

1-1-2011

Organic solar cells: Evaluation of the stability of P3HT using time-delayed degradation

Chung-How Poh
University of Newcastle

Chung-Kiak Poh
ckp600@uow.edu.au

Glenn Bryant
University of Newcastle

Warwick Belcher
University of Newcastle

Paul Dastoor
University of Newcastle

Follow this and additional works at: <https://ro.uow.edu.au/engpapers>



Part of the [Engineering Commons](#)

<https://ro.uow.edu.au/engpapers/4577>

Recommended Citation

Poh, Chung-How; Poh, Chung-Kiak; Bryant, Glenn; Belcher, Warwick; and Dastoor, Paul: Organic solar cells: Evaluation of the stability of P3HT using time-delayed degradation 2011, 1-6.
<https://ro.uow.edu.au/engpapers/4577>

Organic solar cells: evaluation of the stability of P3HT using time-delayed degradation

Chung-How Poh^{*a}, Chung-Kiak Poh^b, Glenn Bryant^a, Warwick Belcher^a, Paul Dastoor^a
^aCentre for Organic Electronics, University of Newcastle, University Drive, NSW 2308, Australia;
^bInstitute for Superconducting and Electronic Materials, University of Wollongong/Innovation Campus, Squires Way, Fairy Meadow, NSW 2519, Australia

ABSTRACT

Despite the fact that the performance of organic solar cells is generally susceptible to degradation by moisture exposure, there has been suggestion that the photoactive layer (P3HT) is surprisingly resilient. This work attempts to confirm the stability of P3HT as an organic solar cell material by deliberately introducing water into the photoactive layer. A dramatic step drop in device performance during cell characterization is observed approximately one day after the device has been fabricated. The time-delayed step drop in output efficiency strongly suggests that moisture has little effect on the P3HT conducting polymer.

Keywords: P3HT, PEDOT:PSS, ITO, moisture, hydroscopic, organic, solar cell

1. INTRODUCTION

The P3HT-PCBM solar cell has been a popular choice in the field of organic solar cells owing to the availability and the performance of the materials.¹ Its typical construction is as shown in Figure 1(a). A thin ≈ 30 nm PEDOT:PSS [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)] is normally inserted between the active layer and the ITO (indium tin oxide) for a better work function matching and to enable hole extraction and transport to the anode.² As demonstrated in Figure 1(b) the P3HT [poly(3-hexylthiophene)] solar cell is capable of generating a spectral response that spans nearly the entire visible spectrum, omitting only wavelengths longer than 625 nm (and those shorter than 350 nm).

The fact that it has such a considerable spectral range makes it a tentative material for solar cell application. However, the performance of the solar cell is not sustained in ambient air. Upon exposure to moist air the cell performance will deteriorate rapidly. The red dotted curve in Figure 2 depicts an example of the decay.³ Fortunately, this decay seems to be attributed primarily to the hydroscopic PEDOT:PSS rather than the P3HT photoactive material.⁴ Replacing the PEDOT:PSS with a suitable p-type material such as the NiO has substantially stabilized the cell performance.^{5,6} An inverted architecture as illustrated in Figure 2 has also been shown to have improved stability in ambient air.^{3,7} This may be that with the inverted architecture, the hydroscopic PEDOT:PSS does not come into direct contact with the ITO.

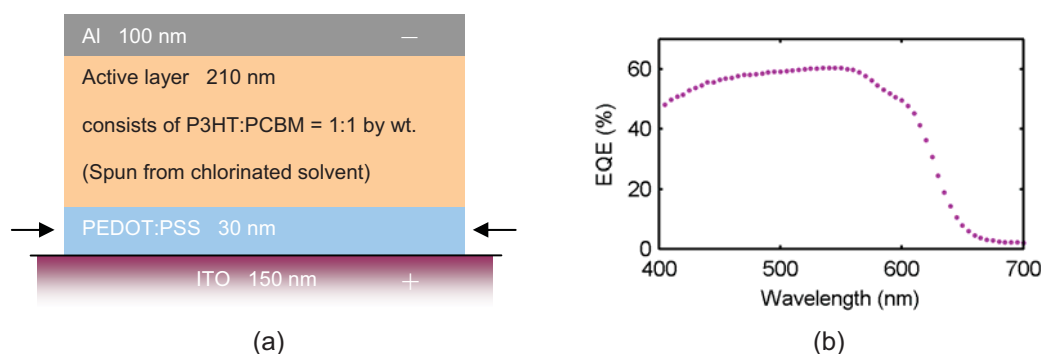


Figure 1. a) Typical P3HT-PCBM solar cell structure. b) Spectral response of the photovoltaic cell.

*Chung-How@ieee.org

Smart Nano-Micro Materials and Devices, edited by Saulius Juodkazis, Min Gu, Proc. of SPIE Vol. 8204, 82040W · © 2011 SPIE · CCC code: 0277-786X/11/\$18 · doi: 10.1117/12.903251

Proc. of SPIE Vol. 8204 82040W-1

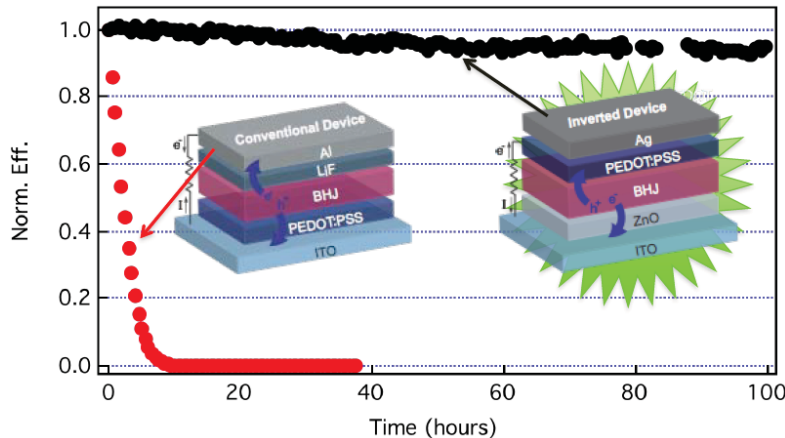


Figure 2. The decay curves of two different device architectures.

It is thought that when exposed to ambient air the hydroscopic PEDOT:PSS takes up the moisture through “edge-in” diffusion,³ as indicated by the arrows in Figure 1(a). In this work we attempt to visualize the propagation of the moisture through the film by using a physical model. We demonstrate that the instantaneous “unaffected” area corresponds to the output power of the degrading device. We then incorporate moisture directly into the active layer of the device by spin cast the layer from water saturated solvent to determine the effect of moisture on the active layer itself.

2. EXPERIMENTAL PROCEDURES

2.1 Verifying the moisture diffusion pathway

The physical model consisted of a glass substrate with a Glu Tack positioned in the center. To simulate the propagating moisture wetting the PEDOT:PSS, water was added to the perimeter of the Glu Tack after it has properly been dried. The Glu Tack turned blue on contact with water. This provided a visual indication of the progress of the moisture. The dry region remained transparent, which represents the available functional area for electrical conduction in the solar cell. It is assumed that the affected area will no longer contribute to the output power, i.e. the instantaneous output power,

$$P_{out} \propto A_{eff} \quad (1)$$

where A_{eff} is the remaining unaffected area. Thus, by monitoring the size of the transparent region around the middle of the glass substrate, it will be possible to simulate the way the output power decays when moisture is diffusing into the PEDOT:PSS layer via the edges. The sample appearance was recorded by a flatbed scanner every 30 seconds for 13 minutes until the moisture propagation has become slow. Edge detection was performed on the recorded images to determine the instantaneous size of the available area.

For the purpose of cross checking, a standard P3HT solar cell with structure as depicted in Figure 1(a) was fabricated so that its decay profile under ambient air conditions could be acquired. The maximum output power of the solar cell was noted at a 20 minute interval over a period of 18 hours. Green LED with peak wavelength at 530 nm was used to illuminate the solar cell. The LED was only turned on long enough to determine the cell maximum power point. This helped to ensure that the decay was caused solely by the presence of the moist air.

2.2 Effect of moisture in the active layer

Once the moisture diffusion pathway has been satisfactorily determined, we turned our attention to investigate the effect of moisture that it would have on the active layer. As before, standard devices with structure as shown in Figure 1(a) were fabricated. However, in order to be able to incorporate moisture selectively into the active layer, the photoactive film was spin cast from a blend solution made from water saturated chloroform (i.e. wet solvent). Figure 3 shows the preparation scheme. A dry and a wet chloroform sources were first prepared. To ensure the solvent was water saturated, deionized water was added to the anhydrous solvent and left overnight before used. A portion of the water saturated solvent was then taken and mixed with the anhydrous chloroform in 1:4 mixing ratio to yield a solvent with 20% water content.

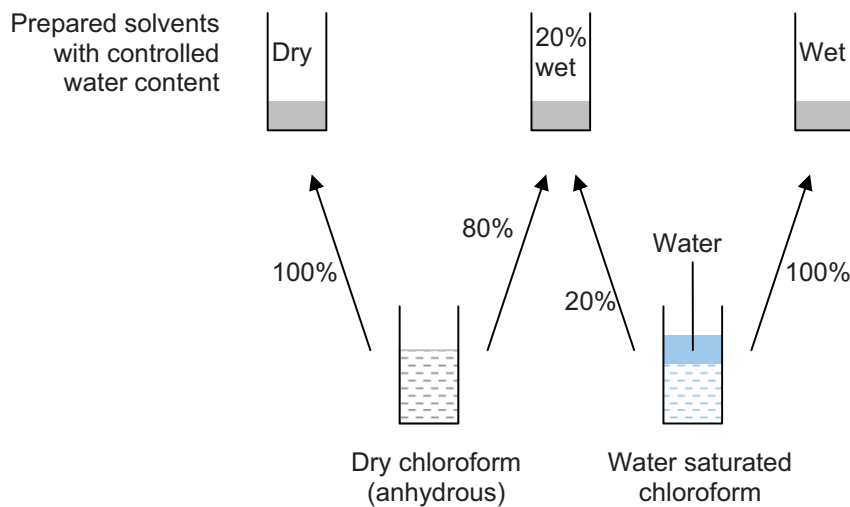


Figure 3. Preparation scheme to yield solvents with the desired water content.

The three resultant solvents with varying moisture content were used to fabricate three photovoltaic devices and the process is summarized in Table 1. The device spun from the Dry blend solution was to serve as a controlled sample. The finished devices were tested under A.M. 1.5.

Table 1. The prepared blend solutions with varying moisture content.

Blend solution	Water content (%)	Labeled as	Number of devices made
1	0	Dry	1
2	20	20% wet	1
3	100	Wet	1

2.3 Identifying the moisture accumulation point

We attempted to find out where water will accumulate within the photovoltaic cell after it has been exposed to moisture. For the purpose of the work in this section, a cell with structure as shown in Figure 1(a) was submerged in water for about 5 minutes. It was then carefully blown dry with nitrogen and transferred into the antechamber of a glovebox.

3. RESULTS

3.1 Moisture diffusion pathway

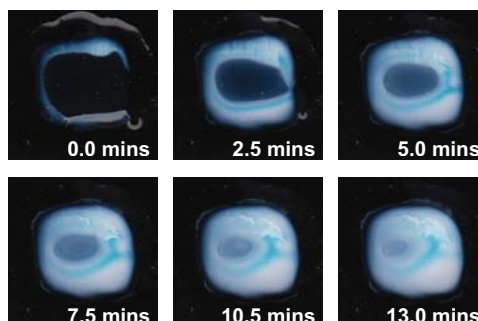


Figure 4. The propagation of moisture on the Glu Tack model after water was added to the perimeter.

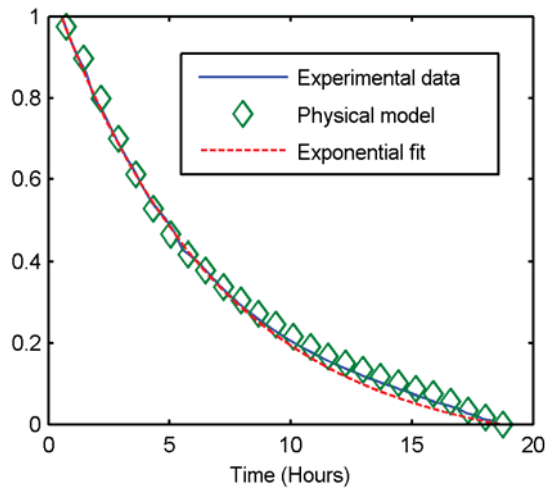


Figure 5. Comparing the decay profiles predicted by the physical model and that of a real P3HT solar cell. An exponential decay function was also included.

Figure 4 shows the moisture propagation on the Glu Tack model at a 2.5 minute interval after water was added to the perimeter. The processed data points are as shown in Figure 5 (in green, diamonds). Similar to the red dotted curve as presented in Figure 2, the obtained output power was noted to reduce to half of its initial value in about 6 hours. The experimentally obtained decay curve has been added to Figure 5 (the blue solid curve) to contrast with that given by the physical model (green, diamonds).

The comparison yields a close agreement between the two curves. This validates the fact that when the photovoltaic structure was exposed to ambient air, moisture diffused into the PEDOT:PSS layer through the edges of the solar cell, analogous to the propagation of moisture on the Glu Tack model (Figure 4). An exponential decay curve was also included in Figure 5 (the red dashed curve). Evidently, the decay process may also be closely modeled by the exponential function as pointed out in the literature.⁵ However, it is noted that there is an increasing discrepancy towards the end of the process, while the decay curve offered by the physical model is able to fit the experimental data entirely.

3.2 Moisture in active layer

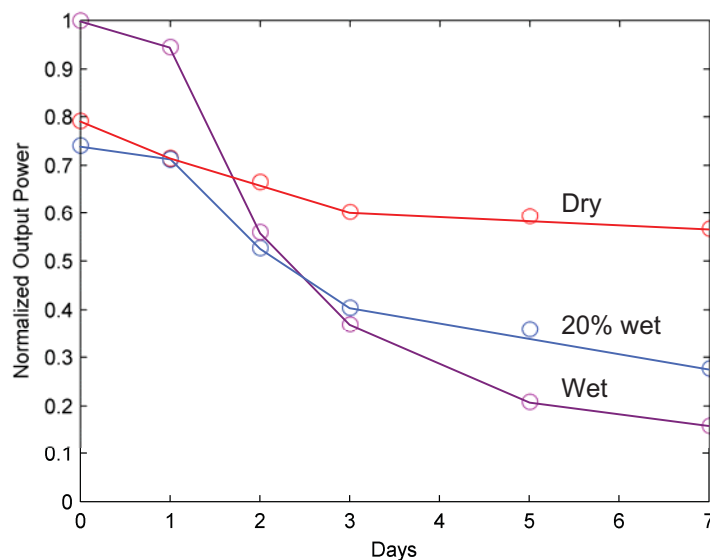


Figure 6. The performance of the devices monitored over the course of 7 days.

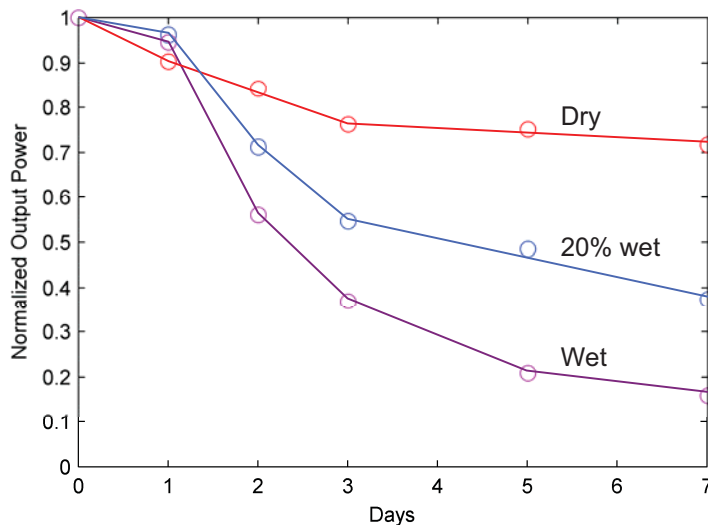


Figure 7. The three decay curves with their initial output powers normalized to 1.0.

Our automated testing stage at that time was still at the planning phase so the data density has been rather minimal. Figure 6 shows the daily test results. We were initially surprised that the devices showed no response to the use of the wet solvent. Ironically, with a power conversion efficiency of about 3.0% the Wet device has been demonstrating the highest output power among the three devices. However, after more than a day later, the devices fabricated from the wet solvent showed a noticeable drop in the output power. Solid lines in Figure 6 have been added to aid the eyes.

Figure 7 depicts the three decay curves as in Figure 6 but with their initial power normalized to 1.0 to emphasize their initial rate of decay. Up until Day 1, the device spun from anhydrous solvent (the Dry device) appeared to have the fastest decay rate among the three samples (the red curve in Figure 7). Notably the size of the error bar for the data points is approximately the diameter of the circle marker.

The delay in response to the moisture in the solvent is seen as an important aspect of the result. It suggests that the active layer (comprises both P3HT and PCBM components) is unaffected by the present of the moisture within it. However, when the moisture is released into the adjacent materials, the moisture starts to disrupt the operation of the cell. It is suspected that the moisture from the active layer was primarily taken up by the PEDOT:PSS. This helps to explain the existence of a correlation between the rate of decay and the amount of moisture introduced into the blend solution (comparing the Wet and the 20% wet data points in Figure 7). It is known that the acidity of the PEDOT:PSS depends on the amount of moisture it absorbed. Therefore, when significantly more moisture is available to the PEDOT:PSS layer as in the Wet device, it turned correspondingly acidic and started to impact on the underlying ITO.

3.3 Water accumulation point

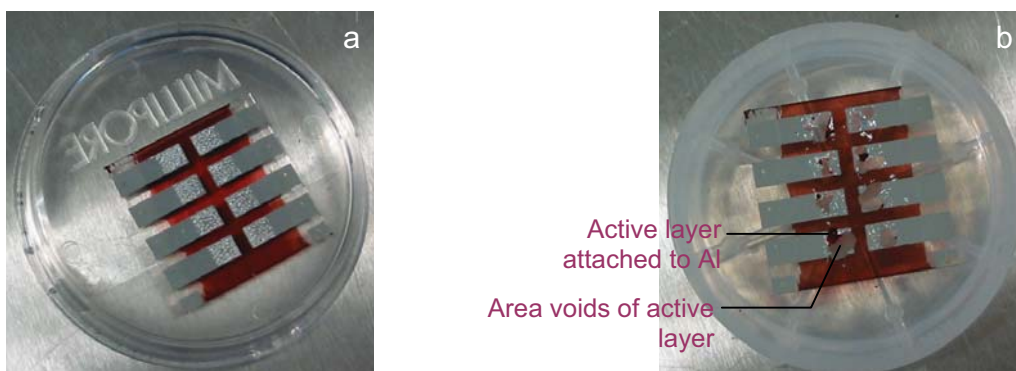


Figure 8. Identifying the point of explosion within the cell structure.

Figure 8(a) shows what happened to the sample after it been submerged for 5 minutes in water. When the antechamber was being pumped down the structure was ruptured by the vapor pressure of the trapped moisture in the cell. Close examination of Figure 8(b) reveals that the active layer has remained attached to the aluminum electrode after it has been ejected from the ITO. This indicates that the point of explosion is between the ITO and the active layer and therefore provides the evidence showing that after a cell has been exposed to water, majority of the moisture will accumulate in the PEDOT:PSS.

4. DISCUSSIONS

The three devices were identically kept in a glovebox and it could be seen that the box has not been particularly dry at that time. This is evident from the substantial background decay demonstrated by the Dry device, losing by almost 10% of its efficiency overnight (Figure 7). Perhaps, it is such humidity level that made it possible to retain the diminutive amount of moisture present in the blend solutions. We have tried to repeat the experiment for improved data resolution with our automated testing stage in a new glovebox environment where both the moisture and oxygen levels are effectively kept below 2 ppm. The acquired data, however, revealed no obvious step drop in the device performance. It is thus suspected that the dryness of the new box has caused the moisture in the active layer to escape. From OPV fabrication point of view, this may imply that with a sufficiently dry glovebox, moisture in solvent will have little effect on the fabricated devices.

5. CONCLUSION

We have devised a physical model to visualize the way the effective area of the organic solar cell diminishes when the cell is exposed to ambient air conditions. The obtained decay profile of the cell power agreed closely with the experimental data. The wet solvent test has indicated that the added moisture has no observable effect on the active layer (P3HT + PCBM) until the moisture has made it sufficiently into adjacent layers. The available evidence indicates that the hygroscopic PEDOT:PSS serves as a water accumulation center and thus may have absorbed most of the moisture present in the active layer as a result of the use of the wet solvent. The moisture activates the high acidity of the PEDOT:PSS, explaining the existence of the correlation between the rate of performance decay and the moisture content in the prepared blend solutions.

REFERENCES

- [1] Ouyang, J. and Xia, Y., "High-performance polymer photovoltaic cells with thick P3HT:PCBM films prepared by a quick drying process", *Sol. Energy Mater. Sol. Cells* 93(9), 1592-1597 (2009).
- [2] Steirer, K. X., Chesin, J. P., Widjonarko, N. E., Berry, J. J., Miedaner, A., Ginley, D. S. and Olson, D. C., "Solution deposited NiO thin-films as hole transport layers in organic photovoltaics", *Organic Electronics* 11(8), 1414-1418 (2010).
- [3] http://www1.eere.energy.gov/solar/review_meeting/pdfs/prm2010_nrel_lloyd.pdf
- [4] Kawano, K., Pacios, R., Poplavskyy, D., Nelson, J., Bradley, D. D. C. and Durrant, J. R., "Degradation of organic solar cells due to air exposure", *Sol. Energy Mater. Sol. Cells* 90(20), 3520-3530 (2006).
- [5] Betancur, R., Maymó, M., Elias, X., Vuong, L. T. and Martorell, J., "Sputtered NiO as electron blocking layer in P3HT:PCBM solar cells fabricated in ambient air", *Sol. Energy Mater. Sol. Cells* 95(2), 735-739 (2011).
- [6] Irwin, M.D., Buchholz, D.B., Hains, A.W., Chang, R.P.H. and Marks, T.J., "p-Type Semiconducting Nickel Oxide as an Efficiency-Enhancing Anode Interfacial Layer in Polymer Bulk-Heterojunction Solar Cells", *Proc. Nat. Acad. Sci* 105(8), 2783-2787 (2008).
- [7] Hau, S. K., Yip, H.-L., Baek, N. S., Zou, J., O'Malley, K. and Jen, A. K.-Y., "Air-stable inverted flexible polymer solar cells using zinc oxide nanoparticles as an electron selective layer", *Appl. Phys. Lett.* 92(25), 253301 (2008).