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

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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.

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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].

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

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C_{61}-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/cm^2 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