



ELSEVIER

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Investigating electrodes degradation in organic photovoltaics through reverse engineering under accelerated humidity lifetime conditions



Vasileios M. Drakonakis, Achilleas Savva, Maria Kokonou, Stelios A. Choulis*

Molecular Electronics and Photonics Research Unit, Mechanical Engineering and Materials Science & Engineering Department, Cyprus University of Technology, 45 Kitiou Kyprianou St., 3041 Limassol, Cyprus

ARTICLE INFO

Article history:

Received 29 April 2014

Received in revised form

24 July 2014

Accepted 31 July 2014

Keywords:

Organic photovoltaics

Reverse engineering

Humidity lifetime performance

Degradation mechanisms

Electrodes

PEDOT:PSS

ABSTRACT

Exposure to accelerated humidity lifetime conditions has been proved to have detrimental effects on organic photovoltaics (OPV) performance, because of the deterioration of the electrodes of the device rather than the active layer. Normal and inverted OPV devices are investigated in order to identify their main degradation mechanisms under accelerated humidity lifetime conditions. Reverse engineering can be a useful technique to probe main degradation mechanisms of the top electrode of both normal and inverted organic photovoltaic (OPVs). By using reverse engineering methods, we show that the major degradation mechanism of inverted OPVs under accelerated humidity lifetime conditions, is due to PEDOT:PSS hole selective top contact.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Environmental lifetime factors such as water, oxygen [1], high temperature [2], and light exposure, have a strong influence on the stability of the structural layers in OPVs. For instance, conjugated polymers that comprise the active blend of OPVs, are unstable in air [3] and react through photolytic and photochemical reactions when exposed to sunlight causing photodegradation of the polymer [4]. However, such mechanisms can be much slower than degradation occurring within the electrode layers of the device such as oxidation of the metal contact [5–7]. Hence, the sources leading to these degradation mechanisms must also be addressed.

OPVs rapidly degrade due to the susceptibility of metals, usually used for the back electrode, to oxidation in the presence of absorbed oxygen molecules [7]. The degradation of the metal electrode leads to the formation of thin insulating oxide barriers, hindering electric conduction and collection of the charge carriers [8,9]. Certain metals such as Al, Ca and Ag are commonly used as electrodes in OPV devices because of their high electrical conductivity, and suitable work function. Interestingly, two basic degradation mechanisms of the metal electrode have been identified. Those are, primarily, oxidation [10], and secondarily, chemical interaction with polymers within the active layer interface [11].

* Corresponding author.

E-mail address: stelios.choulis@cut.ac.cy (S.A. Choulis).

The degradation due to oxidation at the electrode/polymer interface can result in the formation of an oxide layer on the top metal surface as well as within the metal/polymer interface [10]. This oxidation layer hinders the charge selectivity of the electrode, thus reducing device performance. For example, in Ca/Al electrodes, the oxide formation is faster due to Ca presence; it has been reported that Ca/Al electrode degradation in air is due to considerable changes at the metal–organic interface [10]. Cross-sectional TEM studies have revealed the formation of void structures to be the primary degradation mechanism for Ca/Al contacts. These structures grow as the electrode ages and become oxidized. For Ag electrodes, it has similarly been observed that the electrode becomes oxidized and that an interfacial layer of silver oxide is formed over time. Nevertheless, its oxidation is much slower compared to Al-based electrodes [12].

In addition, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is an essential hole selective contact for achieving efficient normal and inverted OPV devices. This particular buffer layer is extremely sensitive to moisture and oxygen. The detrimental effects of atmospheric air on the electrical properties of this material have been studied by Vitoratos et al. [13,14], who show that when the PEDOT:PSS layer absorbs water, it promotes irreversible structural modification of its networks due to its highly hygroscopic nature, resulting in conductivity reduction which may consequently result in shortage of device lifetime. Moreover, the PEDOT:PSS layer can influence the degradation of the active layer [1]. It has also been reported that the PEDOT:PSS layer can induce degradation of P3HT:PCBM (poly(3-hexylthiophene): [6,6]-phenyl

C₆₁-butyric acid methylester) OPVs, which is demonstrated by a decrease in the absorbance and the formation of aggregates in the active layer [15].

Additionally, it has been observed that the acidity of the PEDOT:PSS layer can cause etching of the indium within the ITO (indium tin oxide) electrode, liberating indium ions, which then diffuse throughout the device [16]. This process is accelerated in the presence of moisture, as shown by de Jong et al. [17] due to moisture absorbance during the spin coating process. A mechanism of ITO etching by PEDOT:PSS has been investigated and proposed [18]. However, this mechanism has been conclusively proven only for organic light emitting diodes (OLEDs), therefore, the investigation of failure mechanisms in OPVs is a challenging task and due to the different nature of the application, the extensive know-how developed for OLED degradation mechanisms cannot be directly transferred to OPVs. Voroshazi et al. have demonstrated that the hygroscopic behavior of PEDOT:PSS, and not its acidic one, is responsible for the device degradation through comparable degradation of PEDOT systems with pH values of 5 and 7 [12]; nevertheless an electrical conductivity comparison between the two PEDOT systems could make a stronger point on the fatality of PEDOT:PSS hygroscopic behavior over its acidic one. Finally, due to the aforementioned difference between OPV and OLED application, questions arise as to what extent the ITO etching occurs in OPVs.

Furthermore, extensive work has been performed in characterizing OPVs and deriving conclusions for the degradation mechanisms of the electrodes of OPVs [19]. OPVs fabricated by different groups were exposed to accelerated illumination conditions [20] under the well-established ISOS protocols [21,22]. Later, these particular OPV devices [20] were extensively characterized through Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS) [16,23], Incident Photon-to-Electron Conversion Efficiency (IPCE) [24], and imaging techniques [25], demonstrating the convergence in identifying the degradation mechanisms by different characterization methods. Such works have been proven extremely useful for OPV lifetime performance investigations.

Fabrication through doctor blading or other coating or printing technologies over spin coating can be more relevant to OPV product development processing targets [26]. In this study non-encapsulated OPV devices processed by doctor blading have been studied in order to collectively understand, identify, and verify major sources of electrode degradation under accelerated humidity lifetime conditions. It is verified through reverse engineering that the oxidation of the top electrode (Al) in normal OPVs has a major impact on the lifetime performance under humidity, whereas the deterioration of the transparent electrode ITO/PEDOT:PSS has a secondary role. Normal OPVs, using alternative top electrodes such as ZnO/Al, ZnO/Ag, Cr/Al, and Cr/Ag, as well as neutral PEDOT:PSS as a bottom electrode alternative are also fabricated and investigated under the same experimental conditions. As expected, despite the increase using the aforementioned collective alternatives, the lifetime of the normal OPVs is still significantly lower than the lifetime of the inverted OPVs. Importantly, by using reverse engineering, we prove that the major source of degradation in inverted OPVs under accelerated humidity lifetime conditions, is due to the PEDOT:PSS hole selective contact.

2. Experimental

For the scope of this work both normal and inverted reference OPVs were fabricated. The pre-sputtered glass-ITO substrates (Microliquid) were sonicated in acetone and subsequently in isopropanol for 10 min. For normal OPVs, PEDOT:PSS was diluted

in IPA (ratio 1:3.2) and then deposited through doctor blading, resulting in a layer thickness of ~50 nm as measured by Dektak 150 stylous profilometer. Upon annealing of PEDOT:PSS for 30 min at 140 °C, P3HT:PCBM (ratio 1:0.8, 36 mg/ml in chlorobenzene) solution was doctor bladed on top of PEDOT:PSS resulting in a thickness of 230 nm; devices were then transferred into a nitrogen filled glove-box. An Al layer of 120 nm was thermally evaporated and the devices were annealed for 22 min at 140 °C. For the alternative top electrodes, Cr and Ag were evaporated to form layers of 2 nm and 100 nm respectively.

For the fabrication of inverted devices, ZnO was deposited on the pre-cleaned ITO substrates using a sol-gel method described in detail elsewhere [27]. The active layer was bladed on top of ZnO from the same solution used for normal OPVs, resulting in a layer thickness of 180 nm. PEDOT:PSS (70 nm) was then deposited with a mixture of zonyl and dynol wetting agents on the active layer surface [28]. The devices were annealed inside a glovebox at 140 °C for 20 min and after that a silver layer with a thickness of 100 nm was thermally evaporated on top of PEDOT:PSS.

The *J/V* characteristics were measured with a Keithley source measurement unit (SMU 2420). For illumination a calibrated Newport solar simulator equipped with a Xe lamp was used, providing an AM1.5G spectrum at 100 mW/cm² as measured by an Oriel 91150V calibrated silicon cell equipped with KG5 filter.

Electrical conductivity measurements were performed through a four point-probe conductivity meter (Jandel RM3000). Atomic Force Microscopy was performed in tapping mode using a table-top system (Nanosurf easy scan 2). The aging of the devices and the films was performed in an environmental chamber (Binder) for the desired time under relative humidity of RH 85% and 30 °C temperature.

3. Results and discussion

Humidity affects both electrodes of the OPV device. The main objective of the present work is to address the main sources of electrode degradation by using reverse engineering. Normal and inverted OPV structures have been studied under accelerated humidity lifetime conditions (85% RH, 30 °C in a dark chamber). In order to control the environmental factor causing the degradation, we chose to expose the samples to severe humidity only, as it is the condition affecting device electrodes/interfaces the most. Devices are not encapsulated in order to accelerate degradation process observation.

3.1. Comparison of top-electrodes in normal non-encapsulated OPVs under accelerated humidity lifetime conditions

The top electrode of the reference normal device is severely susceptible to oxidation, as it has been investigated by others in the literature as well [25,29]. The degradation processes of the electrodes of the normal OPVs have been well described when devices undergo illumination or dark within a variety of atmospheres [29,30]; however, the present study investigates these processes under humidity only. Consequently, other electrodes, more resistant to humidity deterioration, have been utilized in order to improve the lifetime of the normal device. Fig. 1 summarizes the lifetime of the normal and inverted OPVs studied in this work.

Initially, in an attempt to prevent the degradation of the top electrode in normal OPV, a buffer n-type layer was added between the active layer and the metal electrode. Heeger et al. utilized an n-type oxide (TiOx) as a buffer layer in order to decelerate the oxidation of the metal through photo-oxidation [32]. In our study, ZnO was utilized as a buffer layer between aluminum and the

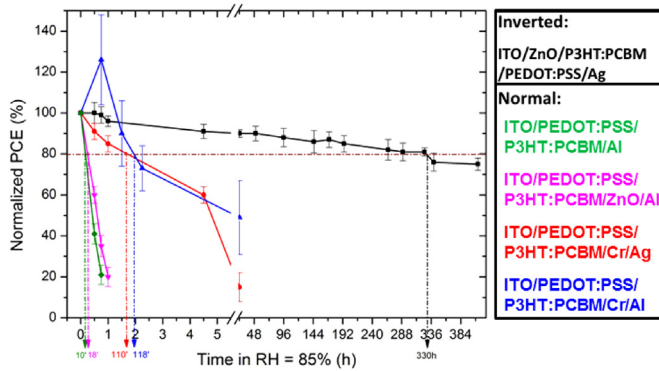


Fig. 1. Comparison of non-encapsulated normal with inverted OPVs under accelerated lifetime conditions of relative humidity RH=85%.

active layer. Devices with ZnO interlayer demonstrate higher stability of more than 50% when compared to reference normal OPVs under humidity (Fig. 1). This is shown by the T80 value (time at which 80% of the initial power conversion efficiency (PCE) upon fabrication is reached [22]) which increases from 10 min to 18 min.

The same interlayer was then implemented with a more stable metal electrode. Ag, known for its resistance to oxidation, was evaporated on top of ZnO in a normal OPV; however, its performance was much lower than the reference normal device, even when the annealing process conditions were investigated in detail. The optimum efficiency for those devices is without further annealing of the ZnO interlayer apart from the standard normal OPV device annealing step prior to evaporation.

In a second attempt to decelerate the oxidation mechanisms of the top electrode in normal OPVs, a thin layer of chromium (Cr) (Thickness between 1 and 3.5 nm – indicatively, Cr thicker than 3 nm resulted in PCEs below 1%) was evaporated between the photoactive layer and either Ag or Al. Cr has been utilized as an electrode material in other works as well, with increased thickness (i.e., 5 nm [33] or 15 nm [23]) and mainly as an electrode in ITO free OPVs together with Al [20,23,33,34]. Although the initial Cr-based device PCE was ~30% lower than the reference device, Cr-based devices demonstrated significantly increased accelerated lifetime. The reduction in PCE is attributed to the non-optimized Cr layer in those devices. The two different top electrodes, Cr/Ag and Cr/Al, present 11 times and 12 times improvement respectively (T80 increases from 10 min to 110 and 118 min respectively), when compared with the reference device accelerated lifetime under RH 85% (Fig. 1). This improvement may be attributed to a delay of oxidation and/or chemical interaction of metals with the active layer [10,11].

As Fig. 1 demonstrates, the introduction of interlayers between the top metal electrode and the active layer improves the lifetime of normal OPVs under accelerated humidity lifetime conditions (almost 12 times higher than the reference lifetime in the case of Cr/Al). Despite the stability improvement, the increase in lifetime when inverted OPVs are utilized is 2000 times higher (Fig. 1).

3.2. Reverse engineering of the degraded top electrode in non-encapsulated normal OPVs

Starting with the cathode of the normal OPV, non-encapsulated reference devices with average initial PCE of 2.6%, reached T80 within several minutes (~10 min) when exposed to RH of 85%. In order to identify the contribution of the top electrode degradation to the overall device degradation, we used reverse engineering on the same devices after one hour of exposure to RH 85%, where the PCE had dropped below 40% of its initial value. The initially evaporated aluminum was removed using simple scotch tape

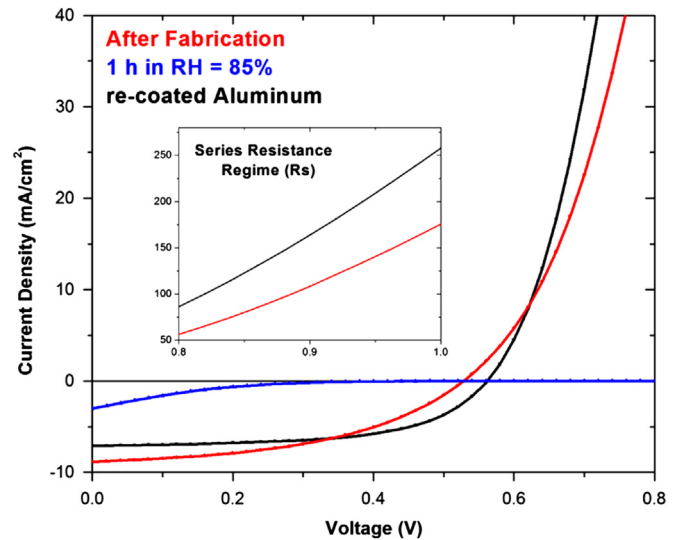


Fig. 2. J/V characteristics of normal structured OPVs after fabrication (red), upon exposure to RH=85% for 1 h (blue) and after reverse engineering (black). The insert represents the R_s regime of all the aforementioned normal OPVs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and fresh aluminum was re-evaporated on top of the devices under the same conditions as during the first evaporation.

Fig. 2 depicts representative J/V curves of the as fabricated devices compared with the same devices after 1 h under harsh humidity lifetime conditions and after re-evaporation of the top electrode.

Interestingly, upon re-fabrication of the top electrode, the device is still operational with similar or higher performance (see $J-V$ characteristics) compared to the as fabricated devices. Re-fabrication of the top electrode demands re-annealing of the device as well for achieving an effective adhesion between the active layer and the re-evaporated electrode [35,36]. Re-annealing however usually deteriorates the active layer properties [36]. It is observed that the active layer together with the fresh electrode interface give a similarly efficient or slightly improved device in terms of FF and V_{oc} . Notably, this behavior is not observed when the annealing period during the first fabrication of the device is simply doubled.

The behavior of the normal OPV under reverse engineering demonstrates that the metal-polymer interface quickly oxidizes in a highly humid environment [12]. Furthermore, it suggests that despite both electrodes being responsible for device degradation when exposed to a highly humid environment; the top electrode degradation process is dominant. Other works have shown that the oxidation of the metal is the most detrimental factor in OPV degradation when exposed even to ambient conditions [12].

3.3. PEDOT:PSS degradation

In order to identify the source of degradation in the anode (ITO/PEDOT:PSS) of normal OPVs, plain ITO and PEDOT:PSS coated ITO layers were fabricated and tested in the same accelerated humidity lifetime conditions. PEDOT:PSS in this test is more exposed than in the case of the device, where it is sandwiched, thus somewhat protected between ITO and active layer. However, the degradation of the PEDOT:PSS layer through its separate characterization still provided important conclusions for the source of degradation of the bottom electrode in normal and the top electrode in inverted OPVs.

Films of PEDOT:PSS were prepared on ITO-glass substrates. Plain ITO-glass, PEDOT:PSS-coated ITO-glass and PEDOT:PSS-glass

specimens were characterized in accelerated humidity lifetime conditions in order to examine and verify with available literature [16–18], whether humidity or acidity of PEDOT:PSS system, upon water absorbance, affects ITO. Specimens were evaluated in electrical conductivity and topography after each cycle of exposure to humidity starting from 1 h to 180 h. pH-Neutral PEDOT:PSS (clevis JET-NV2), deposited with zonyl and dynol surfactants [28], was also evaluated as a potential replacement of PEDOT:PSS in normal OPVs, as it exhibited much higher conductivity.

The exposition of specimens to humidity demonstrated that PEDOT:PSS loses its conductivity (Fig. 3). The characterization of PEDOT:PSS/ITO layers taking place in this work raises some doubts over the etching mechanism of ITO relevant to OPV stability. Specifically, it has been reported that the acidity of PEDOT:PSS affects ITO, causing loss of its conductivity over time [16–18]. Fig. 3 depicts electrical conductivity measurements of ITO and PEDOT:PSS samples as those have been previously described. It can be seen that in all cases, PEDOT:PSS conductivity is detrimentally reduced whereas the ITO conductivity remains relatively constant. Other works in literature have also underlined the hygroscopic and not the acidic behavior of PEDOT:PSS as responsible for the electrode degradation [12,15].

In order to further examine the effect of PEDOT:PSS acidity on device lifetime under accelerated humidity lifetime conditions, two different PEDOT:PSS systems were compared. PEDOT:PSS Jet NV2 layers were compared with PEDOT:PSS PH layers under

humidity (electrical conductivity/pH values of $210 \text{ S cm}^{-1}/5\text{--}7$ for Jet NV2 system and $10 \text{ S cm}^{-1}/1.5\text{--}2.5$ for PH system for a layer thickness of $\sim 125 \text{ nm}$). Fig. 3 demonstrates a drop in electrical conductivity over time for both systems. Nevertheless, NV2 exhibits lower reduction rate in electrical conductivity ($\sim 40\%$ compared to $\sim 70\%$ for PH) as a function of time exposure to humidity (RH 85%). Additionally, from the graph (Fig. 3) it can be derived that the water absorption has a saturation point that occurs around 48 h of exposure to humidity for both systems; after that, conductivity reduces at a small rate. It is suggested that in the bottom electrode degradation of normal OPVs, the major reason of deterioration is PEDOT:PSS hole selective contact, rather than the etching of ITO because of PEDOT:PSS acidity. This is also supported by Fig. 3b, where the surface topography of ITO before fabrication and upon removal of PEDOT:PSS after 180 h of exposure in RH 85%, is presented. It can be seen that there is no significant difference on the surfaces of ITO before and after exposure to humid environment.

Normal devices fabricated with neutral PEDOT:PSS as a hole-transport layer demonstrated approximately constant series resistance (R_s) and improved parallel resistance (R_p) compared to the reference devices, resulting in a slight PCE increase from 2.58% to 2.64%. Indicatively, the R_s and R_p values (at 1 V and -1 V respectively) are approximately 74Ω and $5.56 \text{ k}\Omega$ for the reference device, and 44Ω and $55.56 \text{ k}\Omega$ for the device with the neutral PEDOT:PSS. However, when it comes to lifetime, due to the

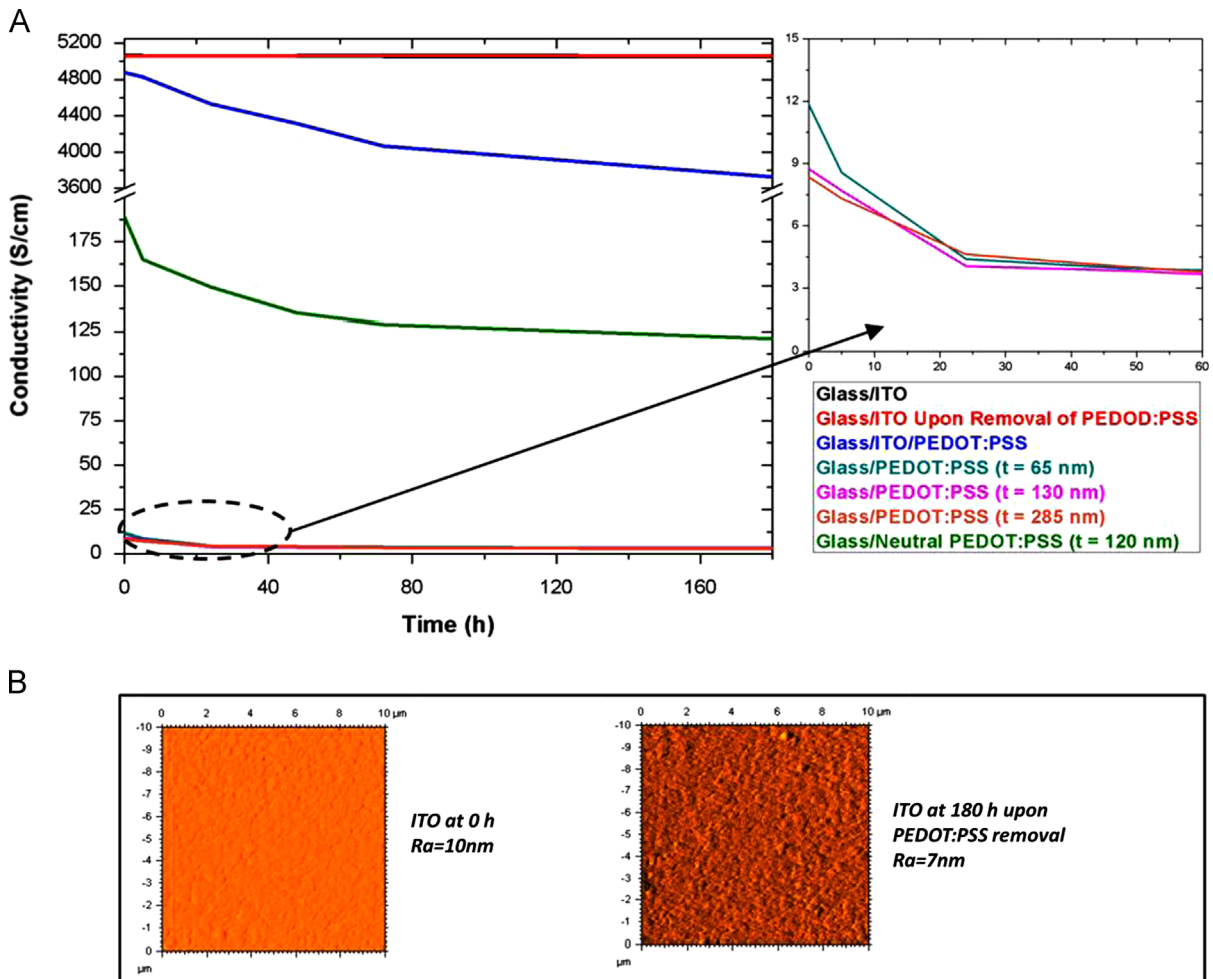


Fig. 3. (A) Electrical conductivity of ITO, PEDOT (PEDOT:PSS PH pH ~ 1.5) and neutral PEDOT (PEDOT:PSS JetNV2 pH $\sim 5\text{--}8$) as a function of exposure to highly humid environment (RH=85%). (B) ITO AFM characterization before fabrication and upon removal of PEDOT:PSS after 180 h of exposure in RH 85%. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

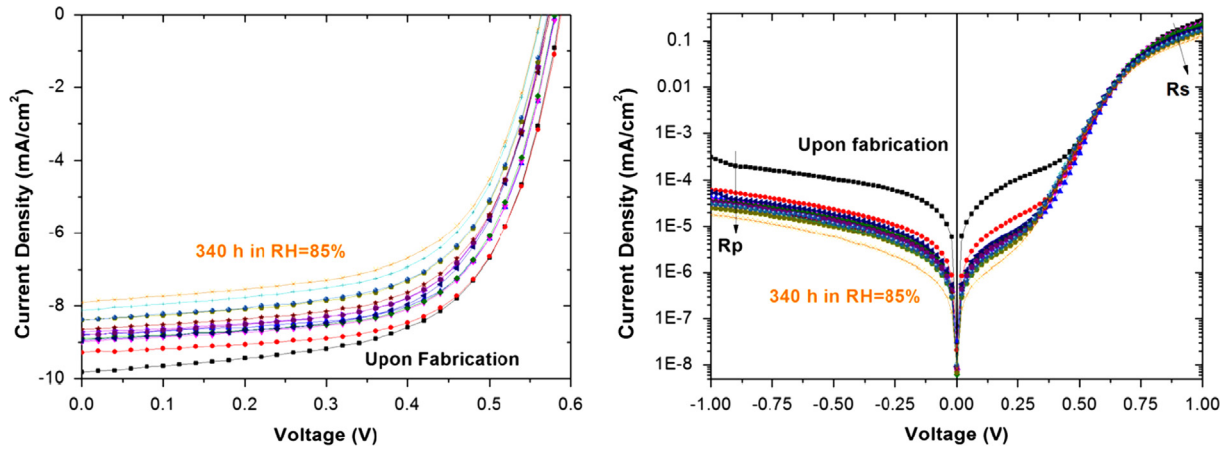


Fig. 4. J/V characteristics of inverted OPV cells which were exposed under humidity lifetime of RH 85% for more than 300 h.

dominant effect of aluminum oxidation, devices with NV2 reached T80 as fast as the reference devices under RH of 85% (Fig. 1). This behavior further supports the fact that the top electrode degradation is the major reason for the rapid degradation of normal OPVs.

3.4. Reverse engineering of the degraded top electrode in non-encapsulated inverted OPVs

Despite the increase in lifetime of normal OPVs using interface engineering, lifetime of inverted OPVs is still significantly longer, as presented in Fig. 1. The reason for such a great difference in lifetime is mainly the much slower oxidation mechanism of Ag compared to Al. Several studies under illumination and ambient environment have investigated in detail the degradation processes of the electrodes of inverted OPVs [20,29,30,37]. Krebs et al. has studied the differences between normal and inverted OPVs (similar to our references) exhibiting inverted structures superiority in stability by exposing them to illumination under different environments such as ambient, nitrogen, humid nitrogen, and dry oxygen [30]. Similarly, Sachs-Quintana et al. demonstrate the superiority of the inverted structure over normal under exposure to heat [31].

Fig. 4 depicts the J/V characteristics of a representative inverted OPV measured periodically during the lifetime investigation in dark, RH=85%, and $T=30^\circ\text{C}$. In the illuminated curves (Fig. 4a) it can be seen that the fill factor, Voc, and Jsc decrease at a constant rate. The dark curves (Fig. 4b) present a constant increase in the device internal resistances, R_s and R_p . The observed increased R_s could indicate charge transport impedance from the active layer to the terminal of the device. The latter could be related to the loss of conductivity of PEDOT:PSS over time under humidity (Fig. 1). This is in good agreement with literature reports that demonstrate an increase in device R_s when lower conductivity buffer layers are used [38]. However, the observed increased R_p is a strong indication that the conductivity reduction of PEDOT:PSS over time in humidity is not the only mechanism that should impede the charge transport to the electrodes [39]; The increased R_p can be attributed to PEDOT:PSS interfaces and/or interaction with the P3HT:PCBM layer. This sensitive interface could be affected by PEDOT:PSS vertical segregation forming a barrier between PEDOT:PSS and thus reducing the leakage current of the device (Fig. 4b). Nevertheless, the mechanism is not currently clear and needs to be further investigated. Based on the systematic study of J/V characteristics over time of exposure, we suggest that PEDOT:PSS deterioration is a major degradation mechanism of inverted OPVs, caused either by its hygroscopic nature or its sensitive interface with the active layer.

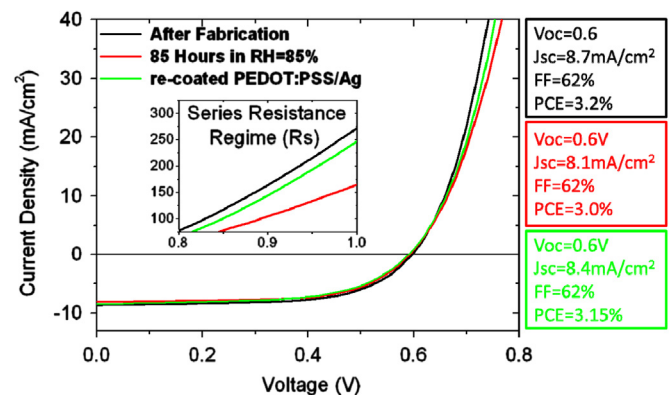


Fig. 5. J/V characteristics of inverted OPVs after fabrication (black), upon exposure to RH=85% for 85 h (red) and after reverse engineering (green). The insert represents the R_s regime of all the aforementioned inverted OPVs. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The suggested degradation mechanisms are in accordance with several studies found in literature which have addressed degradation of PEDOT:PSS as the primary reason for inverted OPVs degradation [12,15,37,40]. Krebs et al. have shown that the mechanism responsible for the degradation of inverted OPVs which are exposed to dark ambient environment is the phase separation of PEDOT:PSS due to water and oxygen molecules absorbance as well as the interaction between PEDOT:PSS and the active layer [41].

Finally, in order to verify the assumption that inverted OPVs degrade due to the deterioration of PEDOT:PSS, the top electrode was reverse engineered after a certain time of exposure to humidity. PEDOT:PSS and Ag were removed and re-fabricated similarly to the first inverted device fabrication. The already evaporated electrode was extracted with a simple scotch tape and observed in optical microscopy for traces of PEDOT:PSS. The scotch tape technique was performed in devices that were exposed for different periods of time in humidity. It was found that up to 85 h of exposure the PEDOT:PSS has a stronger interface with Ag than with the active layer. At larger periods of exposure, traces of PEDOT:PSS on the scotch taped active layer were observed in optical microscopy. After recoating PEDOT:PSS on top of the active layer, the device was re-evaporated with Ag. Fig. 5 compares the same inverted OPV J/V curves after fabrication, after 85 h of exposure to 85% humidity environment and after subjection to reverse engineering with re-fabrication of the top electrode.

Fig. 5 demonstrates increased R_s and reduced J_{sc} after 85 h under high humidity lifetime conditions and thus reduced device performance. When the old PEDOT:PSS/Ag electrode is removed and a fresh one is re-fabricated, a decrease in R_s and increase in J_{sc} is observed. Increased and decreased R_s are strongly correlated with degraded and fresh PEDOT:PSS respectively, something which strongly indicates that the degradation of the PEDOT:PSS hole selective top contact is a major source of degradation for inverted OPVs.

4. Conclusions

The present work examines the sources of degradation of the electrodes of OPVs under accelerated humidity lifetime conditions. Reverse engineering can be a useful technique to identify main degradation OPV mechanisms. In agreement with current literature, it is observed that the dominant degradation mechanism in normal OPVs is the oxidation of the top electrode. The OPV performance dropped below 40% of the initial PCE within only 45 min of exposure to RH=85%. Upon re-fabrication of the top electrode, the PCE exhibited similar values with the initially fabricated OPVs. In addition, buffer interlayers found in literature such as ZnO and Cr [23,32,33] have been collectively implemented either with Al or Ag resulting in significant increase (12 times) on the stability of normal OPVs. However, in the case of Cr, the increase on the stability of OPVs is not escorted by preservation or increase of the PCE. Furthermore, it is observed that the bottom electrode degradation of normal OPVs acts as a secondary source of degradation originating from the PEDOT:PSS hole selective contact. Electrical conductivity measurements upon exposure to highly humid environment demonstrated that the conductivity of PEDOT:PSS is significantly reduced, whereas ITO conductivity remained constant. As expected, even though the stability of normal OPVs was increased using alternative buffer layers (Cr, ZnO etc.), the improvement was still very limited when compared to the stability of inverted OPVs. Importantly, reverse engineering of the top electrode demonstrates that the major source of degradation for inverted OPVs under accelerated humidity lifetime conditions is due to PEDOT:PSS hole selective contact.

Acknowledgments

This work was co-funded by the European Regional Development Fund and the Republic of Cyprus through the Research Promotion Foundation (Strategic Infrastructure Project NEA ΥΠΟΔΟΜΗ/ΣΤΡΑΤΗ II /0308/06).

References

- [1] K. Kawano, R. Pacios, D. Poplavskyy, J. Nelson, D.D.C. Bradley, J.R. Durrant, Degradation of organic solar cells due to air exposure, *Sol. Energy Mater. Sol. Cells* 90 (2006) 3520–3530.
- [2] S. Bertho, G. Janssen, T.J. Cleij, B. Conings, W. Moons, A. Gadisa, J.D. Haen, E. Goovaerts, L. Lutsen, J. Manca, D. Vanderzande, Effect of temperature on the morphological and photovoltaic stability of bulk heterojunction polymer: fullerene solar cells, *Sol. Energy Mater. Sol. Cells* 92 (2008) 753–760.
- [3] J. Morgado, R.H. Friend, F. Cacialli, Environmental aging of poly(p-phenylene-vinylene) based light-emitting diodes, *Synth. Met.* 114 (2) (2000) 189–196.
- [4] D. Sutherland, J. Carlisle, P. Elliker, G. Fox, T. Hagler, I. Jimenez, H. Lee, K. Pakbaz, L. Terminello, S. Williams, F. Himpel, D. Shuh, W. Tong, J. Lia, T. Callcott, D. Ederer, Photooxidation of electroluminescent polymers studied by corelevel photoabsorption spectroscopy, *Appl. Phys. Lett.* 68 (1996) 2046–2048.
- [5] N. Grossiord, J.M. Kroon, R. Andriessen, P.W.M. Blom, Degradation mechanisms in organic photovoltaic devices, *Org. Electron.* 13 (3) (2012) 432–456.
- [6] M. Lira-Cantu, D.M. Tanenbaum, K. Norrman, E. Voroshazi, M. Hermenau, M.T. Lloyd, G. Teran-Escobar, Y. Galagan, B. Zimmermann, M. Hösel, H.F. Dam, M. Jørgensen, S. Gevorgyan, L. Lutsen, D. Vanderzande, H. Hoppe, R. Rösch, U. Würfel, R. Andriessen, A. Rivaton, G.Y. Uzunoglu, D. Germack, B. Andreasen, M.V. Madsen, E. Bundgaard, F.C. Krebs, Combined characterization techniques to understand the stability of a variety of organic photovoltaic devices: the ISOS-3 inter-laboratory collaboration, in: *Proceedings SPIE 8472, Reliability of Photovoltaic Cells, Modules, Components, and Systems 847203*, October 2012, 10.1117/12.929579.
- [7] L. Do, E. Han, Y. Nidome, M. Fujihira, T. Kanno, S. Yoshida, A. Maeda, A. Kushima, Observation of degradation processes of Al electrodes in organic electroluminescence devices by electroluminescence microscopy, atomic force microscopy, scanning electron microscopy, and Auger electron spectroscopy, *J. Appl. Phys.* 76 (9) (1994) 5118–5121.
- [8] C.J. Brabec, A. Cravino, D. Meissner, N. Sariciftci, M. Rispens, L. Sanchez, J. Hummelen, T. Fromherz, The influence of materials work function on the open circuit voltage of plastic solar cells, *Thin Solid Films* 403–404 (2002) 368–372.
- [9] M. Schaer, F. Nuesch, D. Berner, W. Leo, L. Zuppiroli, Water vapor and oxygen degradation mechanisms in organic light emitting diodes, *Adv. Funct. Mater.* 11 (2) (2001) 116–121.
- [10] M.O. Reese, A.J. Morfa, M.S. White, N. Kopidakis, S.E. Shaheen, G. Rumbles, D.S. Ginley, Short-term metal/organic interface stability investigations of organic photovoltaic devices, in: *Proceedings of the 33rd IEEE Photovoltaic Specialists Conference*, San Diego, California, 2008.
- [11] M. Wang, F. Xie, J. Du, Q. Tang, S. Zheng, Q. Miao, J. Chen, N. Zhao, J.B. Xu, Degradation mechanism of organic solar cells with aluminum cathode, *Sol. Energy Mater. Sol. Cells* 95 (2011) 3303–3310.
- [12] E. Voroshazi, B. Verreet, A. Buri, R. Müller, D. Di Nuzzo, P. Heremans, Influence of cathode oxidation via the hole extraction layer in polymer:fullerene solar cells, *Org. Electron.* 12 (2011) 736–744.
- [13] E. Vitoratos, S. Sakkopoulos, E. Dalas, N. Paliatas, D. Karageorgopoulos, F. Petraki, S. Kennou, S.A. Choulis, Thermal degradation mechanisms of PEDOT:PSS, *Org. Electron.* 10 (2009) 61–66.
- [14] E. Vitoratos, S. Sakkopoulos, N. Paliatas, K. Emmanouil, S.A. Choulis, Conductivity degradation study of PEDOT: PSS films under heat treatment in helium and atmospheric air, *Open J. Org. Polym. Mater.* 2 (2012) 7–11.
- [15] M.T. Lloyd, D.C. Olson, P. Lu, E. Fang, D.L. Moore, M.S. White, M.O. Reese, D.S. Ginley, J.W.P. Hsu, Impact of contact evolution on the shelf life of organic solar cells, *J. Mater. Chem.* 19 (2009) 7638–7642.
- [16] C.W.T. Bulle-Lieuwma, W.J.H. van Gennip, J.K.J. van Duren, P. Jonkheijm, R.A. J. Janssen, J.W. Niemantsverdriet, Characterization of polymer solar cells by TOF-SIMS depth profiling, *Appl. Surf. Sci.* 203 (2003) 547–550.
- [17] M.P. De Jong, L.J. van Ijzendoorn, M.J.A. de Voigt, Stability of the interface between indium-tin-oxide and poly(3,4-ethylenedioxythiophene)/poly(styrenesulfonate) in polymer light-emitting diodes, *Appl. Phys. Lett.* 77 (2000) 2255–2257.
- [18] S.D. Yambem, K.-S. Liao, N.J. Alleya, S.A. Curran, Stable organic photovoltaics using Ag thin film anodes, *J. Mater. Chem.* 22 (2012) 6894–6898.
- [19] M. Jørgensen, K. Norrman, F.C. Krebs, Stability/degradation of polymer solar cells, *Sol. Energy Mater. Sol. Cells* 92 (2008) 686–714.
- [20] D.M. Tanenbaum, M. Hermenau, E. Voroshazi, M.T. Lloyd, Y. Galagan, B. Zimmermann, M. Hösel, H.F. Dam, M. Jørgensen, S. Gevorgyan, S. Kudret, W. Maes, L. Lutsen, D. Vanderzande, U. Würfel, R. Andriessen, R. Rosch, H. Hoppe, G. Teran-Escobar, M. Lira-Cantu, A. Rivaton, G.Y. Uzunoglu, D. Germack, B. Andreasen, M.V. Madsen, K. Norrman, F.C. Krebs, The ISOS-3 inter-laboratory collaboration focused on the stability of a variety of organic photovoltaic devices, *RSC Adv.* 2 (3) (2012) 882–893.
- [21] S.A. Gevorgyan, M. Jørgensen, E. Bundgaard, S.R. Kurtz, D.S. Ginley, D.C. Olson, M.T. Lloyd, P. Morvillo, E.A. Katz, A. Elschner, O. Haillant, T.R. Currier, V. Shrotriya, M. Hermenau, M. Riede, K.R. Kirov, G. Trimmel, T. Rath, O. Inganäs, F. Zhang, M. Andersson, K. Tvingstedt, M. Lira-Cantu, D. DarinLaird, C. McGuinness, S.(J.) Gowrisanker, M. Pannone, M. Xiao, J. Hauch, R. Steim, D.M. DeLongchamp, R. Rosch, H. Hoppe, N. Espinosa, A. Urbina, G.Y. Uzunoglu, J.-B. Bonekamp, A.J.J.M. van Breemen, C. Grotto, E. Voroshazi, F.C. Krebs, Consensus stability testing protocols for organic photovoltaic materials and devices, *Sol. Energy Mater. Sol. Cells* 95 (2011) 1253–1267.
- [22] M. Jørgensen, K. Norrman, S. Gevorgyan, T. Tromholt, B. Andreasen, F.C. Krebs, Stability of Polymer Solar Cells, *Advanced Materials* 24 (2012) 580–612.
- [23] B. Andreasen, D.M. Tanenbaum, M. Hermenau, E. Voroshazi, M.T. Lloyd, Y. Galagan, B. Zimmermann, S. Kudret, W. Maes, L. Lutsen, D. Vanderzande, U. Würfel, R. Andriessen, R. Rosch, H. Hoppe, G. Teran-Escobar, M. Lira-Cantu, A. Rivaton, G.Y. Uzunoglu, D.S. Germack, M. Hösel, H.F. Dam, M. Jørgensen, S. A. Gevorgyan, M.V. Madsen, E. Bundgaard, F.C. Krebs, K. Norrman, TOF-SIMS investigation of degradation pathways occurring in a variety of organic photovoltaic devices – the ISOS-3 inter-laboratory collaboration, *Phys. Chem. Chem. Phys.* 14 (33) (2012) 11780–11799.
- [24] G. Teran-Escobar, D.M. Tanenbaum, E. Voroshazi, M. Hermenau, K. Norrman, M.T. Lloyd, Y. Galagan, B. Zimmermann, M. Hösel, H.F. Dam, M. Jørgensen, S. Gevorgyan, S. Kudret, W. Maes, L. Lutsen, D. Vanderzande, U. Würfel, R. Andriessen, R. Rosch, H. Hoppe, A. Rivaton, G.Y. Uzunoglu, D. Germack, B. Andreasen, M.V. Madsen, E. Bundgaard, F.C. Krebs, M. Lira-Cantu, On the stability of a variety of organic photovoltaic devices by IPCE and in situ IPCE analyses – the ISOS-3 inter-laboratory collaboration, *Phys. Chem. Chem. Phys.* 14 (33) (2012) 11824–11845.
- [25] R. Rosch, D.M. Tanenbaum, M. Jørgensen, M. Sealand, M. Barenklau, M. Hermenau, E. Voroshazi, M.T. Lloyd, Y. Galagan, B. Zimmermann, U. Würfel, M. Hösel, H.F. Dam, S. Gevorgyan, S. Kudret, W. Maes, L. Lutsen,

- D. Vanderzande, R. Andriessen, G. Teran-Escobar, M. Lira-Cantu, A. Rivaton, G.Y. Uzunoglu, D. Germack, B. Andreasen, M.V. Madsen, K. Norrman, H. Hoppe, F.C. Krebs, Investigation of the degradation mechanisms of a variety of organic photovoltaic devices by combination of imaging techniques—the ISOS-3 inter-laboratory collaboration, *Energy Environ. Sci.* 5 (2012) 6521–6540.
- [26] P. Schilinsky, C. Waldauf, C.J. Brabec, Performance analysis of printed bulk heterojunction solar cells, *Adv. Mater.* 16 (2006) 1669–1672.
- [27] A. Savva, S.A. Choulis, Cesium-doped zinc oxide as electron selective contact in inverted organic photovoltaics, *Appl. Phys. Lett.* 102 (23) (2013) 233301–233305.
- [28] A. Savva, M. Neophytou, C. Koutsides, K. Kalli, S.A. Choulis, Synergistic effects of buffer layer processing additives for enhanced hole carrier selectivity in inverted organic photovoltaics, *Org. Electron.: Phys. Mater. Appl.* 14 (11) (2013) 3123–3130.
- [29] S. Gevorgyan, M. Jørgensen, F.C. Krebs, K.O. Sylvester-Hvid, A compact multi-chamber setup for degradation and lifetime studies of organic solar cells, *Sol. Energy Mater. Sol. Cells* 95 (2011) 1389–1397.
- [30] F.C. Krebs, S.A. Gevorgyan, J. Alstrup, A roll-to-roll process to flexible polymer solar cells: model studies, manufacture and operational stability studies, *J. Mater. Chem.* 19 (2009) 5442–5451.
- [31] I.T. Sachs-Quintana, T. Heumüller, W.R. Mateker, D.E. Orozco, R. Cheacharoen, S. Sweetnam, C.J. Brabec, M.D. McGehee, Electron barrier formation at the organic-back contact interface is the first step in thermal degradation of polymer solar cells, *Adv. Funct. Mater.* 24 (2014) 3978–3985.
- [32] K. Lee, J.Y. Kim, S.H. Park, S.H. Kim, S. Cho, A.J. Heeger, Air-stable polymer electronic devices, *Adv. Mater.* 19 (2007) 2445–2449.
- [33] M. Manceau, D. Angmo, M. Jørgensen, F.C. Krebs, ITO-free flexible polymer solar cells: from small model devices to roll-to-roll processed large modules, *Org. Electron.* 12 (2011) 566–574.
- [34] N. Espinosa, R.G. Valverde, A. Urbina, F. Lenzenmann, M. Manceau, D. Angmo, F.C. Krebs, Life cycle assessment of ITO-free flexible polymer solar cells prepared by roll-to-roll coating and printing, *Sol. Energy Mater. Sol. Cells* 97 (2012) 3–13.
- [35] J. Kniepert, I. Lange, N.J. Van Der Kaap, L.J.A. Koster, D. Neher, A conclusive view on charge generation, recombination, and extraction in as-prepared and annealed P3HT:PCBM Blends: combined experimental and simulation work, *Adv. Energy Materials* 4 (2) (2014) 11 (Art. No 1301401).
- [36] S.R. Dupont, E. Voroshazi, P. Heremans, R.H. Dauskardt, The effect of anneal, solar irradiation and humidity on the adhesion/cohesion properties of P3HT:PCBM based inverted polymer solar cells, in: *Proceedings of the 38th IEEE Photovoltaic Specialists Conference*, Austin, TX, USA, 2012, Art. No 6318272, pp. 3259–3262.
- [37] M.T. Lloyd, C.H. Peters, A. Garcia, I.V. Kauvar, J.J. Berry, M.O. Reese, M.D. McGehhe, D.S. Ginley, D.C. Olson, Influence of the hole-transport layer on the initial behavior and lifetime of inverted organic photovoltaics, *Sol. Energy Mater. Sol. Cells* 95 (2011) 1382–1388.
- [38] P. Schilinsky, C. Waldauf, J. Hauch, C.J. Brabec, Simulation of light intensity dependent current characteristics of polymer solar cells, *J. Appl. Phys.* 95 (5) (2004) 2816–2819.
- [39] A.W. Hains, Z. Liang, M.A. Woodhouse, B.A. Gregg, Molecular semiconductors in organic photovoltaic cells, *Chem. Rev.* 110 (11) (2010) 6689–6735.
- [40] C. Waldauf, M. Morana, P. Denk, P. Schilinsky, K. Coakley, S.A. Choulis, C.J. Brabec, Highly efficient inverted organic photovoltaics using solution based titanium oxide as electron selective contact, *Appl. Phys. Lett.* 89 (23) (2006) 3 (Art. No 233517).
- [41] K. Norrman, M.V. Madsen, S.A. Gevorgyan, F.C. Krebs, Degradation patterns in water and oxygen of an inverted polymer solar cell, *J. Am. Chem. Soc.* 132 (2010) 16883–16892.