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# The effect of hole transport layer on the thermal stability of inverted polymer solar cells



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Stability

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#### ABSTRACT

In this article, the effect of hole transport layer (HTL) on the thermal stability of inverted polymer solar cells (PSCs) consisting of the blend of poly(3-hexylthiophene) (P3HT) and (6,6)-phenyl-C<sub>60</sub> butyric acid methyl ester fullerene derivative (PCBM) as active layer (AL) is investigated. The two conventional HTLs, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) and MoO<sub>3</sub>, were used in this study to demonstrate the effect of HTLs on the thermal stability of PSCs. The inverted devices were heated at 80 -110 °C as accelerated test for different time intervals to illustrate the temporal variation of performance. The different temporal behaviors during (1) metastable period and (2) thermally unstable period are described here. Moreover, the effect of photoactive film thickness on the thermal stability of devices based on the two HTLs was considered. This study shows that the spin- and spray-coated devices exhibit different characteristics of thermal stability for the PSCs with MoO<sub>3</sub> and PEDOT:PSS as HTLs, respectively. The temporal behavior caused by the effect of HTL during the thermally-unstable period is quantitatively studied. This study could provide vital information required to develop high durability in commercial PSCs.

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#### 1. Introduction

Polymer solar cells (PSCs) have attracted a lot of attention in the past decades due to several advantages they offer, such as light weight, low energy requirement in manufacturing, low manufacturing costs, solution processability, ease of large-area fabrication, and mechanical flexibility [1–3]. Many research groups have made efforts to improve the power conversion efficiency (PCE) of PSCs, and most of the groups focus on the synthesis of low band-gap polymers to effectively harvest incident photons [4–7], improving the bulk heterojunction structure (BHJ) of PSCs [8–10], and enhancing charge transport by interfacial engineering [11–13]. In the conventional PSC devices, the conducting polymer, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), is usually deposited between the AL and ITO electrode as the hole transporting layer (HTL), and the low work function (WF) metal is used as the metal electrode. However, the stability of

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.10.014 0141-3910/© 2016 Elsevier Ltd. All rights reserved. these conventional PSCs is limited due to the low WF metal electrode and ITO degradation by the acidic nature of PEDOT:PSS [14]. In addition, the hygroscopic nature of PEDOT:PSS would adsorb water molecules, which diffuse through the active layer and to the electrode and cause the oxidation of the low work function electrode [15]. Therefore, the inverted PSCs with good device stability are broadly investigated, aimed at PSC commercialization. Inverted PSCs, in general, use metal oxide, such as ZnO, TiO<sub>x</sub>, as the electron transport layer (ETL) between ITO and AL. In addition, less air sensitive high WF metal electrodes, such as Au or Ag, are used in the inverted PSC. However, most of the inverted PSCs show poor stability after prolonged exposure to heat due to the aggregation of PCBM [16]. Considering the fact that the AL of PSCs is subjected to serious phase separation due to high temperature, enhancing the thermal stability is of critical importance. In order to improve the thermal stability of PSCs by controlling the AL morphology, many strategies have been devised, which include addition of polymer compatibilizers [17], and the use of fullerene derivative [18-20] or thermally cross-linkable donor or acceptor materials within the AL [21,22]. By applying these strategies, the thermal stability of PSCs could be improved dramatically even at an elevated temperature of



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Fig. 1. The schematics of devices and the corresponding bandgap diagram based on (a, c) MoO<sub>3</sub> and (b, d) PEDOT:PSS as the HTL.



**Fig. 2.** Current-voltage curves of four types of spin-coated devices based on two active layer thicknesses and two HTLs (PEDOT:PSS and MoO<sub>3</sub>).

over 150  $^{\circ}$ C. However, most of these studies focus on the control of AL morphology evolution. There are only few studies describing the thermal stability due to the interfacial interaction between AL and

HTL. As reported in these studies such interface can effectively influence the performance of PSCs. It might be expected that the interfacial interaction between different HTLs and AL can cause the degradation of performance due to thermal effect that served as the motivation behind the present study. On the other hand, the P3HT:PCBM blend is generally adopted as the model system with good stability. Herein, the effect of HTLs on the thermal stability of PSCs based on inverted structures with different thicknesses of AL is reported. The two commonly used HTLs, PEDOT:PSS and MoO<sub>3</sub>, were adopted in this study to demonstrate the different thermal stability behavior. The PEDOT:PSS and MoO<sub>3</sub> devices were prepared using spin- and spray-coated processes, respectively. The results of this research open up new venues for high thermal stability PSCs.

#### 2. Experiment

#### 2.1. Materials

P3HT and PCBM were purchased from Rieke Metals. Indium tin oxide (ITO) coated glass substrate was used as transparent electrode and was obtained from Optical Filter Ltd (EMI-ito 15). The ZnO ETL was synthesized by sol-gel method, and the ZnO precursor was prepared as reported in our previous study [23]. The two HTL materials, PEDOT:PSS and MoO<sub>3</sub>, were purchased from Heraeus (Clevios AI 4083) and Aldrich, respectively.

#### Table 1

Performance characteristics of spin- and spray-coated devices based on two HTLs (PEDOT:PSS and MoO<sub>3</sub>).

AL concentration (mg/ml)	HTL	J <sub>sc</sub> (mA/cm <sup>2</sup> )	V <sub>oc</sub> (V)	FF (%)	PCE (%)	PCE <sub>max</sub> (%)
Spin devices						
10	PEDOT:PSS	$6.63 \pm 0.15$	$0.62 \pm 0.00$	$57.3 \pm 0.7$	$2.33 \pm 0.04$	2.4
	MoO <sub>3</sub>	$7.03 \pm 0.09$	$0.57 \pm 0.00$	$58.3 \pm 0.9$	$2.33 \pm 0.04$	2.4
15	PEDOT:PSS	$7.21 \pm 0.08$	$0.61 \pm 0.01$	$52.9 \pm 0.1$	$2.30 \pm 0.01$	2.3
	MoO <sub>3</sub>	$6.75 \pm 0.12$	$0.58 \pm 0.00$	$56.0 \pm 1.6$	$2.20 \pm 0.07$	2.3
Spray devices						
10	PEDOT:PSS	$8.76 \pm 0.09$	$0.58 \pm 0.00$	52.6 ± 1.3	$2.68 \pm 0.10$	2.80
	MoO <sub>3</sub>	$8.64 \pm 0.07$	$0.59\pm0.00$	$54.5 \pm 2.3$	$2.78 \pm 0.13$	2.90

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