

Solution processed, ionic compound dispersed with small molecular effective interfacial layer for Polymer Light-Emitting Devices

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We have fabricated highly efficient polymer light-emitting devices (PLED) from ionic compound (cesium carbonate) dispersed with organic molecular compound 2-(4-*tert*-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD), which was used as hole blocking and electron transport layer (HB-ETL) on the top of commercially available light emitting polymer. The device with HB-ETL showed a maximum current efficiency of 2.5 cd/A, while the one without HB-ETL showed an efficiency of 1.3 cd/A. They propose that the better performance in PLED with PBD layer was to a well-balanced charge injection in emitting layer after the enhanced electron transport due to ionic compound in the PBD layer.

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Keywords: Polymer light emitting devices, Interfacial layer, Charge injection, Small molecule

1. Introduction

Polymer light emitting diodes (PLEDs) have attracted considerable attention owing to their potential application in flat panel displays. Friend and co-workers reported PLEDs based on conjugated polymer poly(*p*-phenylenevinylene) as active layer prepared by solution process, suggesting that large area PLEDs could be made in low cost [1-8]. To achieve an efficient electroluminescence (EL) of a PLEDs, a balance in the injection and transport of charge carriers is required. In general indium tin oxide (ITO)/Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is used as the anode to attain hole injection ability. For the cathode, a common approach is the application of a metal with a low work function to realize a lower injected barrier for electrons. However, realize a lower injected barrier for electrons. However, these metals are susceptible to degradation caused by oxygen and moisture. From a practical viewpoint, it is desirable to use a stable metal as the cathode, such as Al and Ag, having a higher barrier for electron injection. To overcome the high electron injection barrier a modification between and EL polymer and the stable metal is required. These metals are very sensitive to moisture and oxygen and form detrimental quenching sites at areas near the interface between the electroluminescence (EL) layer and the cathode [5 – 14]. In addition, metal ions formed at the metal/organic interface tend to migrate into the EL layer, thus, affecting the long-term stability of devices. To improve electron injection from high work function metals into the emitting layer, numerous approaches have been attempted, examples, by inserting a thin layer of insulating species, such as lithium fluoride (LiF), Cesium fluoride (CsF), inorganic salts CH_3COOCs , Calcium(2) acetylacetonate $[\text{Ca}(\text{acac})_2]$, $\text{R}(\text{OCH}_2\text{CH}_2)_n\text{OSO}_3\text{Li}$, Sodium sulfonated polystyrene

(SSPS) ionomer, and NaOH all covered with Al, were all used as a buffer layer to an electron injection layer/cathode in an attempt to enhance the electron injection in the OLEDs or PLEDs [9-21].

Recently, water-soluble conjugated polymers with positive ammonium ions were used as an EIL. Owing to the enhancement in the interfacial dipole between the emitting layer and the metal cathode, it has been reported that this bilayer cathode could improve electron injection. In example neutral surfactants are based on poly(ethylene glycol) (PEG) or poly(propylene glycol) (PPG), and poly[9,9-bis(6-(diethanolamino)hexyl)fluorene] (PFN-OH), were used as an electron injection materials for polymer light emitting diodes. Cesium carbonate is reported to be one of the best electron injection materials, which can be used as electron injection (EIL) by vacuum vapor deposition. Huang et al. spin coated Cs_2CO_3 layer from its dilute solution in 2-ethoxyethanol on top of the emitting polymer, to enhance the electron injection and to block hole carriers at the PFO/ Cs_2CO_3 interface, leading to a better charge balance. Moreover, Hsiao et al. recently reported that few nanometer thickness of PEO doped Cs_2CO_3 spin coated from solution in methanol on top of the PFO emitting polymer, its superior hole blocking with better electron transport capability at the PFO/PEO- Cs_2CO_3 [11-21].

In this letter, we demonstrate highly efficient multilayer PLED by using a insulating salt having promising electron transport (ETL) capability for the electroluminescent polymer MEH-PPV. The composite layer Cs_2CO_3 and 2-(4-*tert*-Butylphenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) spin-coated from alcohol solution onto an emissive layer, and a work functional metal such as Ca/Al thermally deposited on top of the composite layer. This new type of multilayer cathode (PBD: Cs_2CO_3 /Ca/Al) can significantly enhance electron

transport to green electro luminescence polymers, thereby resulting in high efficiency polymer LEDs comparable to those using $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$ cathodes.

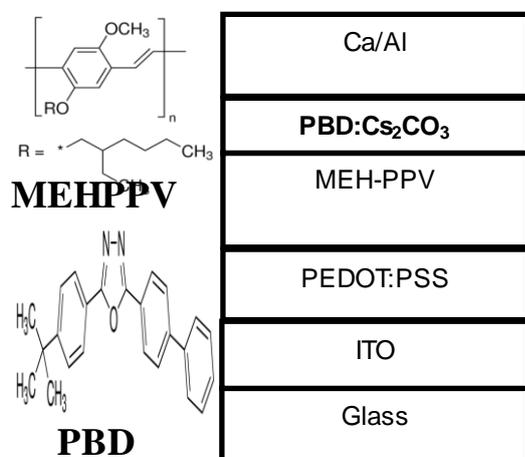


Fig. 1. Chemical structure of the organic materials and a typical device structure of the PLED used in this study

2. Experimental details

OLEDs were fabricated on ITO-coated glass substrates of which sheet resistance were 30 ohm/sq. ITO-coated glass substrate was carefully cleaned in sequence with the acetone, iso-propyl alcohol, methanol, de-ionized water, and then dried with high purity nitrogen gas and oxygen plasma treatment. The device configuration herein is comprised of ITO/glass substrate as the anode, poly(3,4-ethylene dioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS) as the hole transport layer, MEHPPV as the light-emissive layer, and PBD: Cs_2CO_3 as the interfacial layer, and the Ca/Al cathode electrode. The base pressure for thermal vacuum evaporation was 1×10^{-6} Torr.

Fig. 1 shows the device configuration and structure used in this study. The current-voltage (I-V) and brightness-voltage (B-V) characteristics and electroluminescent (EL) spectra of the devices were measured by using computer-controlled Keithley 2400 source-measure and PR650 SpectraScan photometer under the ambient condition.

3. Results and discussion

The device architectures studied are described as follows. The control device is based on ITO/PEDOT:PSS/MEHPPV/ $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$. The improved device with new cathode incorporates a PBD interfacial layer mixed with Cs_2CO_3 layer between the MEHPPV layer and the cathode, ITO/PEDOT:PSS/MEHPPV/PBD: $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$.

Fig. 2 shows the current density versus bias voltage characteristics of the devices with PEDOT:PSS used as the anode buffer layer. Since the energy level of the highest

occupied molecular orbital (HOMO) of PEDOT:PSS is around -5.2 eV and the HOMO level of MEHPPV is around -5.1 eV, there is almost no hole-injection barrier from PEDOT:PSS to MEHPPV. The current density-voltage characteristics show very few difference between $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$ or PBD: $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$ cathodes. Figure 3 shows that brightness versus bias voltage characteristics of the devices [6,13-14]. In sharp contrast to this, the brightness versus bias voltage characteristics differs greatly with changing cathodes as a result of the different hole blocking and electron-injection abilities as well as different degrees of quenching among these two kinds of cathode configurations. Because the energy level of the lowest unoccupied molecular orbital of MEHPPV is around -3.0 eV and the work function of Al and Ca are -4.3 eV and -2.9 eV respectively; there exists a large energy barrier for electron injection when Al alone is used as cathode while there is almost no barrier for Ca cathode. Quite amazingly, simply inserting a layer of Cs_2CO_3 and PBD mixed Cs_2CO_3 between MEHPPV and Cathode lead to an enhanced brightness of the resulting devices. In addition, the Cs_2CO_3 serves to block the diffusion of metal cathodes and thereby prevents the generation of quenching centers during the cathode deposition process. The Cs_2CO_3 serve to protect the polymer against contamination by oxygen and moisture [8,13-14,20-21].

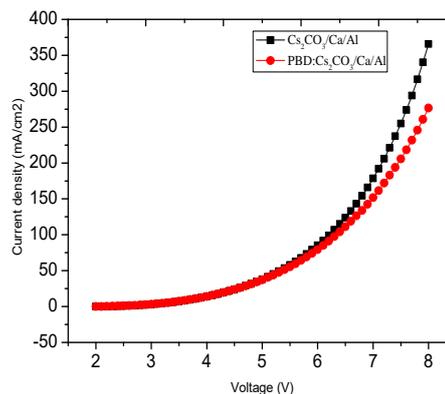


Fig. 2. Current density-Voltage curves of the devices using $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$ and PBD: $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$ as the device cathode.

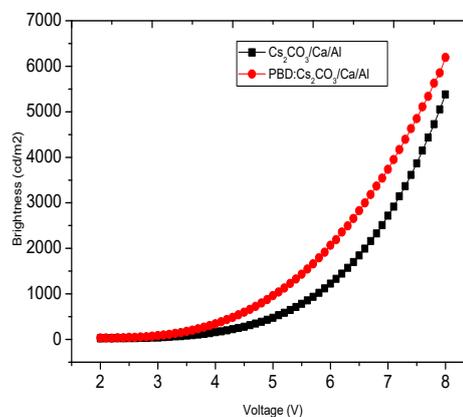


Fig. 3. Brightness-Voltage curves of the devices using $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$ and PBD: $\text{Cs}_2\text{CO}_3/\text{Ca}/\text{Al}$ as the device cathode.

Fig. 4 shows that the devices with PBD:Cs₂CO₃/Ca/Al cathodes have higher current efficiency (2.6 cd/A at 100 A/cm²) than that of the device with Cs₂CO₃/Ca/Al cathode (1.45 cd/A biased at 100 A/cm²). The current efficiency remains high in the high brightness regime when the devices are biased at high current. No variation in the electroluminescence spectra was observed (not shown in here). Therefore, the increases in the current efficiencies for the above devices are due to the improvement in the device performance, but not the color change of the emission[20-21]

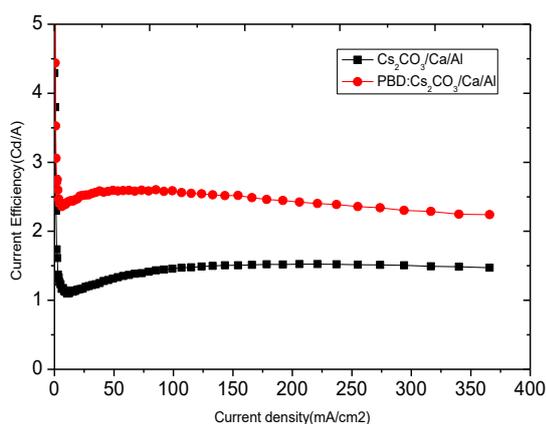


Fig. 4. The current efficiency versus current density for the devices applying Cs₂CO₃/Ca/Al and PBD:Cs₂CO₃/Ca/Al as the device cathode

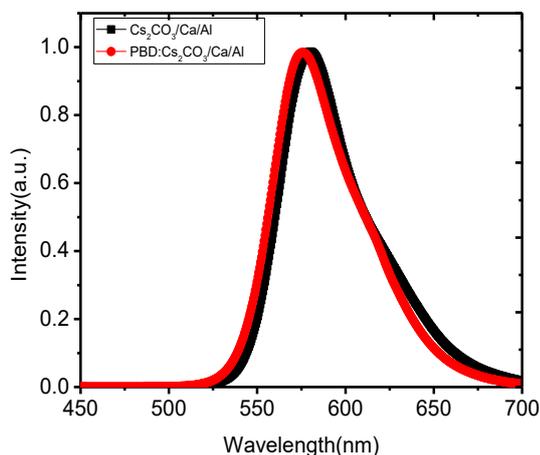


Fig. 5. Normalized electroluminescence of the devices using Cs₂CO₃/Ca/Al and PBD:Cs₂CO₃/Ca/Al as the device cathode

The normalized electroluminescence (EL) as a function of the emission wavelength (nm) of PLEDs with Cs₂CO₃/Ca/Al and PBD:Cs₂CO₃/Ca/Al were shown in Fig. 5. We obvious found that MEH-PPV the emission peak from the inter-chain vibration of MEH-PPV was little reduced, that suppose the possible reason the PBD assist

the polymer arrangement and reduce the conformational disorder of polymer in the emission layer, and then cause the probability for inter-chain emission of device to reduce. It is observed that the emission peak only takes place in the emission layer

4. Conclusions

In conclusion, we demonstrated a efficient PLED that consisted of interfacial layer between an emissive layer and cathode. This improvement can be attributed to the excellent balancing of holes and electrons through increasing electron transporting and blocking holes with reduced surface roughness. The result is a maximum brightness of over 6200 cd/m² and maximum luminance efficiency of 2.6 cd/A. Most importantly, our results indicate that high-performance PLEDs can be fabricated by processing all the layers from solution. We regard the formation of specific interaction and reaction at the interfacial layer during the cathode deposition which results in the enhanced injection of electrons.

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