Oxygen- and water-induced degradation of an inverted polymer solar cell: the barrier effect

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Abstract. The work focuses on the degradation of performance induced by both water and oxygen in an inverted geometry organic photovoltaic device with emphasis on the accumulated barrier effect of the layers comprising the layer stack. By studying the exchange of oxygen in the zinc oxide (ZnO) layer, the barrier effect is reported in both a dry oxygen atmosphere and an oxygen-free humid atmosphere. The devices under study are comprised of a bulk heterojunction formed by poly(3-hexylthiophene) and [6,6]-phenyl-C61-butyric acid methyl ester sandwiched between a layer of zinc oxide (electron transporting layer) and a layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (hole transport layer) and the two electrodes indium tin oxide and silver. Time-of-flight secondary ion mass spectrometry is employed to characterize the accumulated barrier effect. A pronounced barrier effect is observed in the humid atmosphere, correlating well with a long observed lifetime in the same atmosphere. © 2011 Society of Photo-Optical Instrumentation Engineers. © 2011 Society of Photo-Optical Instrumentation Engineers (SPIE). [DOI: [10.1117/1.3544010](https://doi.org/10.1117/1.3544010)]

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1 Introduction

In recent years polymer solar cells have presented themselves as an upcoming technology in the commercial photovoltaic market. The existence of companies developing and marketing polymer solar cells is evidence that the technology is maturing rapidly. The main driver behind the commercialization of polymer solar cells is the production scalability. Production involving only printing techniques have been demonstrated, either without any vacuum steps involved¹⁻³ or starting from an indium tin oxide (ITO) covered substrate.^{4,5} Performance issues with polymer solar cells include the limited efficiency and lifetime. Efficiencies are typically in the region of 5% with a few reports of efficiencies approaching higher values in the 6 to 8% range.^{6,7} Polymer solar cells have been produced on a pilot scale and demonstrated in real world situations⁸ with an inferior efficiency, which suggests that efficiency is not a significant obstacle for the technology to reach a production stage. In this regard stability and lifetime is a more pressing issue. Today, lifetimes on the order of a few years are being recorded with good stability for air stable devices, encapsulated devices, and devices exposed to outdoor conditions.⁹⁻¹⁴ An effective encapsulation is in many cases the enabling technology for stable polymer solar cells. However, the use of expensive barrier materials is not desirable from a production point of view. Characterizing the performance of the solar cell under different atmosphere conditions can experimentally determine the stability of the cell toward a specific atmosphere,¹⁵ but do not in any way quantify the degree of oxidation caused by the atmosphere. Furthermore, as each layer in the cell acts as a barrier, changing a layer may change the overall need for encapsulation. In this study the

Fig. 1 Schematic illustration of partial (a)–(c) and complete (d) solar cell devices.

barrier effect was determined by studying the oxygen exchange inside the solar cell caused by an isotopically labeled dry oxygen ($^{18}\text{O}_2$) atmosphere or an oxygen-free humid (H_2^{18}O) atmosphere by employing time-of-flight secondary ion mass spectrometry (TOF-SIMS).

2 Experimental

A series of four partial and complete solar cells of inverted geometry were prepared, see Fig. 1. The solar cell is comprised of an ITO electrode, an electron transporting layer (ZnO), an active layer poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PCBM), a hole transport layer poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), silver electrode stripes, and an Alcan encapsulation. One set of complete and partial devices were subjected to an isotopically labeled dry oxygen ($^{18}\text{O}_2$) atmosphere and another set was subjected to an oxygen-free isotopically labeled humid (H_2^{18}O) atmosphere. The atmosphere exposure time was set to 21 days (504 h) where the devices were subjected to 330 W m^{-2} of illumination at $65 \pm 2^\circ\text{C}$. The accumulated barrier effect was measured by TOF-SIMS at the ZnO surface inside the solar cell (after layer removal).

2.1 Photovoltaic Preparation

Complete and partial solar cell devices were prepared on ITO coated glass substrates. ZnO nanoparticles were prepared by a method similar to the one described earlier, however, with the ink prepared in acetone instead of o-xylene/WS-1.⁴ The ZnO particles were stabilized with 10% methoxyethoxyacetic acid and filtered ($0.45 \mu\text{m}$) prior to use. The final concentration of the ZnO solution was 42.5 mg mL^{-1} . The ZnO solution was spin-coated using a rotational speed of 1000 rpm and subsequently annealed for 5 min at 140°C . The P3HT:PCBM ink was prepared by dissolving P3HT (Sepiolid P200 from BASF) and PCBM (99%, Solenne BV) in half the required volume of 1,2-dichlorobenzene at 110°C for 2 h followed by the addition of one volume of chloroform. The final concentrations were 24 mg mL^{-1} for P3HT and 22 mg mL^{-1} for PCBM. The P3HT:PCBM solution was spin-coated using a spin speed of 1000 rpm and subsequently annealed for 2 min at 140°C . The PEDOT:PSS was (EL-P 5010 from Agfa with a conductivity of $\sim 30 \text{ Ohm square}^{-1}$) diluted with isopropanol (10:5 w/w) to give a final viscosity of $270 \text{ mPa} \cdot \text{s}$. The PEDOT:PSS solution was spin-coated using a rotational speed of 1000 rpm and subsequently annealed for 5 min at 140°C . The silver ink was from Dupont (PV410) and printed on without modification in a stripe pattern with stripes being 0.2 mm wide and spaced by 0.8 mm. A stripe pattern was used to mimic the conditions used for R2R fabricated devices, where a stripe pattern is employed to reduce cost. The active areas of the devices were $\sim 3 \text{ cm}^2$.

2.2 Control of Atmosphere

The influence of the atmosphere was established by illumination (330 W m^{-2} , $65 \pm 2^\circ\text{C}$) in chambers equipped with a quartz window allowing for control of the atmosphere.¹⁵ Prior to the experiment a pressure of $\sim 10^{-4}$ mbar was established and the entire system was purged with nitrogen (99.9%) and pumped back down to $\sim 10^{-4}$ mbar. One chamber was then injected

Fig. 2 Normalized PCE describing the degradation in performance of encapsulated (gray) and nonencapsulated (black) devices under continuous illumination (330 W m^{-2} , AM1.5G, $65 \pm 2^\circ\text{C}$).

via a septum with H_2^{18}O (97%, 5 mL, $\sim 20 \text{ mmol}$). The entire system has a volume of 2.5 L resulting in a saturated isotopically labeled atmosphere. Another chamber was filled with 1 atm of $^{18}\text{O}_2:\text{N}_2$ (20:80).

2.3 Accessing the ZnO Layer

In order to study the ZnO surface the preceding layers need to be removed. Since the layers comprised the cell where the solution was processed, the organic layers can subsequently be re-dissolved and removed. The PEDOT:PSS layers were removed by either delamination in the case of the encapsulated device or by gently swiping the surface with a cotton stick soaked in pure water. The underlying P3HT:PCBM layers were removed using the same procedure by substituting water with chloroform. Delamination of encapsulated devices is accomplished by peeling off the encapsulation. The delamination occurs at the PEDOT:PSS-P3HT:PCBM interface as verified by TOF-SIMS mass spectra (not shown).

2.4 Chemical Characterization

Analysis of the ZnO surface was performed using a TOF-SIMS IV (ION-TOF GmbH, Münster, Germany) with 25-ns pulses of 25-keV Bi^+ (primary ions), bunched to form ion packets with a nominal temporal extent of $< 0.9 \text{ ns}$ at a repetition rate of 10 kHz yielding a target current of 0.9 pA. These primary ion conditions were used to obtain 10 mass spectra for each sample acquired on a $100 \times 100 \mu\text{m}^2$ surface area for 20 s. The intensity of the ^{18}O signal describes the oxygen exchange that has taken place in accordance with the reaction shown below.

By comparing the ^{18}O signal intensities for the different surfaces (Fig. 1), semiquantitative information on the barrier effect was extracted.

3 Results and Discussion

Two functional solar cells were produced, as depicted in Fig. 1(c) and Fig. 1(d). Both were performance tested prior to the degradation experiments. This was done in both an oxygen-free humid atmosphere and a dry oxygen atmosphere.

3.1 Cell Performance

Figure 2 depicts a comparison of the degradation of the solar cell performance in a dry oxygen atmosphere and an oxygen-free humid atmosphere. Both encapsulated and unencapsulated

devices, corresponding to Fig. 1(c) and Fig. 1(d), were tested. The mounting process took 1 h. Power conversion efficiency (PCE) was measured before and after the mounting process, which revealed a small insignificant drop in the PCE. Figure 2 shows the temporal development of PCE after the mounting process and exchange of the atmospheres.

It is observed that both atmospheres lead to fast degradation of the initial response for the unencapsulated devices. However, a clear difference is seen in device stability in the two atmospheres. The dry oxygen atmosphere led to complete degradation of the solar cell properties in roughly 20 h with all parameters showing fast decay. On the contrary the device in the oxygen-free humid atmosphere remained nearly constant after the initial performance drop. During the 480 h time frame of the experiment the cell had not reached the end of its functional lifetime.

3.2 Barrier Effect

Complete and partial devices were placed in the atmosphere chambers for 504 h (21 days) and subjected to light for the entire duration. After the exposure to the atmosphere the devices were removed from the atmosphere chamber, the ZnO layer was exposed, and TOF-SIMS mass spectra were obtained. Figure 3 shows a plot of the degree of oxygen exchange that took place during the experiment at the ZnO surface inside the cell. The normalized intensities are based on the integrated ^{18}O signal normalized to the largest degree of oxygen exchange. TOF-SIMS is not directly quantitative, however, since the substrate is the same in each case the intensities can be compared semiquantitatively.

At the directly exposed ZnO surface [Figs. 3(a) and 1(a)] a higher degree of oxygen exchange (roughly a factor of 2) is observed in an oxygen-free humid atmosphere as compared to a dry oxygen atmosphere. ZnO is expected to exchange oxygen easily; hence the oxygen uptake at the ZnO surface cannot directly be correlated to degradation. However, it can be used to determine the accumulated barrier effect of the preceding layers. The explanation for the difference in oxygen uptake at the directly exposed ZnO surface can be found in the different trapping mechanisms for oxygen and water. The exchange with $^{18}\text{O}_2$ is expected to take place through trapping of superoxide radicals at the surface of the ZnO nanoparticles, whereas the exchange with H_2^{18}O is expected to take place through the exchange of hydroxide on the surface of the ZnO nanoparticles.

In the dry oxygen atmosphere a clear barrier effect is observed for all layers [Figs. 3(b)–3(d), white columns]. It is seen that each layer has a distinctive effect as a barrier. An accumulated effect is therefore seen. In the oxygen-free humid atmosphere the active layer is observed to have a pronounced barrier effect [Fig. 3(a) and 3(b), striped columns] to such an extent that

Fig. 3 Normalized ^{18}O intensities for partial (a)–(c) and complete (d) solar cells. The values have been normalized to the largest degree of oxygen exchange seen in the oxygen-free humid atmosphere. (c) The functional cell without encapsulation, (d) the same cell with encapsulation, and (a) and (b) partial devices (see Fig. 1).

the active layer effectively shields the effect of the preceding layers as the difference between B and C lies within the error bars (i.e., a bottleneck effect). The elevated ^{18}O intensity for the encapsulated device [Fig. 3(d), striped column] can seem puzzling as it intuitively was expected to show the lowest value. One possible explanation could be that the adhesive used for the Alcan encapsulation is hygroscopic, i.e., the adhesive acts as a reservoir for water.

4 Conclusion

Barrier effects against molecular oxygen and water in an inverted geometry polymer solar cell (Alcan-Ag-PEDOT:PSS-P3HT:PCBM-ZnO-ITO) were determined using TOF-SIMS in conjunction with isotopic labeling. In an oxygen-free humid atmosphere the barrier effect of the active layer (P3HT:PCBM) is demonstrated to be very pronounced. The barrier effect of the active layer effectively overshadows the effect of the preceding layers (i.e., a bottleneck effect). In a dry oxygen, atmosphere barrier effects of similar magnitudes are observed for the various layers giving rise to a steady increase in the accumulated barrier effect. These results provide information on how much of the atmosphere reached the ZnO surface during the experiment, it does not directly provide information on the degree of oxidation/degradation in the organic materials, and does not provide information on where oxidation/degradation took place. It is therefore not possible to relate these results to the relative lifetime in molecular oxygen and water.

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References

1. F. C. Krebs, M. Jørgensen, K. Norrman, O. Hagemann, J. Alstrup, T. D. Nielsen, J. Fyenbo, K. Larsen, and J. Kristensen, “A complete process for production of flexible large area polymer solar cells entirely using screen printing—First public demonstration,” *Sol. Energy Mater. Sol. Cells* **93**, 422–441 (2009).
2. F. C. Krebs, “All solution roll-to-roll processed polymer solar cells free from indium-tin-oxide and vacuum coating steps,” *Org. Electron.* **10**, 761–768 (2009).
3. F. C. Krebs, “Roll-to-roll fabrication of monolithic large-area polymer solar cells free from indium-tin-oxide,” *Sol. Energy Mater. Sol. Cells* **93**, 1636–1641 (2009).
4. F. C. Krebs, S. A. Gevorgyan, and J. Alstrup, “A roll-to-roll process to flexible polymer solar cells: model studies, manufacture and operational stability studies,” *J. Mater. Chem.* **19**, 5442–5451 (2009).
5. F. C. Krebs, H. Spanggaard, T. Kjaer, M. Biancardo, and J. Alstrup, “Large area plastic solar cell modules,” *Mater. Sci. Eng., B* **138**, 106–111 (2007).
6. S. H. Park, A. Roy, S. Beaupré, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, and A. J. Heeger, “Bulk heterojunction solar cells with internal quantum efficiency approaching 100%,” *Nature Photonics* **3**, 297–303 (2009).
7. H. Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, and G. Li, “Polymer solar cells with enhanced open-circuit voltage and efficiency,” *Nature Photonics* **3**, 649–653 (2009).
8. F. C. Krebs, T. D. Nielsen, J. Fyenbo, M. Wadstrøm, and M. S. Pedersen, “Manufacture, integration and demonstration of polymer solar cells in a lamp for the Lighting Africa initiative,” *Energy Environ. Sci.* **3**, 512–525 (2010).
9. E. A. Katz, S. Gevorgyan, M. S. Orynbayev, and F. C. Krebs, “Out-door testing and long-term stability of plastic solar cells,” *Eur. Phys. J. Appl. Phys.* **36**, 307–311 (2006).

10. J. A. Hauch, P. Schilinsky, S. A. Choulis, R. Childers, M. Biele, and C. J. Brabec, "Flexible organic P3HT:PCBM bulk-heterojunction modules with more than 1 year outdoor lifetime," *Sol. Energy Mater. Sol. Cells* **92**, 727–731 (2008).
11. F. C. Krebs and K. Norrman, "Analysis of the failure mechanism for a stable organic photovoltaic during 10 000 h of testing," *Prog. Photovoltaics* **15**, 697–712 (2007).
12. F. C. Krebs, "Air stable polymer photovoltaics based on a process free from vacuum steps and fullerenes," *Sol. Energy Mater. Sol. Cells* **92**, 715–726 (2008).
13. F. C. Krebs, Y. Thomann, R. Thomann, and J. W. Andreasen, "A simple nanostructured polymer/ZnO hybrid solar cell—preparation and operation in air," *Nanotechnology* **19**, 424013–434025 (2008).
14. B. Zimmermann, U. Würfel, and M. Niggemann, "Longterm stability of efficient inverted P3HT:PCBM solar cells," *Sol. Energy Mater. Sol. Cells* **93**, 491–496 (2009).
15. S. A. Gevorgyan, M. Jørgensen, and F. C. Krebs, "A setup for studying stability and degradation of polymer solar cells," *Sol. Energy Mater. Sol. Cells* **92**, 736–745 (2008).

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