Minimal Long-Term Intrinsic Degradation Observed in a Polymer Solar Cell Illuminated in an Oxygen-Free Environment

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S *Supporting Information*

Polymer solar cells (PSCs) have attracted substantial attention over the past decade,[1,2] and research devoted to increasing the starting power conversion efficiency (PCE) has driven it above 10%.[3,4] While promising, this value only represents the initial performance of the PSCs—how the PCE of the solar cell degrades with time is also of critical importance. Commercial silicon modules are typically warrantied for 25 years, which sets the standard for the photovoltaic community.[5] PSCs that are exposed to continuous illumination and monitored over time are observed to degrade on two time scales. First, there is an initial fast degradation, called burn-in, that slows down with time. After burn-in ends, there is a second period of linear degradation. The slope of this linear portion determines a PSC's lifetime, which is chosen to be the time over which it takes the solar cell to reach 80% (T_{80}) of post-burn-in efficiency.[6] If linear degradation proceeds slowly and T_{80} is not reached while the solar cells are monitored, then the lifetime is determined from a linear extrapolation of the performance after burn-in ends.

Oxygen and water, extrinsic to PSCs, are known to affect their lifetimes;[7,8] PSCs without any packaging degrade in air in minutes.[9] While the performance of flexible plastic barrier materials has improved,[10,11] PSCs packaged with PET films demonstrate lifetimes of only several hundred to a thousand hours.[12−14] Glass-on-glass packaging has improved the observed lifetimes of several types of PSCs. When solar cells made with the polymer poly(3-hexylthiophene-2,5-diyl) (P3HT) are encapsulated in glass-on-glass packaging and illuminated for several thousand hours, extrapolated lifetimes of 5000−6000 h are observed.[6,15] PSC's with the polymer poly[9′-hepta-decanyl-2,7-carbazole-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT) have demonstrated even better extrapolated lifetimes, on the order of 12 000−18 000 h.[9,15] Assuming there are on average 5.5 h of sunlight in 1 day, 2007 h of constant illumination correspond to 1 year of operational lifetime. Thus, PSCs in flexible packaging might be expected to last 6 months, while PCDTBT solar cells in glass-on-glass packaging might last 6−9 years. It is encouraging that improvements in packaging translate into improved observed lifetimes, but important questions remain. When using encapsulated PSCs to evaluate lifetimes, there is always the question of whether the degradation rate is determined by the packaging leak rate, however small it may be. This may be from residual water in the packaging materials outgassing over time[16] or in glass-on-glass encapsulation, the leak rate of the epoxy used to seal the devices. Most importantly, it is unknown whether polymer materials, and completed PSCs, are intrinsi-cally stable enough to withstand repeated photo-excitation for the span of 25 years.

To test the intrinsic stability of PSCs in a controlled environment and to minimize extrinsic degradation through any uncertainty of package leaking, we constructed a portable environmental chamber that can hold PSCs at their maximum power point and simultaneously measure their current−voltage (*IV*) characteristics at fixed time intervals in an atmosphere with less than 0.1 ppm water and oxygen. We fabricated PSCs in both the standard and the inverted architectures, loaded them into the environmental chamber, and exposed them to continuous illumination for 7700 h (>9 months). We observed a slower burn-in for inverted architecture devices, though ultimately both standard and inverted devices lost ~40% PCE. Once burn-in ended, the linear degradation proceeded slowly. In fact, the degradation rate for many of the monitored devices was so slow that accurately assigning device lifetimes became difficult. By minimizing oxygen and water content in the atmosphere for the duration of the lifetime test, we observed that, on average, PSCs can operate with minimal intrinsic degradation for thousands of hours with extrapolated lifetimes beyond 15 years.

We fabricated PSCs using the polymer PCDTBT and the fullerene [6,6]-phenyl C_{70}-butyric acid methyl ester (PC$_{71}$BM) as the semiconducting materials (Figure 1). We chose PCDTBT because it is well studied, so it offers a point of comparison, and has previously shown promising stabil-ity.[14,15,17,18] Furthermore, it has a sufficiently high glass transition temperature (~135 °C), such that temperature induced degradation is minimal and the primary degradation is photoinduced.[17,19] We chose PC$_{71}$BM to avoid the photo-dimerization that occurs in PC$_{61}$BM.[20−22] In addition to the standard architecture, which uses PEDOT:PSS to collect holes and calcium to collect electrons, we fabricated inverted devices that use zinc oxide nanoparticles as the electron collector and molybdenum oxide as hole collector to eliminate low work function metals from the PSC. Aluminum and silver were used as reflective electrodes for the standard and inverted devices, respectively (Figure 1). Before loading the environmental chamber, IV curves of all devices were taken. The average PCE of the standard and inverted devices monitored in the lifetime test was 5.3% and 5.1%, respectively.

A

PCDTBT

PC₇₁BM

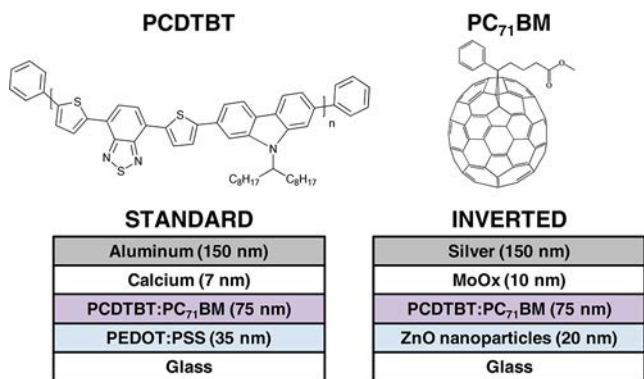| STANDARD	INVERTED
Aluminum (150 nm)	Silver (150 nm)
Calcium (7 nm)	MoOx (10 nm)
PCDTBT:PC₇₁BM (75 nm)	PCDTBT:PC₇₁BM (75 nm)
PEDOT:PSS (35 nm)	ZnO nanoparticles (20 nm)
Glass	Glass

Figure 1. Polymer PCDTBT and fullerene derivative PC$_{71}$BM were used as the semiconducting materials in the PSCs (top). Both standard (left, bottom) and inverted (right, bottom) architecture devices were monitored for 7700 h.

Over a span of 7700 h, two time scales of PSC degradation are observed, a burn-in period followed by a linear degradation (Figure 2). During burn-in, degradation is dominated by losses in open circuit voltage (Voc) and fill factor (FF). The PSCs with an inverted architecture burn-in at a slower rate than the standard ones, but ultimately both types of PSCs lose nearly 40% of their starting efficiencies. After nearly 3500 h, the slope of the PCE loss for the standard architecture devices stops changing and the linear degradation period begins. Burn-in extends another 500 h for the inverted devices, but after 4000 h they also begin the linear degradation period. The average slope of the post-burn-in efficiency loss-rate is used to calculate the life times for individual PSCs following eq 1:

$$\text{lifetime [years]} = \left(\frac{0.2}{\text{SLOPE}} \right)$$
$$\times \left(\frac{1}{365 \text{ [days/year]} \cdot 5.5 \text{ [hrs sunlight/day]}} \right) \tag{1}$$

Although linear regression is used to calculate the slopes, assigning precise lifetimes to many of the individual solar cells is difficult, as small fluctuations in the slope can create large differences in lifetime (Supporting Information Figure S3). The linear regressions for a few of the PSCs are even slightly positive, which we take to indicate essentially no degradation for 4200 h after burn-in ends. We note that the extrapolated lifetimes of a few individual solar cells in the standard architecture exceed 25 years (Supporting Information Table S2). However, when we calculate the average over all standard architecture devices, we cap the extrapolation for those solar cells to 25 years, and the extrapolated lifetimes average greater than 20 years (Table 1). The average extrapolated lifetime for

Table 1. Average Extrapolated Solar Cell Lifetimes

architecture	lifetime (hours simulated sunlight)	lifetime (years)
standard	41 000	20
inverted	16 000	8

inverted architecture devices, which clearly have a steeper degradation slope, is greater than 7 years. Over all devices, the average lifetimes we extrapolate exceed 15 years.

After 7700 h of illumination, we removed the solar cells from the environmental chamber and retested their IV characteristics using a solar simulator (Figure 3 and Supporting Information Table S1). We note that the final PCE of the standard devices measured by the solar simulator differs by 10% from what the degradation curve presented in Figure 2 implies. This stems
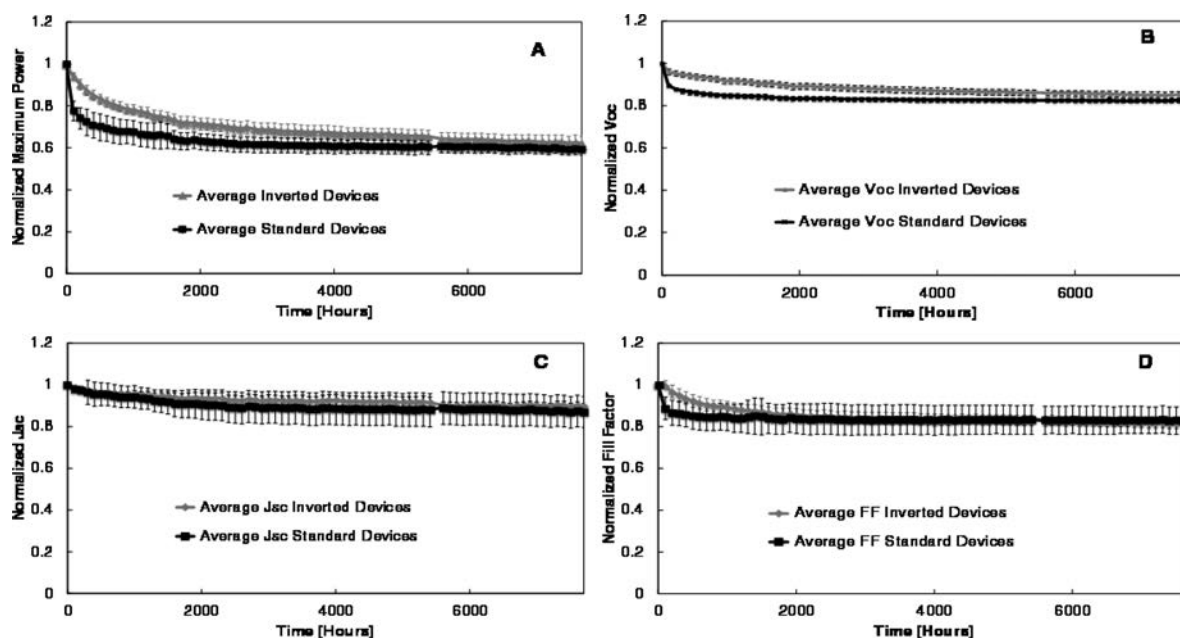

Figure 2. Normalized PCE (A), Voc (B), Jsc (C), and FF (D) for both inverted and standard devices are shown for over 7500 h (>9 months) of continuous illumination. Each data point represents the average over multiple devices every 100 hours, and the error bars represent standard deviation of these data. While a burn-in of nearly 40% occurs over the first 3500 h, mostly due to Voc and FF loss, the devices become very stable for the next 4000+ hours. Lifetimes exceeding 15 years are observed.
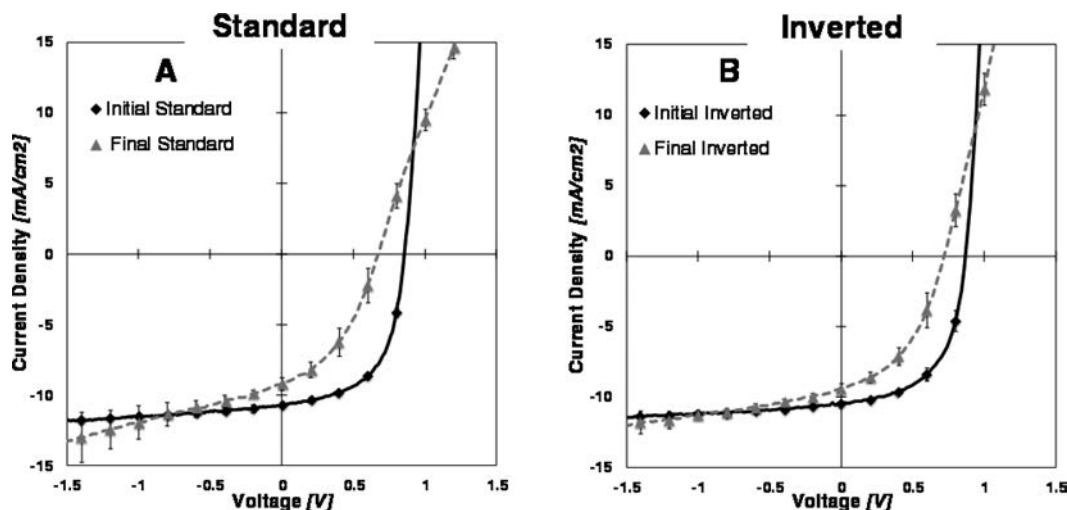
Figure 3. IV curves were taken using a solar simulator before and after the PSCs were loaded into an environmental chamber and illuminated for 7700 h. The initial performances of the standard architecture (A) and inverted architecture (B) PSCs are similar. The final IV curves of the standard architecture PSCs show a larger series resistance, probably due to brief ambient exposure after removal from the environmental chamber.

primarily from a reduced fill factor compared to the degradation curve. Indeed, the average series resistance after being removed from the environmental chamber for standard devices appears worse than that observed in the average inverted device. We believe this discrepancy occurred because of a brief exposure to ambient when removing the solar cells from the environmental chamber before placing the cells back into a glovebox, where the final measurements were taken. While the inverted devices were barely affected, the standard devices likely suffered some degradation of the calcium contacts.

Substantial loss in Voc and FF during burn-in has previously been observed for encapsulated standard architecture PCDTBT solar cells.[9,15] It has been shown to occur independent of the choice of electrodes and is considered to be the result of a photoinduced chemical reaction in the bulk materials.[17,23] That the inverted architecture devices in the present study also show burn-in dominated by Voc and FF loss only further suggests such a bulk process. Furthermore, the burn-in occurs in an environment that has very little, if any, oxygen, which strongly suggests that oxygen is not involved. We considered that residual oxygen from processing might remain in the PSCs and photo-oxidize the polymer, causing the observed burn-in. In a back-of-the-envelope calculation, we estimated the ratio of oxygen molecules to PCDTBT molecules left in the films after processing in a glovebox with 5 ppm of O_2 to be $\sim 10^{-10}$ (Supporting Information Section 3). If every oxygen molecule photo-oxidized a monomer on a PCDTBT chain, the total trap concentration would be 6 orders of magnitude below the concentration of $1/10\,000 - 1/1000$ ($10^{-4} - 10^{-3}$) that has been shown to reduce solar cell performance to the level observed after burn-in.[24−26] Thus, it is unlikely that either oxygen from the PSC's environment or residual oxygen in the films causes burn-in degradation. While aging PSC's in an oxygen-free environment does not reduce burn-in, using polymers with greater crystallinity does.[27] PSCs made from the amorphous polymers regiorandom P3HT and PCDTBT burn-in more severely than PSCs made from the more crystalline regioregular P3HT and KP115. Finding ways to inhibit burn-in degradation is critical, as a 40% loss of PCE is highly undesirable.

It is encouraging that once burn-in ends the PSCs degrade very little over more than 4000 h of continuous photo-excitation. However, with such a low water and oxygen composition, the atmospheric conditions inside the environmental chamber are nearly ideal. Any commercial PSC will be encapsulated, and the requirements of such encapsulation should be evaluated. Organic light emitting diodes (OLEDs) use similar organic semiconductors and low work function metals, and packaging is required to protect the layers from ambient atmosphere.[28,29] To reduce electrode degradation from water vapor to less than 20% over 10 000 h of operation,[30,31] Burrows estimates that the water vapor transport rate (WVTR) of an encapsulate layer must be less than 10^{-5} g/(m^2 day).[32] For a 25-year lifetime, the packaging WVTR requirements are five times stricter. Oxygen is known to react with organic semiconductor materials themselves in the presence of light, and thin films of organic semiconductors left in air and exposed to light typically photobleach in a matter of several to tens of hours.[33−36] We can apply a method similar to the one Burrows uses[32] to estimate the packaging requirements necessary to protect the organic materials from oxygen while exposed to light. Assuming the PCDTBT PSC structure, there are 1.4×10^{-4} moles in one square meter of active area. If a PCE degradation of 20% corresponds to the photo-oxidation of 1 in every 10 000 monomer units,[24−26] then about 1.4×10^{-8} moles O_2/m^2 is required to cause such degradation (Supporting Informatoin Section 4). The corresponding daily leak rate to ensure a 25-year lifetime equates to 2.0×10^{-12} moles of $O_2/(m^2$ day). Converting to the units typically used to discuss oxygen transport rate (OTR) yields an OTR of less than 4.5×10^{-8} cm^3/(m^2 day). Both the WVTR and OTR packaging requirements are several orders of magnitude lower than those of common plastic packaging such as PET films. As with OLEDs, PSCs will likely need glass-on-glass encapsulation or multilayer organic−inorganic films[37,38] with an additional getter or desiccant material in the packaging to further minimize degradation.[39−42]

Moving forward, steps need to be taken to reduce the effect of burn-in in PSCs, as burn-in is the predominant loss mechanism over the lifetime of the solar cells. More closely studying the solid state photochemistry of these PSC materials

will help elucidate the underlying chemical mechanisms and hopefully aid in materials design. In the absence of oxygen and water, the PSCs degrade very little for over 4000 h, and lifetimes exceeding 15 years are observed. With sufficient packaging, some PSCs can be intrinsically stable under continuous photoexcitation.

■ ASSOCIATED CONTENT

ⓈSupporting Information

Experimental details, tabulated device performance, and example calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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