produced by the infinitesimal segments of the photo-active layer ($j(V)$) and the current in the resistive ITO bottom electrode ($I(x)$).

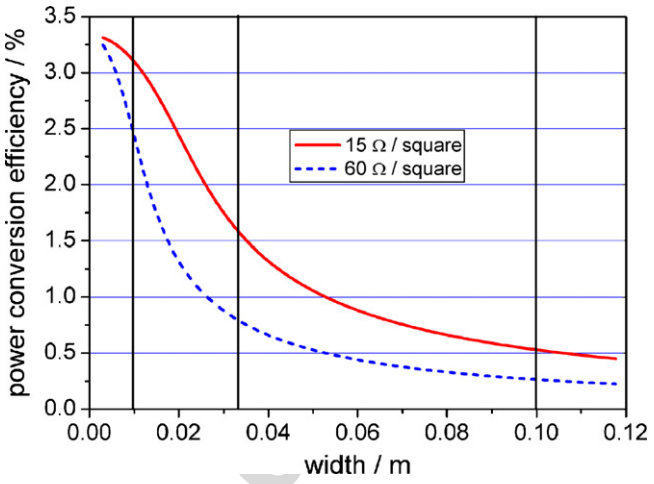

Fig. 3. Calculated theoretical power conversion efficiency of a P3HT:PCBM-based single rectangular organic solar cell as a function of the width of the electrode. Two cases are shown, an ITO sheet resistance of 15 Ω/square (solid line) and 60 Ω/square (dashed line). The vertical lines indicate the widths of the electrodes compared in Table 1.

Table 1
Calculated theoretical power conversion efficiencies of a P3HT:PCBM-based single rectangular organic solar cells. Three device dimensions are compared

Shape	Length (cm)	Width (cm)	Sheet resistance (Ω/square)	Efficiency (%)
Square	3.3	3.3	15	1.6
Square	3.3	3.3	60	0.8
Broad stripe	1	10	15	0.5
Broad stripe	1	10	60	0.25
Narrow stripe	10	1	15	3.1
Narrow stripe	10	1	60	2.4

To effectively cover large surface areas, it has to be divided among separate, but interconnected devices.

3.2. Series connected solar cell devices

Organic solar cells operated to produce the maximum power output typically deliver a voltage of around 500 mV. For most applications higher voltages are desirable. As the produced current scales with the active area of the photovoltaic device, large solar cells are needed to produce more electrical power. To meet both demands, solar cell modules have to be created in which the photovoltaic units are connected in series to add up the produced voltage.

We have manufactured organic solar cell modules with a total active surface area of up to 17.1 cm^2, showing power conversion efficiencies of 1.5%.

Fig. 4 shows the I–V characteristics of these large-area organic solar cell modules consisting of two or three solar cells connected in series. These modules are built on ITO/glass substrates. The photovoltaic performance is shown in more detail in Table 2. From the theoretical considerations

presented in Fig. 3, much higher power conversion efficiencies are expected. We explain this deviation with a high degree of inhomogeneity and defects. These are increasingly difficult to avoid with larger surface areas as the samples have not been prepared in clean room conditions. Furthermore, we believe shorts between the electrodes are responsible for a decreased V_{OC} of nominally less than 600 mV for each single cell (Table 2). The series connection (Fig. 1), as described in Section 2.1, is done manually and therefore does not represent a viable procedure to be realized on an industrial scale. For a scaled-up production, different techniques are necessary. We have demonstrated a process based on selective laser scribing of the various layers of the organic solar cell [7]. This process is analogous to the established technology used in amorphous silicon.

3.3. Solar cell performance under various illumination conditions

Even when the losses upon upscaling are minimized, the power conversion efficiency of bulk heterojunction solar cells operated under AM1.5 conditions does not reach that of established technologies based on inorganic semiconductors or even dye sensitized solar cells (DSC) [8]. One of the reasons for this is the incapacity of the most widely used organic donor/acceptor blends such as P3HT:PCBM to convert low energy photons into current. This drawback is less pronounced if not sunlight but artificial light is collected, i.e., indoor applications are targeted. Especially, fluorescent tubes emit light mostly below 600 nm, a region in which P3HT:PCBM solar cells efficiently absorb light and convert it into electric current.

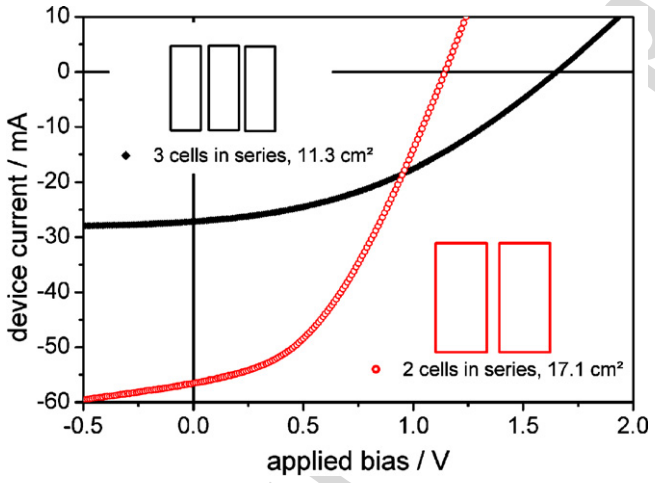

Fig. 4. *I–V* characteristics under simulated solar irradiation of an organic, P3HT:PCBM-based solar cell module on ITO/glass substrates consisting of two (circles) or three (diamonds) cell connected in series.

In Fig. 5, solar cells based on various technologies are compared to P3HT:PCBM bulk heterojunction modules on ITO/glass substrates sealed with a glass plate. Under the favorable lighting from fluorescent tubes, especially at lower illumination levels, our organic solar cells are competitive with commercially available products. The highest power conversion efficiencies among the studied systems are found in monocrystalline silicon cells (SunPower A300), small area DSC (0.16 cm^2 active area, made at Solaronix) and solar cells based on amorphous silicon (7 cell module on glass for low-light applications, SOLEMS S.A.). At illumination levels as low as 400 lux (typical office lighting) the manually made, lab standard organic solar cells are already in the range of CdTe-based devices (Panasonic BP-378234, 8 cell module for low-light applications) and outperform flexible competitors based on amorphous silicon (early prototype, 9 cell module on polyimide made by Flexcell) and DSC technology (Ti-foil and ITO coated poly(ethylene terephthalate) (PET) as electrodes). The power output of the organic solar cell also decreases less with the illuminance than most other technologies. At 2000 lux, the power per unit area generated by the crystalline silicon-based cell is almost four times the power of the P3HT:PCBM cell. This ratio is reduced to less than two for the 400 lux intensity. The lower graph in Fig. 5 illustrates this effect. By plotting the normalized power output the decrease of the performance with the light intensity is revealed. The P3HT:PCBM-based solar cells deliver at 400 lux about 20% of the power at 2000 lux hence losing less in efficiency than all other tested technologies. We attribute this favorable behavior to an only slight dependence of V_{OC} and a linear dependence of I_{SC} on the light intensity [9] in the measured range of illuminance.

3.4. Flexible super-barrier material for encapsulation of organic solar cells

A common drawback of most organic solar cells is their sensitivity to moisture and oxygen. Both, the photoactive layer and the top electrode material are affected [10–12]. It is therefore necessary to protect them by a gas tight encapsulation. A straightforward solution is to cover the solar cells with glass plates. Though ensuring optimum

Table 2
Measured power conversion efficiencies of P3HT:PCBM-based organic solar cell modules. Typical photovoltaic performance of two and three cell devices

Cells	Length (cm)	Width (cm)	Total area (cm^2)	V_{OC} (V)	I_{SC} (mA)	Fill factor	Efficiency (%)
2 ×	5.9	1.4	17.1	1.14	56.5	0.416	1.5
3 ×	3.9	0.95	11.3	1.66	27.2	0.39	1.5

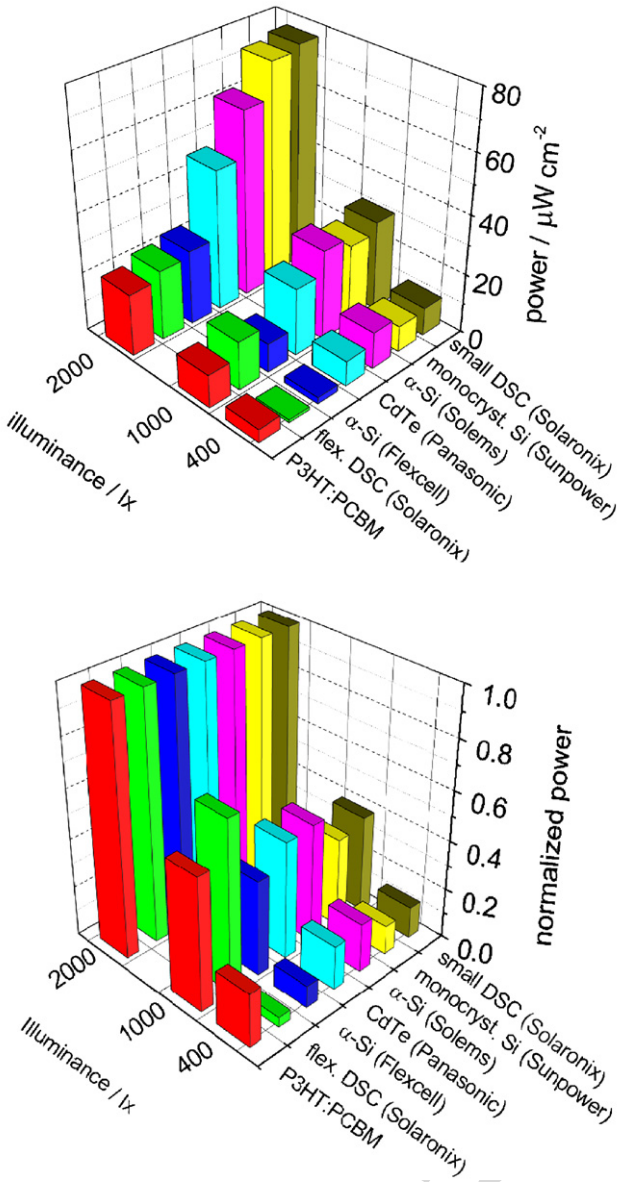

Fig. 5. Absolute (upper graph) and normalized (lower graph) power output per surface area of diverse solar cell technologies under illumination with fluorescent tubes yielding various illuminance levels.

encapsulation, one of the most important advantages of the organic solar cell concept is sacrificed: the mechanical flexibility.

To the best of our knowledge, only timid steps have been undertaken to produce large-area organic solar cells on flexible substrates, announcing single cells with an active area of less than 2 cm^2 [13,14]. We have demonstrated large area modules consisting of three interconnected solar cells of 11.3 cm^2 total active area produced on flexible ultra-high barrier foils. Fig. 6 compares their photovoltaic performance to the same design on ITO/glass. While the power conversion efficiency of the second type of device reaches 1.5% (Table 2), only 0.5% ($I_{SC} = 13.9$ mA, $V_{OC} = 1.38$ V, FF = 0.29) are achieved on the flexible substrates. We attribute this not only to the inferior sheet resistance of the ITO, but as well to its higher surface roughness and inhomogeneity of the available ultra-high barrier ITO coating.

To be competitive on the market, solar cells not only have to be produced cost-effective but also they need to show reasonable power conversion efficiencies, and also long lifetimes are desirable. Keeping 50% of the initial efficiency for at least 10000 h under illumination was found to be the lower limit for a viable product [15].

Figs. 7 and 8 show the results of shelf lifetime studies performed on flexible, encapsulated organic solar cells based on two different material combinations. The MDMO-PPV:PCBM devices remain above 50% of their

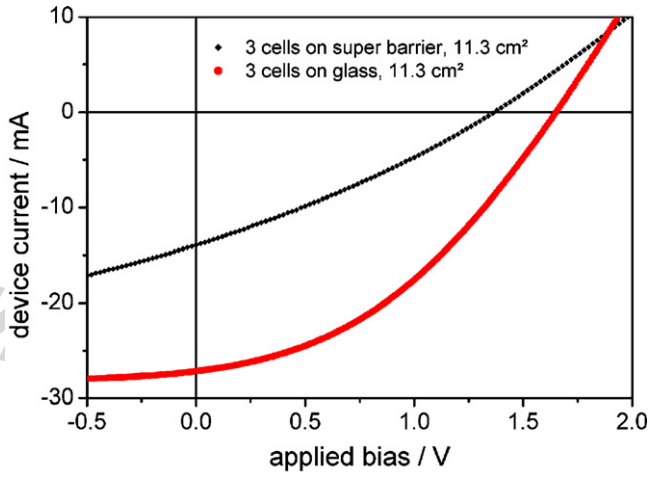

Fig. 6. *I–V* characteristics under simulated solar irradiation of an organic, P3HT:PCBM-based solar cell module (11.3 cm^2 active area) consisting of three cells connected in series on ITO/glass (circles) and ITO/ultra-high barrier substrate (diamonds).

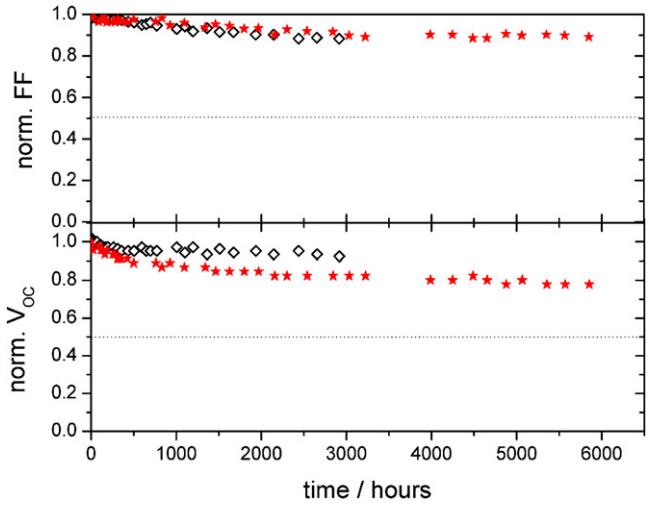

Fig. 7. Normalized V_{OC} and FF of solar cells based on MDMO-PPV:PCBM blends (open diamonds) and P3HT:PCBM blends (stars) encapsulated with flexible gas barrier material versus storage time in the dark under ambient air.

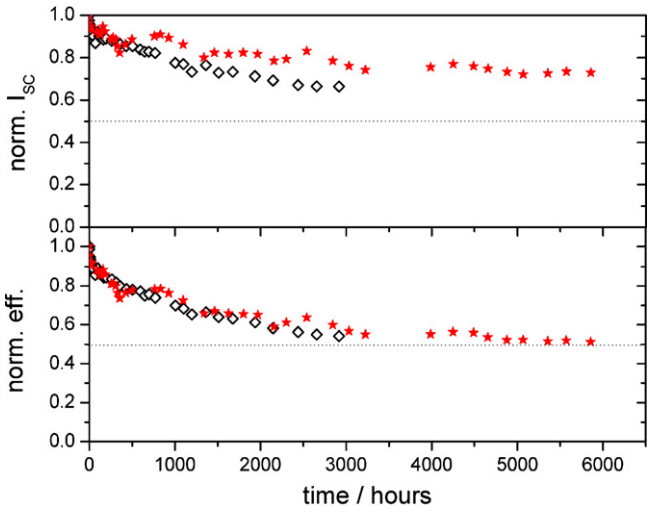

Fig. 8. Normalized I_{SC} and efficiency of solar cells based on MDMO-PPV:PCBM blends (open diamonds) and P3HT:PCBM blends (stars) encapsulated with flexible gas barrier material versus storage time in the dark under ambient air.

initial efficiency for more than 3000 h. During this time, the V_{OC} stays remarkably constant and even after 3000 h, I_{SC} and the efficiency possess 67% and 54% of their initial values, respectively. A significant part of the observed performance drop occurs during the first 50 h of the experiment. Qualitatively the degradation of P3HT:PCBM solar cells follows a similar behavior, but happens on a longer time scale. The FF is stable over long times, degrading only slowly. While V_{OC} decays faster than in the case of MDMO-PPV-based samples, I_{SC} decreases significantly slower from the initial value. The efficiency figure accumulates all these contributions and stays above 50% of its starting value up to 6000 h. The flexible gas barrier encapsulation used in this study drastically increases the lifetimes of conjugated polymer:fullerene solar cells. While a simple PET film as encapsulation provides a shelf lifetime of less than 6 h [2,7], our ultra-high barrier material yields lifetimes exceeding 3000 h in MDMO-PPV:PCBM. This is comparable to those reported for the same type of cells encapsulated between glass plates [16] suggesting that degradation may not be related to the flexible gas barrier itself, but to the intrinsic instability of the photo-active material. This is supported by the significantly longer lifetimes achieved by using P3HT:PCBM blends as active layers of the solar cell devices. The 6000 h of device stability achieved so far is not sufficient for a product viable on the market, but certainly shows the effectiveness of the ultra-high barrier foils.

4. Conclusion

We have demonstrated interconnected large-area, organic solar cells both on glass substrates as well as on flexible ultra-high barrier foils. Though less efficient than their rigid counterparts, we have realized 0.5% efficient flexible solar cell modules consisting of three series connected devices having a total active surface area of around 11 cm^2. The ultra-high barrier material is capable of sustaining a shelf lifetime of 6000 h, or more than 8 months, in the case of the P3HT:PCBM-based cells.

Furthermore, we could show that our efficient solar cell modules on high-quality ITO/glass substrates are competitive in their photovoltaic performance to established technologies in typical indoor-office lighting.

Acknowledgments

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