Grain size dependence of degradation of aluminium/calcium cathodes in organic solar cells following exposure to humid air

T.S. Glen [a], N.W. Scarratt [b], H. Yi [c], A. Iraqi [c], T. Wang [b], J. Kingsley [d], A.R. Buckley [b], D.G. Lidzey [b], A.M. Donald [a,*]

[a] University of Cambridge, Cavendish Laboratory, J J Thomson Avenue, Cambridge CB3 0HE, United Kingdom
[b] University of Sheffield, Department of Physics and Astronomy, Hicks Building, Hounsfield Road, Sheffield S3 7RH, United Kingdom
[c] University of Sheffield, Department of Chemistry, Dainton Building, Brook Hill, Sheffield S3 7HF, United Kingdom
[d] Ossila Limited, Kroto Innovation Centre, Broad Lane, Sheffield S3 7HQ, United Kingdom

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ABSTRACT

Cross-sectional TEM and SEM have been used to study the degradation of organic solar cells when exposed to a high humidity environment. Two obvious effects were caused by this exposure: voids at the aluminium/calcium interface and large bubble like protrusions on the top surface. Water ingress was found to occur mainly from the edge rather than through pinholes or defects in the aluminium film. The grain size of the aluminium used in the cathode was varied and small grained devices were found to have degraded faster. The importance of minimising water ingress into devices through cathode design and choice of materials is highlighted.

1. Introduction

Organic materials can potentially provide cheap, flexible, thin film solar cells that are easily manufactured in large volumes and contain no hazardous materials [1,2]. However, organic photovoltaic (OPV) devices still have low efficiencies compared with other materials and have lifetime problems due to sensitivity to ultraviolet light, water and oxygen [3,4]. Whilst a lot of work has been directed towards increasing efficiencies, the longevity and operational performance over time of these devices are just as important and is a growing area of interest in the field.

Degradation of OPV performance is complex and cannot be described by a single process. This is mainly due to the multi-layered structure and finely balanced morphology of the active layer. Lifetimes for unencapsulated devices are often a day or less. Encapsulation techniques can improve that considerably, but add additional costs and processing stages [5,6].

Much previous work has focused on monitoring the electrical performance of devices over time [7–9], with some observing the effect of exposure to different environments [10–12]. This is useful in that it provides quantitative values and practical parameters that can be seen to worsen. However it is not straightforward to separate the various causes of degradation and to identify which, if any, are dominant. Different techniques are needed in conjunction in order to understand all of the different degradation mechanisms and hence interpret the decreased lifetime.

One study used air exposure at various stages of device fabrication to determine which layer is being affected by air [13]. When tested, samples in which organic layers were previously exposed to air showed no difference to freshly made devices. It was thus concluded that the measured increase in series resistance with time as devices were aged was due to the oxidation of the aluminium at the aluminium/active layer interface. Using impedance spectroscopy it was proposed that this layer of aluminium oxide acts as a charge-blocking layer and grows thicker with time.

Another study used X-ray photoelectron spectroscopy (XPS) depth profiles to show the presence of aluminium oxide at the interface after ageing and that the use of PEDOT:PSS as the hole transport layer led to faster formation of this oxide layer, as well as faster degradation of the device performance [14].

Stability measurements have been made on devices with various cathodes and exposures [15]. Strong evidence was found that changes at the metal/active layer interface can account for a significant amount of the total loss of efficiency. These studies show

* Corresponding author.
  E-mail address: amd3@cam.ac.uk (A.M. Donald).

the importance of the cathode/active layer interface in organic solar cells.

The first reports of 'bubbles' forming in cathodes of organic devices came in the 90s in work on organic light emitting diodes (OLEDs) [16–18]. These bubbles were attributed to electrochemical reactions with water and oxygen, producing hydrogen and oxygen, which became trapped and caused delamination of the layers of the device.

Cross-sectional transmission electron microscopy (TEM) has previously been used to study degradation in OPVs. Thermal annealing has been used to drive phase separation and consequent growth of the P3HT:PCBM active layer into elongated protrusions [19], which were observed and studied using cross-sectional TEM alongside other techniques. It was found that these protrusions were formed from the lateral diffusion of the active layer and that the metal cathode remained intact until over 100 h of annealing.

The same technique has also been used to study the aluminium/active layer interface and an intermixed layer of ~3 nm was reported [20]. It was argued that this could not be an oxide layer as the devices were fabricated in a nitrogen glovebox, contrary to similar TEM work done on deposited aluminium films [21]. However, an intermixing layer of 2 nm at an aluminium/P3HT interface was also reported by another group using X-ray reflectivity [22]. Clearly there is some doubt regarding the details of this interface.

Small holes, or 'voids', at an aluminium/calcium interface have been previously reported [23]. In this study devices were kept in the dark and performance was monitored before cross-sectional TEM images were taken. Relatively stable open circuit voltage (V_{oc}) and a sharp drop in the short circuit current density (J_{sc}) combined with the TEM images suggested that the observed voids were the main cause of degradation in device performance with calcium and aluminium cathodes. These were thought to have been caused by oxygen and water, which are thought to ingress through grain boundaries and pinholes present in the cathode [24,25].

Another study found that water ingress was significant from both pinholes and from the edge of devices [26]. They also found that the rate of degradation was quicker at the edge of devices than around even large pinholes, but edge effects could be reduced by appropriate lateral design of the device. Indeed, it was found that if the cathode extended beyond the active area the degradation was significantly reduced.

Water diffusion from the edges through the PEDOT:PSS layer has been linked with the oxidation of the cathode and loss of J_{sc} [27]. By replacing the cathode on aged devices the J_{sc} could be fully recovered. The use of alternative hole transport layers was also found to reduce the observed degradation.

Recently, an adapted calcium test was used to measure the water ingress into non-encapsulated small molecule solar cells [28]. The calcium test is described in detail elsewhere [29]. It was found that most of the water ingress was through macroscopic defects in the aluminium top layer, and a few large (radius >300 nm) defects contributed to most (>72%) of the permeation. It has been argued that water is the primary source of degradation in devices [4,28].

We have studied the exposure of OPV devices to high humidity air. Unencapsulated devices have been exposed to humid air in order to accelerate any possible damage caused by water ingress. The use of a dual-beam Focussed Ion Beam–Scanning Electron Microscope (FIB-SEM) allows fabrication of cross-sectional site specific TEM samples. These TEM images obtained showed both large scale bubble defects and also smaller voids at the cathode-polymer interface.

The grain size of the evaporated aluminium used in the cathode was varied by changing the rate of deposition.This has been shown

to change the rate of degradation, which, to our knowledge, is an effect which has not been previously reported.

It was found that degradation at the cathode interface is the cause of device failure in humid conditions, and have proposed the formation of voids at the interface as a key degradation mechanism. Water ingress and dependence on the grain size of the aluminium used in the cathode was explored.

This work links previously reported void formation [23] with water ingress and used electron microscopy to confirm ingress from the edges of devices [26] and to view the effects of water on the cathode and PEDOT:PSS in operational devices.

2. Experimental

2.1. Device fabrication

OPV devices were fabricated on pre-patterned indium tin oxide (ITO) substrates provided by Ossila Ltd. The size of the substrates used was 20×15 mm, with six active pixels of 4 mm^2 on each. The substrates were cleaned by sonication; first with a Hellmanex® solution, then dilute sodium hydroxide (NaOH) and finally isopropyl alcohol.

The polymer used in the active layer for this study was poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′, 7′-di-2-thienyl-2′, 1′, 3′-othiadiazole)], known as PCDTBT, synthesised by Yi as reported previously [30]. The electron acceptor used was [6,6]-phenyl-C_{71} butyric acid methyl ester ($PC_{70}BM$), provided by Ossila Ltd. The active layer was dissolved in a polymer:$PC_{70}BM$ ratio of 1:4 at a concentration of 8 mg/ml in chlorobenzene.

The architecture of devices was ITO/PEDOT:PSS/PCDTBT-$PC_{70}BM$/calcium/aluminium, as shown in the schematic in Fig. 1. The PEDOT:PSS was spun cast onto ITO patterned substrates in air to form a layer ~20 nm thick before being annealed for 5 min at 130 °C to remove absorbed moisture. The PCDTBT-$PC_{70}BM$ active layer was spun cast in a nitrogen glovebox to form a layer ~70 nm thick. The PEDOT:PSS and active layer were then wiped off the cathode ITO contact using chlorobenzene and a cotton bud.

The cathode was thermally evaporated using the chamber in the glovebox. A ~8 nm thick layer of calcium was deposited by evaporation followed by ~75 nm of aluminium. The aluminium grain size was varied between devices by changing the rate of deposition. A rate of ~1 nm/s was found to give large grains, whilst ~0.01 nm/s was used for small grain films. Grain size was measured using a TEM to image the top surface of grains deposited onto a TEM grid placed alongside devices in the evaporator. The area of the large grains was measured at 6900 ± 2000 nm^2, whilst the slower rate produced grains of 110 ± 10 nm^2, where the errors are the standard error of the mean. Figs. S1–S4 show TEM images of small and large grain films. Finished devices were left
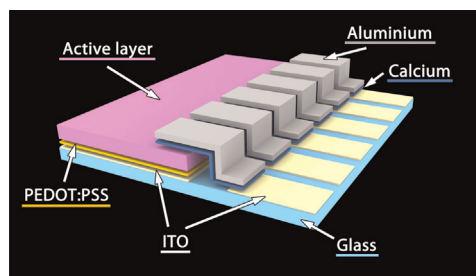

Fig. 1. Organic photovoltaic device structure. Photocurrent is collected at the aluminium/calcium cathode or at the ITO anode. This strip of aluminium/calcium is later referred to as a 'stripe', and connects the active area to another ITO contact for ease of electrical connection. The spin coated PEDOT:PSS and active layer are wiped away from the ITO connecting with the cathode. The active region of the device is the part with all the layers present, shown in the middle.