Analysing impact of oxygen and water exposure on roll-coated organic solar cell performance using impedance spectroscopy

B. Arredondo[a,b,*], B. Romero[a], M.J. Beliatis[c], G. del Pozo[a], D. Martín-Martín[a], J.C. Blakesley[b], G. Dibb[b], F.C. Krebs[c], S.A. Gevorgyan[c], F.A. Castro[b]

[a] *Área de Tecnología Electrónica, Universidad Rey Juan Carlos, C/ Tulipán s/n, 28933 Móstoles, Spain*
[b] *National Physical Laboratory, Hampton Rd, Teddington TW11 0LW, UK*
[c] *Department of Energy Conversion and Storage, Technical University of Denmark, Frederiksborgvej 399, DK-4000 Roskilde, Denmark*

A B S T R A C T

In this work we study the degradation of roll-coated flexible inverted organic solar cells in different atmospheres. We demonstrate that impedance spectroscopy is a powerful tool for elucidating degradation mechanisms; it is used here to distinguish the different degradation mechanisms due to water and oxygen. Identical cells were exposed to different accelerated degradation environments using water only, oxygen only, and both water and oxygen simultaneously, all of them enhanced with UV light. The photocurrent is dramatically reduced in the oxygen-degraded samples. Impedance measurements indicate that this phenomenon is attributed to defects introduced by absorption of oxygen, which results in an increase of the acceptor impurity (N_A) at the cathode interface obtained from a Mott-Schottky analysis. Simultaneously, at the anode interface where PEDOT:PSS is not shielded by the substrate, the nature of degradation differs for the water and oxygen degraded samples. While oxygen + UV light decreases the conductivity of the PEDOT:PSS layer, water + UV light changes the PEDOT:PSS work function inducing a depletion region at the anode.

1. Introduction

Organic photovoltaics (OPV) present several advantages such as lightness, thinness and flexibility [1,2]. Moreover, the active layer can be deposited onto flexible substrates by solution process techniques, allowing low-cost manufacturing processes such as roll-to-roll (R2R) printing for large areas [3–6]. However, OPV technology is limited by reduced power conversion efficiency (PCE) compared to inorganic cells [7]. Moreover, OPV suffers from degradation due to atmospheric agents such as water and oxygen, whose effects are enhanced under illumination [8–11]. In the last years, several groups have been devoted to study the effect of these degrading agents, not only in OPV, but also in dye sensitized solar cells [12,13] and in perovskite solar cells [14,15]. Simultaneously, there has been a great effort to developed robust encapsulation techniques and coatings to prevent degradation in oxygen and water atmospheres, including photopolymerized fluorinated coatings and hybrid coatings [16–18].

The degradation of photovoltaic performance relies on the interplay between interface and active layer degradation. Earlier stability studies have shown that device degradation in air is dominated either by the photo-oxidation of the active material under illumination [19–22] or by

degradation of the interface with the electrodes [10,23,24]. Furthermore, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is widely used as a selective contact in OPVs. The hygroscopic nature of this transport layer makes it particularly sensitive to water and oxygen [25–27], promoting the absorption of water and thus enhancing device degradation.

Extensive work has been performed in studying OPV degradation mechanisms using different characterization techniques such as imaging techniques [28], time of flight secondary-ion mass spectrometry (TOF-SIMS) [29], characterization according to ISOS-3 protocols under different illumination conditions (accelerated full sun simulation, low level indoor fluorescent lighting, and dark storage with daily measurement under full sun simulation) [30] and incident photon-to-electron conversion efficiency (IPCE) [31]. Impedance spectroscopy (IS) has been extensively used to study organic solar cell performance, although its use to study degradation has not been widespread. The aim of this work is to study the effect of oxygen and water in the degradation of roll-coated processed inverted organic solar cells by means of IS.

We present a study of an inverted OPV based on salen-based fluorine polymer (FSP1) [32] blended with phenyl-C_{61}-butyric acid methyl ester (PCBM) on a polyethylene terephthalate (PET) substrate

---

* Correspondence to: Universidad Rey Juan Carlos (Edificio Departamental II, despacho 158), C/ Tulipán s/n, 28933 Móstoles, Madrid, Spain.
E-mail address: belen.arredondo@urjc.es (B. Arredondo).

with structure PET/Ag/PEDOT:PSS/ZnO/FSP1:PCBM/PEDOT:PSS/Ag when exposed to most critical degradation agents: water, oxygen, and water + oxygen, combined with UV light exposure. The structure is designed to be low-cost by not employing indium-tin oxide (ITO), while both the Ag layers are in the form of open grids and consequently do not block the exchange of gas between the active layers and the atmosphere. This structure therefore experiences different degradation mechanisms to other common device structures. Impedance measurements together with equivalent-circuit analysis and simulation are employed to gain insight of kinetics and energetic processes governing the device performance. Moreover, by means of IS analysis, bulk and interfacial degradation mechanisms are elucidated when exposing the sample to different environments [33–36]. Furthermore, we find good agreement between the analysis of small-signal circuital parameters extracted from impedance, the fit of the J-V curve using DC circuits, and numerical simulations of band diagrams and J-V curves using the commercial software Silvaco TCAD.

2. Experimental methods

Devices were fabricated at the Technical University of Denmark and characterised at the National Physical Laboratory. The devices were fabricated on a mini roll coater using a slot-die head for the coating of photoactive layer (FSP1:PCBM) and PEDOT:PSS while a single roll flexography was used for the deposition of Ag back electrode. Active layer thickness is t = 400 nm. Further details on the fabrication process can be found at previous work described in reference [37].

J-V curves and Cole-Cole spectra were measured with a Modulab XM series Electrochemical System. A Xe-lamp based solar simulator (conforming to IEC 60904 9:2007 class AAA) and a custom-made LED system were used for illumination. The latter comprises multiple UV and visible LEDs and is used to provide controllable irradiance while minimising sample heating.

Three nominally identical samples from the same batch were subjected to three different accelerated degradation processes. The studies were performed on unencapsulated devices to execute highly-controlled accelerated aging without the variability that naturally comes from encapsulation. To achieve this, samples were degraded and characterised employing unique portable climate chambers capable of maintaining leak/outgassing rates of < 1 ppm/h for oxygen and water. The three degradation conditions were oxygen (1% O_2), water (0.2% H_2O) and oxygen + water (1% O_2 + 0.2% H_2O) at ambient pressure in a balance gas of purified nitrogen. These low concentrations relative to air were designed to simulate the gradual exposure to contamination, and have been found to produce quantifiable and reproducible degradation on a convenient timescale. Samples were exposed to these conditions for 6 days under UV–vis LED irradiation with a UV (< 400 nm) content of 46 ± 5 W/m^2 centred at 380 nm. At all other times, samples were stored, transported and characterised under controlled conditions with maximum permitted oxygen and humidity of 100 ppm. Such precautions are necessary as very low concentrations of oxygen and humidity in the presence of light can cause both transient and permanent changes to device characteristics [38]. A control sample (fresh) was stored in inert conditions for the sake of comparison. Impedance spectra were recorded by applying a small voltage perturbation (20 mV rms) at a frequency ranging from 1 MHz to 1 Hz in dark and light conditions for voltages varying from −1 V up to 1 V. Illuminated measurements were performed at 1 sun (AM 1.5G, 1000 W/m^2) using the solar simulator and variable irradiance from 0.05 sun up to 1.5 sun equivalent using the LED system under open-circuit conditions.

3. Results and discussion

Fig. 1 shows the current density *vs.* voltage (J-V) characteristics under 1 sun illumination for the three degraded and one fresh samples.
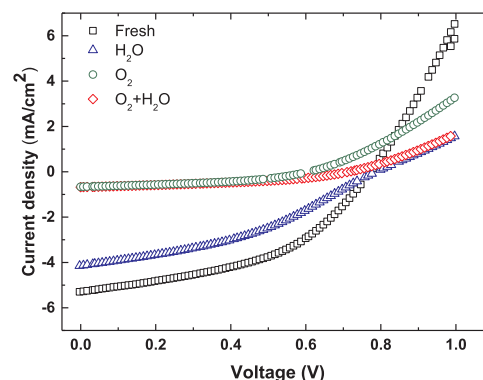

Fig. 1. Experimental J-V characteristics under AM1.5G illumination of fresh and degraded samples in different atmospheres: H_2O, O_2 and O_2 + H_2O (all combined with UV light). Device area = 1 cm^2.

Since the conductivity of ZnO can be changed with exposure to UV light, all samples were pre-treated with UV irradiation for 1 h before characterizing in order to maximize power conversion efficiency [8]. The J-V curves of the degraded samples show a decrease in the short circuit current (J_{SC}) and open circuit voltage (V_{OC}) compared to the fresh sample, as expected. Particularly, the curves exhibit a large decrease of J_{SC} for the samples that have been exposed to oxygen (O_2 and O_2 + H_2O) compared to the sample that has been exposed only to water (H_2O), in agreement with previous results found by other authors [33]. Moreover, the J-V curve of the (H_2O) sample exhibits the well-studied S-shape that results in a decrease of the fill-factor (FF) [39–41]. This S-shape is not visible, at least in the fourth quadrant of the J-V curve, for the oxygen exposed samples (O_2 and O_2 + H_2O). Table 1 summarizes the DC cell performance parameters.

These differences in the J-V behaviour of samples degraded in different atmospheres suggest that different underlying physical mechanisms are taking place and will be discussed later in the article.

Fig. 2 shows V_{OC} versus light intensity for the differently degraded samples. The ideality factor of each cell can be obtained from the slope of the linear fit. In the case of the H_2O + O_2 aged sample, the change of the slope at low light intensity may suggests a shunt resistance, so the ideality factor was calculated avoiding these low light intensities. Similar ideality factors can also be obtained from the dark J-V curves, however by using the measurements at open circuit conditions the effect of the series resistance has been avoided. Results are shown in Table 2.

It is apparent from the comparison of the slopes of all samples that those that have been exposed to oxygen (O_2 and O_2 + H_2O) exhibit a higher ideality factor. This result again suggests that the dynamical mechanisms taking place in the oxygen-degraded samples differ from those occurring in samples exposed to water. Previous theoretical and experimental investigations have linked high ideality factors to the formation of charge traps or shunts [42–45].

In order to gain a deeper insight of the physical mechanisms governing the device, we analyse the dark impedance data using a Mott-Schottky analysis at reverse and low forward bias when no significant charge is injected. For sufficiently thick samples, Mott-Schottky analysis gives information about the flat-band potential (V_{fb}) and acceptor impurity density (N_A) in the region of the metal cathode. The technique is

Table 1
Photovoltaic parameters of degraded and fresh cell under AM1.5G illumination.

	Fresh	H_2O	O_2	H_2O + O_2
V_{OC} (V)	0.71	0.63	0.59	0.63
I_{sc} (mA)	5.3	4.13	0.66	0.67
FF (%)	45.8	39	41.3	41.4
P_{max} (mW)	1.89	1.24	0.17	0.2