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## Efficient organic solar cells with polyfluorene derivatives as a cathode interfacial layer

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#### 1. Introduction

Conjugated polymer-based organic solar cells (OSCs) have received significant attention because they are a cost-efficient and flexible power source. As a result, OSCs have undergone considerable development and the organic syntheses and fabrication methods used in their production have been significantly improved [1–11]. Among the available polymer solar cell systems, poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C<sub>61</sub> (PCBM) blends have efficiencies of up to 4-5%; however, further improvement in efficiency is required for practical applications [9-11].

Typically, P3HT and PCBM based bulk-heterojunction (BHJ) solar cells have a sandwich-like structure consisting of an indium tin oxide (ITO) anode, a photoactive layer, and an Al metal cathode. Here, to achieve high-performance OSCs, the interface between the electrode and active layer must be an Ohmic contact to minimize the contact resistance and to maximize the open circuit voltage  $(V_{\rm oc})$  [12,13]. A preferred and simple method to enhance the contact between the electrode and the active laver is modification of the electrode by insertion of a buffer layer. For example, the insertion of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) between the ITO anode and active layer is commonly used in OSCs to enhance hole collection and increase  $V_{\rm oc}$  [14]. In the case of cathode modification, it was suggested that a thin LiF layer improves cell efficiency through the formation of an interfacial dipole that reduces the







### ABSTRACT

Use of a polyfluorene derivative (WPF-oxy-F) as the cathode interfacial layer was investigated for low-cost and high-efficiency organic solar cells (OSCs) based on poly(3-hexylthiophene) (P3HT) and 1-(3-methoxycarbonyl)-propyl-1-phenyl-(6,6)C<sub>61</sub> (PCBM). Insertion of the WPF-oxy-F interfacial layer between the P3HT/PCBM active layer and the metal cathode increased overall power conversion efficiency from 2.95% to 3.77% primarily due to the improved open circuit voltage and enhanced fill factor, resulting from a reduction of the metal work-function through the introduction of WPF-oxy-F.

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work-function of Al for better electron collection [15]. However, LiF is not an ideal interfacial layer in polymerbased cells for the following reasons: the LiF layer must be very thin (<1.2 nm) [15], which is difficult to achieve; and, vapor deposition of LiF in a vacuum is not well-suited for use in high-throughput roll-to-roll manufacturing, which is the most significant advantage of polymer-based cells [16].

Recently, the use of metal oxides, such as  $TiO_x$  and  $ZnO_y$ as an efficient buffer layer led to significantly enhanced cell efficiency [17-19], and OSCs with SAM-modified ZnO showed dramatic improvements in efficiency, mostly due to enhancements in  $V_{oc}$  and fill factor (FF) resulting from the formation of a favorable interfacial dipole [12,13]. In particular, Zhang et al. demonstrated that a solution-processed poly(ethylene oxide) (PEO) layer can form internal dipoles at the active layer/Al interface, resulting in enhanced the power conversion efficiency (PCE) and  $V_{oc}$ [16]. This organic-based interfacial layer that can be created using a simple solution-based process may be desirable for the realization of low-cost and high-efficiency OSCs. However, until very recently, only a few approaches for an organic-based interfacial layer in OSCs have been reported and, to date, insertion of an organic-based cathode interfacial layer into P3HT/PCBM-based OSCs has not been achieved.

The aim of the present study was to realize a low-cost and high-efficiency organic solar cell by insertion of an organic-based cathode interfacial layer into the cell using a simple solution-based process. We investigated the use of a water-soluble polyfluorene derivative (WPF-oxy-F) as the cathode interfacial layer in polymer solar cells, which was synthesized using a palladium-catalyzed Suzuki coupling reaction [20]. Herein, we demonstrate that simply by spin-coating the WPF-oxy-F, the overall power conversion efficiency of solar cells was increased, mainly resulting from the enhanced  $V_{oc}$  and FF.

#### 2. Experimental

The structure of the solar cell and the chemical structure of the WPF-oxy-F are presented schematically in Fig. 1. To fabricate the OSCs, glass substrates coated with ITO (Samsung Corning Co., Ltd.) having a sheet resistance

> WPF-oxy-F P3HT PCBM PEDOT:PSS ITO

a

of  $\sim 10 \Omega/sq$  were cleaned and PEDOT:PSS (Baytron P VPAI 4083) was spin-coated onto ITO followed by drying at 120 °C for 10 min, with a thickness of ~20 nm. A solution of 30 mg of P3HT (Rieke Metals) and 15 mg of PCBM (Nano-C) in 2 ml of chlorobenzene was then spin-coated on top of the PEDOT:PSS layer, forming the active layer with a thickness of ~80 nm. The WPF-oxy-F, dissolved in methanol at a concentration of 1mg/ml, was spin-coated onto the active layer. Finally, aluminum (100 nm) was thermally evaporated on the WPF-oxy-F layer in a vacuum at 10<sup>-6</sup> Torr. For comparison, solar cells without the WPFoxy-F layer were also fabricated using experimental procedures identical to those used to make the cells with the WPF-oxy-F layer. Photocurrent-voltage (I-V) measurements were performed using a Keithley 4200 instrument under 100 mW/cm<sup>2</sup> illumination from a 1 KW Oriel solar simulator with an AM 1.5 G filter in a N<sub>2</sub>-filled glove box. A calibrated silicon reference solar cell certified by the National Renewable Energy Laboratory (NREL) was used to confirm the measurement conditions.

#### 3. Results and discussion

First, we investigated the effect of the WPF-oxy-F layer and its thickness on the performance of OSCs without thermal annealing of the active layers. A reference cell containing only Al and cells with a WPF-oxy-F layer spin-coated at either 6000, 4000, or 2000 rpm were fabricated. The thicknesses of WPF-oxy-F layers spin-coated at various speeds were as follows:  $\sim$ 3 nm at 6000 rpm,  $\sim$ 4 nm at 4000 rpm, and ~6 nm at 2000 rpm. The photocurrent density-voltage (I-V) characteristics of the cells with a WPF-oxy-F layer are shown in Fig. 2, and detailed information on  $V_{\rm oc}$ , short-circuit current density (Jsc), FF, and PCE, calculated from the I-V curves in Fig. 2a, is presented in Table 1. As shown in Fig. 2b,  $V_{oc}$  values in all cells with a WPF-oxy-F layer were increased by 110 mV. Voc was relatively constant at ~0.68 V, independent of the thickness of the WPF-oxy-F layer, while FF and  $J_{sc}$  were slightly reduced as the thickness of the WPF-oxy-F layer increased. Thus, the cell with the WPF-oxy-F layer that was spin-coated at 6000 rpm had the highest efficiency. Furthermore, compared with the efficiency of the reference cell, the efficiency of each cell with a WPF-oxy-F layer was dramatically enhanced.



b

Fig. 1. (a) Structure of the organic solar cell with a WPF-oxy-F layer. (b) The chemical structure of the WPF-oxy-F polyfluorene derivative.

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