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Organic photovoltaic initial stage degradation analysis using impedance spectroscopy

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ABSTRACT

Shelf lifetime of organic solar cells based on P3HT:PCBM has been investigated using high magnitude and phase resolution impedance spectrometer. From the traditional current–voltage degradation curve, several stages of changes causing the device performance degradation are discussed. Degradation process of the devices has been monitored using impedance spectrometer under light, and dynamic parameters changes have been derived by model fitting, which are unable to provide information regarding the different stages of device changes though. However, layer analysis tested using impedance spectrometer in dark, provided exact information of device's layers and interfaces changes during degradation process. Higher capacitance at PEDOT-ITO interface and higher resistance at PEDOT-P3HT interface, and PEDOT bulk layer's performance fluctuations contributed to the beginning stages of device degradation. The degradation of P3HT:PCBM layer indicates the starting of the final device irreversible degradation.

1. Introduction

In the last decade, bulk hetero-junction organic photovoltaic (BHJ OPV) devices based on polymers have attracted significant interest due to their increasing efficiencies, light-weight, flexibility and low-cost production [1,2]. Power conversion efficiency (PCE) of >9.2% for single junction organic solar cells and ~10% for tandem organic solar cells have been demonstrated recently [3,4]. This results in BHJ OPV having extensive technology potential as a renewable energy source and also a promising alternative to silicon-based solar cells [5,6]. BHJ consists of a blend of an electron acceptor, usually a fullerene that is functionalized to improve the morphology and processing, and a hole transporter, which can be a light absorbing polymer. The two phases in the blend form small aggregates of the order of several nanometers, to facilitate rapid charge separation of electron and holes. A widely studied BHJ OPV device is the mixture of poly(3-hexylthiophehe) (P3HT) as the hole transporter and poly(6, 6-phenyl-C_{61}-butyric acid methyl ester) (PCBM) as an electron acceptor, which when optimized, can reach a maximum power conversion efficiency (PCE) of about 5% at 1 sun (AM1.5G irradiation with total power of 100 mW cm^{-2}) [7–11].

Although much research has been focused on increasing of solar cell efficiency [12–16], the total energy output of a solar cell equals the product of its efficiency and lifetime. Therefore, stability is an important organic solar cell property and the morphology evolution affecting device performance and lifetime is still under investigation. The detailed investigation on the impact of processing parameters on the nanoscale morphology of BHJ blends is challenging, as few techniques are able to characterize such organic thin films with adequate lateral and vertical resolution at the nanoscale. Methods such as transmission electron microscopy and scanning probe techniques have proven to be quite informative [17–19]; however, the relationships between nanoscale morphology, device performance and underlying electrical characteristics of functioning devices are not yet fully understood.

In this work, the INPHAZE impedance spectrometer is used for the characterization of P3HT:PCBM BHJ organic solar cells during device lifetime test. Layer morphology and interface quality have been analyzed to the nanoscale level, which provide exact information of device layers and interfaces changes during degradation process. The device degradation sequence and mechanism during the initial lifetime test have been revealed.

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2. Experiments and instrumentation

2.1. Fabrication process

All the cells reported here were fabricated on pre-patterned ITO-coated glass substrates with sheet resistance ~13 Ω/square. The ITO substrates were pre-cleaned by ultra-sonication in detergent solution, deionized water, acetone and isopropanol sequentially for 10 min each. The washed ITO substrates were further cleaned by exposure to UV–ozone treatment for another 10 min. The devices were then prepared by first applying a PEDOT:PSS layer via spin-coating of a commercial solution (Clevios). After baking at 120 °C for 10 min, a P3HT:PCBM layer was spin-coated via a 2.0 wt% solution of P3HT:PCBM with mixing ratio 1:0.8. Then a capping top electrode of 100 nm of aluminum was deposited in vacuum (2×10^{-4} Pa). Finally, the devices were thermally annealed at 120 °C for 10 min. The thickness of the P3HT:PCBM layer for each device was determined to be 200 nm by a surface profiler (Tencor P15).

2.2. Impedance measurements

The characterization of the BHJ OPV devices are carried out by an INPHAZE high resolution electrical impedance spectroscopy (HiRes EIS) system. The specifications of the INPHAZE impedance spectrometer include an impedance ranging from 0.1 to 10^{10} ohms, frequency range from 0.001 to 10^{6} Hz and configurations of two, three or four electrodes. When devices were tested under light, impedance data were collected and fitted using working equivalent circuit to further understand the electronic behaviors of BHJ OPV solar cells during aging. Based on literature study, the Garcia-Belmonte series model provides a high quality fit of the data over a wide range of conditions, and is applied to the impedance data obtained in this work [20,21]. When devices were tested in dark, the impedance data were collected and modeled as a combination of resistors and capacitors, which are in turn interpreted as the thickness and position of layers forming the surface or interface of the sample. Three pieces devices were applied on each measurement and the data used here are the average values.

3. Results and analysis

3.1. Shelf life study

To better understand the overall stability of the material in BHJ OPV devices, a shelf life study was carried out under normal lab conditions. Measurements of the *I–V* curves are made at an illumination of 1 sun and the results are shown in Fig. 1(a). Parameters such as Voc–Isc fill factor (FF) are extracted and the efficiency was calculated accordingly. The absolute values of these parameters are listed in Table 1. From the table, we can see that all parameters decreased with the time elapse. Fig. 1(b) is the normalized values of these parameters plotted versus time. It is clearly shows that the Isc decreased fastest at every measurement time, while the Voc decreased slowest among the parameters of Voc–Isc and FF. After 1000 h, the Voc decreased about 5% from 0.583 V to 0.569 V and the Isc decreased about 12% from 870 μA to 776 μA.

Voc is determined mainly by the energy difference between the HOMO of the electron donor and the LUMO of the electron acceptor. The decrease in Voc values can be attributed to the degradations of the components in the photoactive bulk layer and/or electrodes, leading to a change of the values of the HOMO of the electron donor and/or LUMO of the electron acceptor. The FF represents the overall quality of the device and provides information about the quality of charge extraction in the device, the evolution of the interfaces between the different layers and the charge transport through each layer. It is determined by intrinsic processes such as recombination losses and the formation of space charges due to unbalanced transport. Decrease in FF values are mostly attributed to the reduction in interfacial charge transfer efficiency between the different layers, e.g., due to degradation of the quality of the interface between the photoactive bulk layer and the electrode interface. Isc is determined by the external quantum efficiency of processes such as light absorption, exaction dissociation at the D/A interface, and free charge transfer and collection at the electrodes. A decrease in Isc during the cell operation corresponds to a decrease of the number of charges collected at the electrodes, which may be caused by various degradations impacting photon absorption, charge dissociation, transport to the electrodes as well as the photoactive layer.

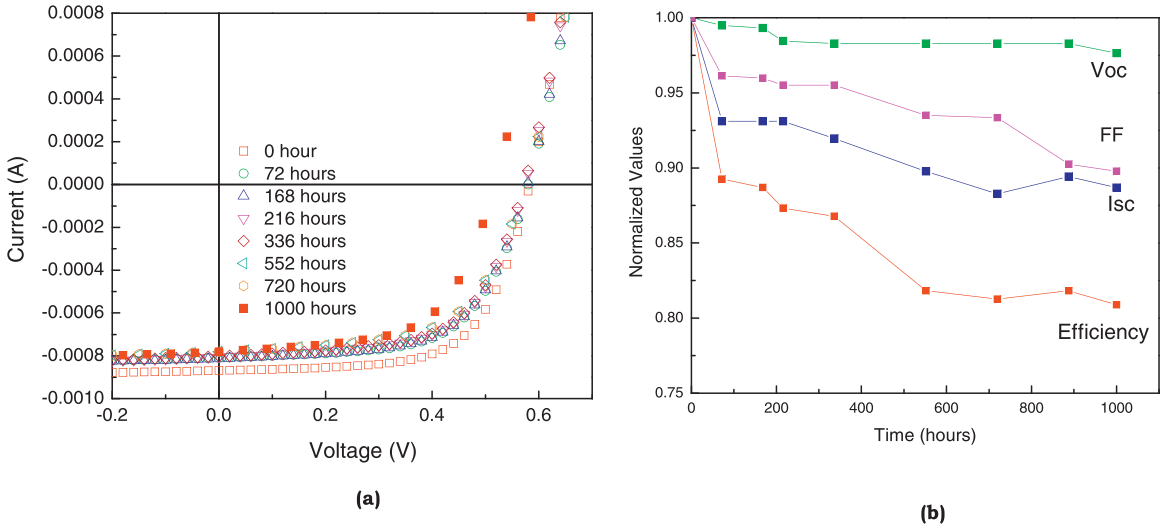

Fig. 1. (a) *I–V* curves measured for the device at 1 sun illumination during the aging process and (b) parameters extracted from the *I–V* measurements, normalized to their initial value.