Cathode Interface Investigation In Polymer/Fullerene Based Organic Solar Cells

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The authors investigate the cathode interface effects in polymer/fullerene based solar cell by using LiF, Liq and/or Bphen as the interfacial layers. Enhanced carrier extracting is observed by using Liq as the electron transport layer. A maximum power conversion efficiency of 3.75\% is obtained in the case of Liq, presenting a 14\% enhancement compared with the device with LiF as the electron transport layer. A detailed analysis of the capacitance as function of frequency and bias yields information about interfacial charges transport as well as the extraction and accumulation of charges is carried out. Cole–Cole impedance plots illustrate the interfacial resistance of different cathode buffer layer based device. The device shows good charge transport and the photo-generated changes could be effectively collected by the electrode and less charge accumulation when Liq is uswed as the cathode buffer layer.

\textbf{Keyword: Cathode interface, Liq, Impedance spectroscopy}

1. Introduction

Organic solar cells (OSCs) based on polymer/fullerene system have drawn more and more attention in resent years due to their advantages of flexibility, light-weight, low-cost and so on.[1-4] Achieving high-efficiency and stable device, which are mainly determined by carrier extraction and recombination properties,[5,6] are still two main motivations for OSCs’ commercialization. The choice of interface materials presents large influence on these carrier properties. Therefore, improving electron extraction and decreasing electron recombination by selecting different cathode structures and/or by synthesizing different electron-transporting materials are important research topics for practical applications of OSCs.[7,8] In a normal device structure of OSCs, LiF/Al cathode usually be selected as the cathode buffer layer. It is known that some other similar cathodes, such as Liq/Al, Bphen/LiF/Al, Bphen/Liq/Al are widely served in organic light emitting diodes (OLEDs).[9-12] It is believed that alkali or alkaline-earth cations, chemically reduced via the reaction between Al and the alkali or alkaline-earth metal compound, can dope the adjacent electron transporting layer to form complexes leading to improved electron injection from the cathode into the electron transporting layer. Generally speaking, the organic alkali or alkaline-earth metal complex/Al cathode, such as Liq/Al, has better thickness tolerance and lower evaporation temperature compared to the inorganic alkali or alkaline-earth metal compound/Al, such as LiF/Al.[13-16]

However, the organic alkali or alkaline-earth metal complex/Al cathode have not been investigated in OSCs. In this work, we investigate the cathode interface effects in polymer/fullerene based solar cell by using LiF, Liq and/or Bphen as the interfacial layers. Liq/Al cathode based device presents excellent character compared to LiF/Al cathode based one. The device Liq/Al cathode
obtain a 14% improvement in power conversion efficiency (PCE) from 3.30% to 3.75% with short-circuit current density ($J_{sc}$) of 9.69 mA/cm$^2$, open-circuit voltage ($V_{oc}$) of 0.59 V and fill factor (FF) of 67%.

2. Experimental

2.1. Device fabrication

OSC devices present a structure of ITO/PEDOT:PSS (35 nm)/P3HT:PCBM (120 nm)/ETL/Al (100 nm). The energy levels of the materials used are shown in Figure 1. The patterned ITO was cleaned by acetone, ethanol and deionized water sequentially, followed an oxygen plasma treatment for 15 min. PEDOT:PSS solution were then spin-coated onto the ITO at 4000 rpm for 60 s, and annealed at 120 °C for 10 min in air. The prepared samples were then transferred into a nitrogen-filled glove box for spin-coating the blend of P3HT and PC$_{61}$BM with 1:1 weight ratio (20 mg/mL each dissolved in 1,2-dichlorobenzene), then the samples were annealed at 110 °C for 10 min on a hotplate. Liq (2 nm)/Al (100 nm), LiF (0.5 nm)/Al (100 nm), Bphen (8 nm)/Liq (2 nm)/Al (100 nm), Bphen (8 nm)/LiF (0.5 nm)/Al (100 nm) were thermally evaporated through a shadow mask as the cathode under a pressure of 2×10$^{-6}$ torr, which defined the device area as 0.09 cm$^2$.

Figure 1. The energy level diagram of materials under investigation.

2.2. Measurements

Current density and voltage ($J$-$V$) characteristics of photovoltaic cells were taken using a Keithley 2400 source measure unit under a simulated AM1.5G spectrum with the intensity of 100 mW/cm$^2$. Impedance spectroscopy (IS) measurements were performed using Wayne Kerr 6550B precision impedance analyzer with 50 mV perturbation oscillation signal in a frequency range from 50 Hz to 20 MHz.

3. Results and Discussion

3.1. Photovoltaic performance

Figure 2. The $J$-$V$ characteristics in the reference device with LiF/Al as cathode, the device with Liq/Al, Bphen/Liq/Al, and the device with Bphen/Liq/Al as cathodes under 100 mW/cm$^2$ AM 1.5G simulated solar illuminations.

Table 1. Short-circuit current density ($J_{sc}$), open-circuit voltage ($V_{oc}$), power conversion efficiency (PCE), fill factor (FF) of various inverted PV devices with different cathode buffer layer.

| Interlayer | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|------------|----------------------|-------------|--------|---------|
| Bphen/Liq  | 7.24                 | 0.57        | 57     | 2.61    |
| Bphen/LiF  | 8.04                 | 0.56        | 56     | 2.33    |
| Liq        | 9.69                 | 0.59        | 67     | 3.75    |
| LiF        | 8.88                 | 0.59        | 62     | 3.30    |

The $J$-$V$ characteristics for photovoltaic cells with Liq/Al, LiF/Al, Bphen/Liq/Al, Bphen/LiF/Al layers as the cathodes are shown in Figure 2. A summary of the device performance is tabulated in Table 1. The reference device based on LiF/Al showed PCE of 3.31% with $V_{oc}$ of 0.59 V, $J_{sc}$ of 8.88 mA cm$^{-2}$, and FF 62% respectively. In the case of using Liq/Al as interlayer, $J_{sc}$ was increased from 8.88 mA cm$^{-2}$ to 9.69 mA cm$^{-2}$ with the PCE of 3.75%. However, the PCE was largely influenced by using Bphen/Liq/Al, Bphen/LiF/Al as the charge injection and transporting layers, the device PCE decreased to 2.61% and 2.33% respectively, which was mainly attributed to the decrease of $J_{sc}$ and FF. We mainly ascribe the decreased $J_{sc}$ of Bphen/Liq/Al, Bphen/LiF/Al based device to following several factors. One is the more suitable energy levels could be observed in Liq/Al, LiF/Al based device since LiF and Liq
are more likely to from tunneling effect when contact with the device active layer, so the lowest unoccupied molecular orbital (LUMO) of the Liq/Al, LiF/Al composites is more closely to the PC$_{61}$BM, so the electrons could be extract effectively. Furthermore, the energy difference between the LUMOs of PC$_{61}$BM and Liq is believed to be small compared to LiF, electrons could be easily extracted. If we increase the LiF thickness to form two interfaces, the electron injection would become worse because LiF is an insulator and could not form an effective band bending region within a thin layer. Liq layer can present better thickness tolerance. Since the better properties of Liq than LiF, Bphen/Liq/Al based device existed better device performance than Bphen/LiF/Al based device. The other reason of decreasing $J_{sc}$ with Bphen/Liq/Al, Bphen/LiF/Al cathodes is that the Bphen layer may cause photoproduction excitons quenching since the limited diffusion length of excitons in OSCs, and the Bphen layer could be easy crystallization, which increase the interface resistance, therefore the deterioration of devices FF.

3.2. Impedance spectroscopy evaluations

Figure 3. Capacitance-frequency plots for different cathode interface layer based OSCs.

In order to further investigate the change of device performance, impedance spectroscopy was utilized to characteristic for Bphen/Liq/Al, Liq/Al, LiF/Al based devices. Figure 3 shows the frequency dependent capacitance at different dc bias values for samples. When the bias voltage $V_0$ equals to 0 V, all organic layers are highly resistive and only geometrical capacitance are measured. There is some difference between these devices at $V_0 = 0$ V, the one with Bphen/Liq having slightly higher values of capacitance, which could be due to a thinner layer of Bphen/Liq compared to Liq and LiF. However, as soon as the bias voltage increased, the measured capacitance corresponds to the value of the electron transport layer. The relaxation frequency at $V_0 = 0.4$ V are changed, the relaxation frequency becomes smaller with Bphen/Liq layer which points toward a deterioration of electron transport to the electron transport layer interface, meanwhile, the LiF based device relaxation frequency is also slightly smaller than the Liq based device, which indicated that the electron transport in Liq based device presents the best performance.

Figure 4. Capacitance (1 KHz) as a function of bias with LiF/Al and Liq/Al as cathode buffer layer.

To confirm the charge accumulation effect in OSCs with different cathode buffer layers, we performed capacitance vs bias ($C$-$V$) measurements, which are shown in Figure 4. The LiF and Liq devices do not show a significant increase in the capacitance at the voltage range between negative bias to $V_{oc}$ (about 0.59 V). It indicates that the photo-generated charges can be effectively collected by the electrode and basically no charge accumulation occurs. However, for the Bphen/Liq based device, a significant increase is observed in the same bias range, which implies the photogenerated carriers are accumulated within the device and cannot be collected by the electrode effectively. The charge accumulation effect can also be used to explain the decrease $J_{sc}$ effect in the $J$-$V$ curves.

To further investigate the charge accumulation effect in the LiF and Liq based devices, Cole-Cole measurements was used. Figure 5(c) presents the equivalent circuit, $R_s$ represents the resistive losses in the electrodes, $R_1$|$C_1$ combination (corresponding to high frequency arc) is related to the bulk resistance and a capacitance that includes both a geometric component and a second component related to photoexcitation events in the
Figure 5. Measured Cole-Cole plots and optimized fittings of the OSCs device with (a) Liq/Al, (b) LiF/Al as cathodes using the equivalent circuit as shown in (c).

film. $R_2$|CPE combination corresponds the low frequency arc which relate to a recombination resistance and chemical capacitance that are associated with the internal charge transfer events at the donor/acceptor interfaces.[22] From Figure 5(a) and 5(b), we can get that the recombination resistance $R_2$ is large of Liq based device but these two device have similar $R_1$, which demonstrated that the carrier recombination in LiF-based device was more serious than that in Liq-based device.[23,24]

4. Conclusion

In summary, we have investigated the cathodes of Bphen/Liq/Al, Bphen/LiF/Al, Liq/Al, LiF/Al in OSCs. A maximum power conversion efficiency of 3.75% is obtained in the case of Liq, presenting a 14% enhancement compared with the device with LiF as the electron transport layer. $C-f$ curves demonstrate the better electron transport in Liq based device, and small charge accumulation occurs in this device by the characterization of $C-V$ and Cole-Cole measurements. The device shows good charge transport and the photo-generated changes could be effectively collected by the electrode and less charge accumulation when Liq as the cathode buffer layer.

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