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The impact of water vapor transmission rate on the lifetime of flexible polymer solar cells

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In this paper we perform accelerated lifetime testing on high efficiency flexible poly(3-hexylthiophene):[6,6]-phenyl C61 butyric acid methyl ester (P3HT:PCBM) solar cells encapsulated with food package quality barrier films with a water vapor transmission rate of 0.2 $g/(m^2\ day)$ at 65 °C/85% relative humidity. We show that lifetimes exceeding 1250 h, even at high temperature/high humidity conditions, may be reached, proving that organic solar cells are significantly less sensitive against the environmental effects of water and oxygen than previously expected. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2975185]

It is well known that organic solar cells are sensitive with respect to oxygen and water in the atmosphere[1,2] and therefore require packaging as protection. Only recently have studies begun to correlate the lifetime of organic solar cells and the properties of the packaging materials that are used to protect them against the environmental influences of oxygen and water.[3–5] Shelf lifetimes of several thousands of hours, for cells packaged with flexible ultrabarrier films with water vapor transmission rates (WVTRs) in the range of 1×10^{-3} $g/(m^2\ day)$, could be demonstrated in some of these experiments. The degradation observed in these trials was mainly related to a degradation of water sensitive electrodes. Recent advances in materials have made it possible to significantly improve the moisture sensitivity of organic photovoltaic (OPV) cells.[5–9] In this paper accelerated lifetime (ALT) testing, with conditions that are chosen close to international standards for inorganic solar cells,[10,11] is used to investigate the degradation of flexible P3HT:PCBM cells with 2.5%–3.5% efficiency (100 mW/cm^2 AM1.5 illumination), which are encapsulated with food package quality barrier films with a WVTR of 0.2 $g/(m^2\ day)$ at 65 °C/85% relative humidity (rh) only.

It is widely known that organic light emitting diodes (OLEDs) require barrier films with a WVTR of 1×10^{-6} $g/(m^2\ day)$ at 25 °C and 40% rh.[12] The general perception is that organic solar cells will require the same level of protection in order to achieve lifetimes in the order of 3–5 years of outdoor exposure. With our measurements we demonstrate that the sensitivity of OPV cells against water and oxygen is significantly lower than that of OLEDs, making low-cost flexible products with a significant lifetime much more feasible.

The barrier films used in this study were characterized with respect to their WVTR using an electrical calcium test.[13] To test the samples a 250 nm thick Ca-sensor was evaporated onto a glass substrate and then contacted with Ag electrodes. The Ca-sensor was then encapsulated under inert atmosphere with the barrier film, and subsequently placed in air inside a climate chamber with controlled temperature and humidity, where the resistance of the Ca-sensor was continuously monitored. The slope of the inverse of the resistance of the Ca-sensor is directly proportional to the WVTR rate of the film. Measurements of two samples are shown in Fig. 1. Three samples of the film were tested at each of two climate conditions, 40 °C/90% rh and 65 °C/85% rh. The WVTR results were cross checked with Mocon measurements[14] performed by the Mocon Testing Service in Minneapolis. Mocon measurements were also used to evaluate the Oxygen transmission rate (OTR) of the barrier films as well. The barrier performance data obtained are summarized in Table I. There is good agreement between the Mocon and the Ca-test data.

To investigate lifetime, OPV cells were prepared on flexible polyethylene terephthalate/indium tin oxide substrates according to the procedure outlined elsewhere.[15–18] All production steps, with the exception of the evaporation of the back electrode, were performed in air. Following production the cells were encapsulated in ambient atmosphere (22 °C/~40% rh) by laminating the barrier film to the front and back sides of the cell. The cells were manufactured on 5×5 cm^2 substrates, with two cells with an area of

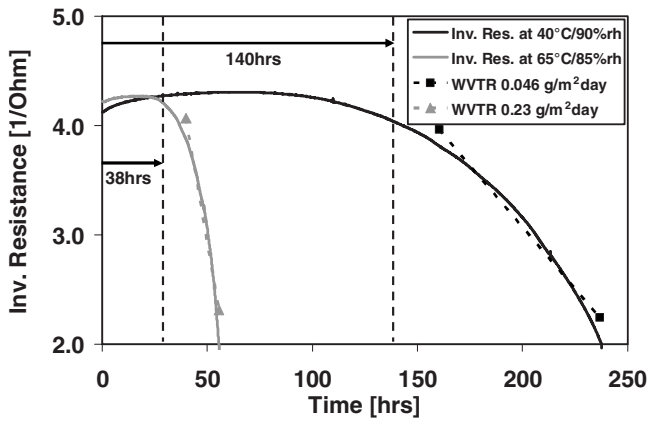

FIG. 1. Inverse resistance of the Ca-sensor vs time for samples of the barrier film at 40 °C/90% rh and 65 °C/85% rh. The soak time at 65 °C/85% rh is around 38 h while it is 140 h at 40 °C/90% rh. In the permeation regime the WVTR rate is obtained from a linear fit to the data.

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TABLE I. Summary of test results obtained for barrier films. The reported Ca-test results are the average of three samples that were measured.

Test	Condition	Soak time	WVTR [(g/m^2 day)]	OTR [cc/(m^2 day)]
Ca-Test	40 °C/90% rh	140 h	0.06 ± 0.015	···
Ca-Test	65 °C/85% rh	38 h	0.2 ± 0.1	···
Mocon	38 °C/100% rh	···	0.06	···
Mocon	65 °C/100% rh	···	0.38	0.12 ± 0.1

1 ± 0.1 cm^2 per substrate. A schematic cross section of the cells is shown in Fig. 2. Prior to characterization the area of each individual cell was measured in order to accurately determine the efficiency. The manufacturing process was repeated multiple times in order to establish the efficiency of the flexible cells in a reproducible standard process. The efficiency versus the number of cells is shown in Fig. 2. Only cells that showed a minimum of 2.5% efficiency and fill factor (FF) $>60\%$ were selected for the degradation trials.

After packaging the cells were placed in a custom measurement holder, which was designed to withstand the environmental tests, and remained in this holder throughout the testing period. The holders had 30×30 mm^2 openings above and below the cell to allow for illumination and atmospheric exposure in the climate chamber. The cells were characterized at ambient atmosphere by measuring their *JV*-characteristics under AM1.5 G illumination at 100 mW/cm^2 with a Steuernagel Solartest 1200 solar simulator and a Keithley 2400 source measurement unit. The mismatch factor of the solar simulator for P3HT:PCBM based solar cells was assessed by cross calibrating to external quantum efficiency measurements. A mismatch factor of 0.75 was determined and all efficiency performance values reported here were corrected by this factor. Prior to measurements the cells were always allowed to cool back down to room temperature in order to eliminate temperature effects from the measurements. For this study 12 cells were placed in air at each of three different climate conditions (36 cells in total): 65 °C (high T storage), 65 °C/1 sun (sun soak), and 65 °C/85% rh (damp heat). At 65 °C and 65 °C/85% rh terminals were kept open during storage while at 65 °C/1 sun the cells were stored at J_{sc} condition (terminals shorted together). From the *JV*-characteristics V_{oc}, J_{sc}, FF, and efficiency were extracted.

Figure 3 shows the evolution of these four performance parameters as a function of time. Each point in Fig. 3 is the

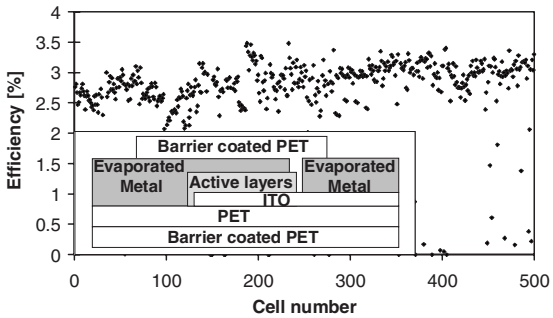

FIG. 2. Efficiency baseline established before the degradation trials to ensure a reproducible process for flexible OPV cells. The efficiency is plotted vs the number of manufactured cells. The inset shows a schematic cross section of the cells.

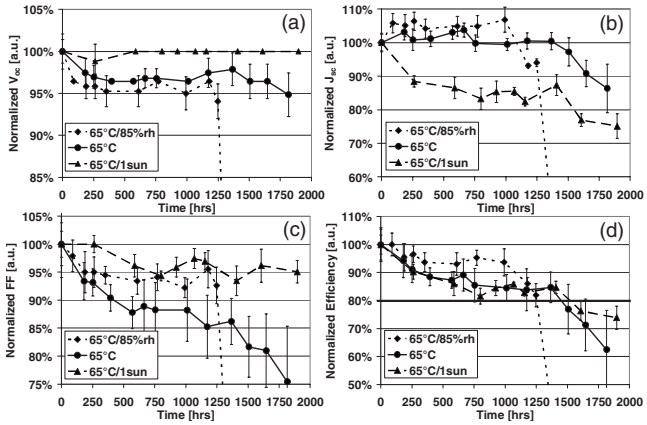

FIG. 3. Evolution of the main performance parameters (a) V_{oc}, (b) J_{sc}, (c) FF, and (d) efficiency for all three degradation conditions—65 °C/85% rh (Diamonds), 65 °C (circles), and 65 °C/1 sun (triangles). Each data point in the figures represents an average over 12 cells. The lines shown are a guide to the eyes.

average over all 12 cells placed at the respective degradation condition. The results are normalized with respect to the initial performance in order to facilitate a direct comparison between the degradation conditions.

V_{oc}, which is representative of the electrode-semiconductor interface in the cell, is very stable for the "dry" conditions 65 °C and 65 °C/1 sun. In damp heat there is a 5% drop in V_{oc} that occurs within the first 100–200 h, which may be attributed to a "soaking" of the cell, equivalent to what is observed in the Ca-test. After soaking, the active layers are assumed to be saturated and in equilibrium with their surroundings, resulting in a period where V_{oc} is stable in humid air until about 1250 h when the cell rapidly fails.

For J_{sc}, both the "dark" storage conditions high T and damp heat show better stability than the sun soaking condition. During illumination with 1 sun, J_{sc} is decreasing faster in the first 250 h than in the final 1000 h. After 1500 h the majority of the cells under illumination had failed. It is noteworthy that hero cells with stable J_{sc} for >2500 h have been measured.

The FF constantly drops for all three degradation conditions. However, despite scatter in the data, there is a difference between the two dark conditions, damp heat and high T, and the sun soak condition is visible. In the dark there is an almost identical trend in FF degradation, but remarkably the FF is more stable under illumination.

The degradation behavior observed under the three conditions shows that different stresses cause different responses. Dry heat induces a drop in FF accompanied by an increase in R_s. Analysis of the *JV*-characteristics also shows a change in the ideality factor n and the saturation current j_o, indicating changes in the morphology of the active layer. Adding light as a degradation factor, while shorting the terminals of the cells, improves the stability of the FF but causes a continual drop in J_{sc}. The loss in J_{sc} is not accompanied by a drop in optical density of the semiconductor layer, which is inconsistent with bleaching of the semiconductor, and at this point in time the reason for the J_{sc} loss is unknown.

When high humidity is added to temperature as a degrading factor, then the most visible difference is a loss in V_{oc} that occurs at the beginning of the degradation. This

indicates comparably fast onsetting change at the electrode interfaces, either through oxidation or through other interactions with water molecules entering the package. However, for a long time this presence of water does not inhibit the functionality of the cell, and only after ~1250 h rapid failure occurs, induced by a complete shunting of the cells.

In this paper we have demonstrated fully flexible P3HT:PCBM bulk-heterojunction solar cells with a well characterized package with a WVTR of 0.2 $g/(m^2\,day)$ at 65 °C/85% rh, lifetime exceeding 1250 h at 65 °C in the dark, 65 °C/1 sun, and 65 °C/85% rh. The degradation of OPV is a complex interaction between the cell and the packaging materials,[1] and we have shown that different environmental stress conditions lead to different types of degradation behavior. In order to understand lifetime it is necessary to look at all of these parameters, such that various degradation mechanisms may be separated. The data clearly show that damp heat is the condition that is most damaging to the cells. However, it is not possible to separate the degrading effects of water and oxygen. The projection of an operational lifetime from ALT testing is difficult, and acceleration factors are subject to controversy. Comparison to results obtained by the authors[5] indicates an outdoor operational life of 2–3 years for the cells investigated in this paper. However, to make meaningful comparisons with stability results obtained from other laboratories, it will be necessary to find common standards for ALT testing. Independent of this the data show that P3HT:PCBM cells are significantly less sensitive to water and oxygen than previously assumed, and that ultrabarrier films are not necessary to achieve lifetimes that are relevant for commercial products.

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