Effects of Inserting Highly Polar Salts Between the Cathode and Active Layer of Bulk Heterojunction Photovoltaic Devices

Sean E. Shaheen, Christoph J. Brabec[1], N. Serdar Sariciftci[1], and Ghassan E. Jabbour
Optical Sciences Center, University of Arizona,
Tucson, AZ 85721, USA
[1]Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University of Linz, A-4040 Linz, Austria

ABSTRACT

Thermal deposition of small amounts of various salts at the interface between the active layer and the aluminum cathode was shown to alter the performance of bulk heterojunction photovoltaic devices. LiF and LiBr were found to enhance the power conversion efficiency as compared to devices with no interfacial salt, but Cs and K compounds were found to severely diminish the device performance. It is suggested that the Li compounds preferentially align to produce a bulk dipole moment at the interface, whereas the Cs and K compounds do not.

INTRODUCTION

Since the discovery of ultrafast photoinduced electron transfer between a conjugated polymer and a fullerene, photovoltaic devices based on blends of these materials have become promising candidates for inexpensive, large scale solar power conversion [1,2]. When blended together, the conjugated polymer and fullerene species form a bulk heterojunction of interpenetrating donor-acceptor networks. Upon absorption of a photon anywhere within the blend, mobile charges are created by electron transfer from donor to acceptor with a timescale of less than 50 fs. The resulting free hole and electron are then driven toward the anode and cathode, respectively, under the influence the built-in electric field that is established by the difference in the work-functions of the electrodes. Recent improvements in the morphology of the conjugated polymer : fullerene blend have resulted in a power conversion efficiency of 2.5% for a device under simulated solar (AM1.5) illumination [3]. This device also contained a small amount of LiF that was thermally deposited onto the active layer surface prior to deposition of the aluminum cathode. This technique was previously demonstrated to improve the electron injection efficiency in organic light emitting diodes (OLEDs). Here we investigate the use of a variety of similar materials at the active layer / cathode interface of the bulk heterojunction solar cell in order to better understand the mechanism by which this enhancement occurs. Materials that were investigated included LiF, CsF, LiBr, CsBr, KBr, and Cs formate.

EXPERIMENT

The structure of the bulk heterojunction solar cell is shown in figure 1. The fabrication of all the devices was performed in an identical manner except for the choice of salt deposited onto the active layer. First, a 150 nm thick film of poly(ethylene dioxythiophene) doped with polystyrene sulphonic acid (PEDOT:PSS, Bayer AG) was first spin-cast from a water solution
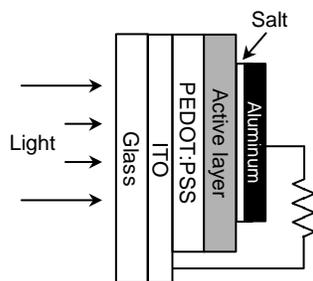
Figure 1. Schematic diagram of the bulk heterojunction photovoltaic device geometry.

onto an indium tin oxide / glass substrate. The PEDOT:PSS layer was then dried in vacuum for 3 hours at 140 $^{\circ}$C. The active layer, consisting of a blend of the conjugated polymer MDMO-PPV (poly(2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylene vinylene) and the methanofullerene PCBM ([6,6]-phenyl C_{61} - butyric acid methyl ester) (1:4 by weight), was then spin-cast onto the PEDOT:PSS layer from a chlorobenzene solution to yield a film with a thickness of 100 nm. The salt was then deposited onto the surface of the active layer from a thermal source at an operating pressure of 10^{-6} Torr. The rate of deposition for the salt was approximately 0.2 nm/min, and the average thickness was 1 nm. However, we emphasize that for thickness values on the order of ~1 nm the salt does not form a continuous film, but instead consists of island clusters on the surface of the active layer. A 130 nm aluminum cathode was then thermally deposited at a rate of 0.2 – 0.6 nm/s through a shadow mask to define a device area of 0.12 cm^2. For characterization, the device was illuminated with the 488 nm line of an argon laser with an intensity of 27 mW/cm^2. The temperature of the device during characterization, performed in an inert environment, was approximately 25 $^{\circ}$C.

RESULTS AND DISCUSSION

The values of the short circuit current density (J_{SC}), open circuit voltage (V_{OC}), fill factor (FF), and efficiency [4] are shown in figure 2 for the devices with various salts inserted at the active layer / aluminum interface. It is seen that devices containing Li compounds at the interface exhibit an increased J_{SC}, and either the same or slightly increased V_{OC} and FF, as compared to the device with no interfacial salt. This results in a relative increase of 10 – 15% in the power conversion efficiency of the devices containing Li compounds. In contrast, the devices containing Cs or K compounds exhibit a severely diminished J_{SC}, V_{OC}, and efficiency. The J-V curves for the devices with LiBr, CsF, and no interfacial salt are shown in figure 3. From this it is seen that insertion of either LiBr or CsF into the interface results in an increased forward injected current in the device. This indicates that the energetic barrier to electron injection from the aluminum cathode is reduced upon insertion of the salts. However, the device containing CsF also exhibits an increased injected current in the reverse direction. At a bias voltage of approximately -1.3 V, a turn-on of carriers injected in the reverse direction can be seen. The rectification property of the active layer / cathode interface is lost to some extent with the insertion of CsF, and the device is a poorer diode.
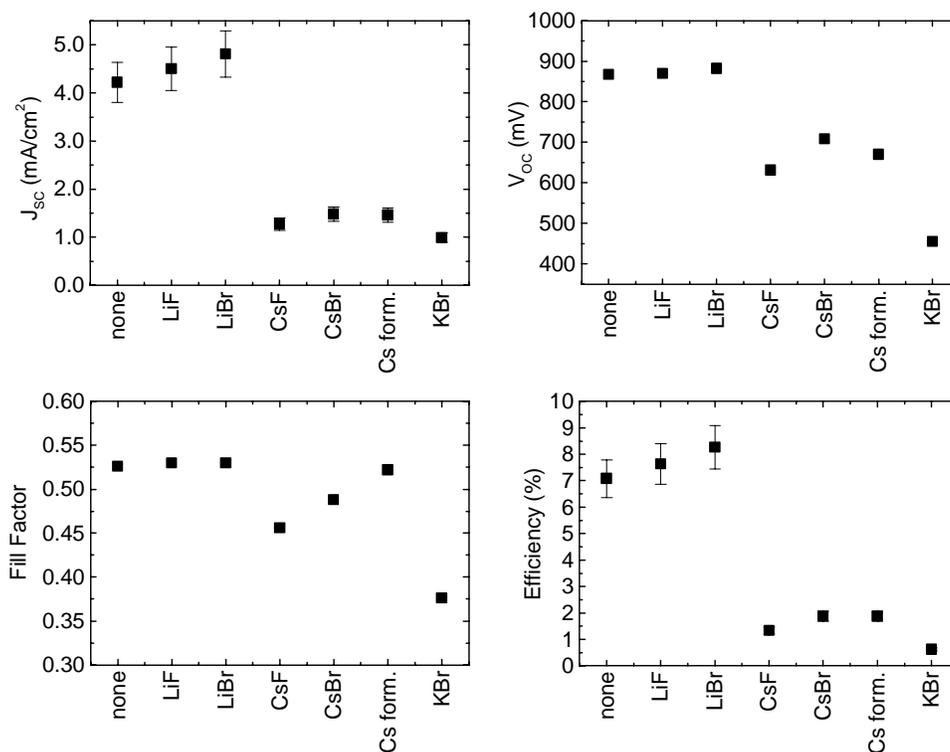
Figure 2. Comparison of short-circuit current density (mA/cm^2), open circuit voltage (mV), fill factor, and power conversion efficiency (%) for various salts inserted into the photovoltaic device with the following structure: glass / ITO / MDMO-PPV:PCBM / salt / aluminum. Error bars in the data are due to uncertainty in the device area.

Enhancement of electron injection from the cathode upon insertion of small amounts of polar salts has previously been found in several studies on OLEDs [5–9]. Several explanations have been proposed thus far for this behavior, including: 1) preferential alignment of the polar salt molecules to form a bulk dipole moment, thus leading to a vacuum level offset between the organic layer and the aluminum, 2) dissociation of the salt to produce, for instance, free Li that forms an alloy with the aluminum resulting in a lower work-function cathode, and 3) dissociation of the salt and subsequent doping of the organic layer by the alkali metal to increase its conductivity [10,11]. The findings in this study suggest that scenario 3) is an unlikely explanation, since either Li, Cs, or K would dope the organic layer in a similar manner. Scenario 2) is also unlikely, given that both CsF and KBr were shown to enhance the performance of OLEDs when inserted between the organic layer and the aluminum cathode [12,13]. We therefore suggest that scenario 1) is the most plausible explanation. The salts in this study have high dipole moments (LiF 6.33 D, LiBr 7.27 D, CsF 7.88 D, KBr 10.63 D) that would produce a substantial vacuum level offset if aligned to form a bulk dipole. The finding that only the Li compounds enhance the performance of the device suggests that, in the presence of an overlying metallic layer, Li$^+$ preferentially adheres to the surface of the MDMO-PPV:PCBM active layer. In the case of the Cs and K compounds, either there is no preferential alignment, or the alignment is in the opposite direction such that the alkali metal is pointing toward the aluminum.
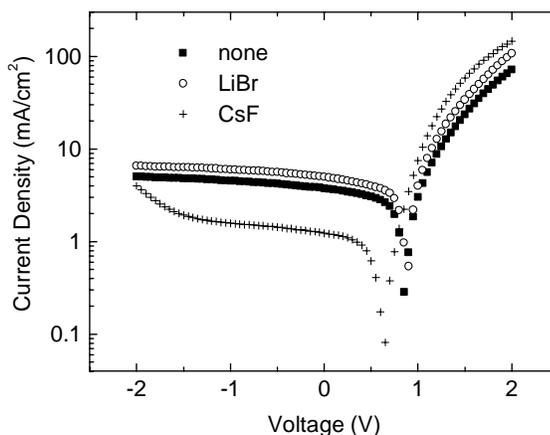
Figure 3. J-V curves for devices containing no interfacial salt (solid square), LiBr (open circle), and CsF (cross).

That CsF and KBr work to enhance the performance of conjugated polymer OLEDs but do not work here in the photovoltaic devices suggests that the fullerenes are largely responsible for the surface properties of the bulk heterojunction blend. Further studies are underway to clarify this issue.

CONCLUSIONS

Insertion of small amounts of various salts between the active layer and cathode of bulk heterojunction photovoltaic devices has been shown to effect the J_{OC}, V_{OC}, FF, and power conversion efficiency. Insertion of Li compounds was shown to enhance the efficiency, whereas Cs and K compounds severely degraded the efficiency. Preferential alignment of the dipole moments at the interface was suggested as the mechanism responsible for the different behaviors.

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4.   The power conversion efficiency η of a photovoltaic device, under illuminaton by a source of arbitary spectrum and intensity, is given by

$$\eta \ = \frac{P_{out}}{P_{in}} = FF \ \frac{V_{OC} \ J_{SC}}{P_{in}}$$

where P_{out} is the output electrical power of the device under illumination, P_{in} is the light intensity incident on the device, V_{OC} is the open-circuit voltage, and J_{SC} is the short-circuit current density. FF is the fill factor, given by

$$FF = \frac{V_{mpp} \ J_{mpp}}{V_{OC} \ J_{SC}}$$

where V_{mpp} and J_{mpp} are the voltage and current density at the maximum power point, respectively.

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