

Hybrid organic-inorganic light-emitting electrochemical cells using fluorescent polymer and ionic liquid blend as an active layer

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We demonstrate enhanced device performance by using a blend of emissive polymer and mobile ionic liquid molecules in hybrid organic-inorganic polymeric light-emitting electrochemical cells with high air stability. The mobile anions and cations redistributed near each electrode/active layer interface make ohmic contacts, thereby enhancing current density and electroluminescence efficiency at relatively low operating voltage. © 2011 American Institute of Physics.

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Great attention has been paid to organic/polymer based light-emitting diodes (LEDs) over the past two decades for solid-state lighting, flat-panel display, and flexible electronic devices.¹ For commercially applicable LEDs, high device efficiency and stable lifetime of organic/polymer LEDs are necessary.

Recently, hybrid organic-inorganic polymeric light-emitting diodes (HyPLEDs) with metal oxides (ZnO, TiO₂, ZnO₂, and MoO₃) as a charge injection layer have been proposed due to the excellent air stability and high device performance.^{2–7} However, these HyPLEDs have intrinsic limitations in producing high device efficiency because of unbalanced charge carrier injection and transport. It has recently been reported that MoO₃ shows ohmic hole injection into materials with ionization potentials significantly deeper than that for poly(9,9'-dioctylfluorene-cobenzothiadiazole) (F8BT).⁸ MoO₃ has also been used in organic thin-film transistors,^{9,10} organic LEDs,¹¹ and HyPLEDs applications for improved hole injection. However, at the interface between the conduction band of ZnO (~4.0 eV) and the lowest unoccupied molecular orbital of an active layer, there exists the large energy barrier (more than 1 eV) in HyPLEDs, which results in poor electron injection efficiency and finally brings serious problems in obtaining highly efficient HyPLEDs.^{4,11} Therefore, interfacial engineering between the organic semiconductor and the inorganic layer is needed to reduce the barrier and balance the charge carrier injection to allow for low operating voltage and high device efficiency. Several methods have been suggested to address this problem: introducing cesium carbonate (CS₂CO₃),^{12,13} lithium fluoride,¹⁴ conjugated polyelectrolytes,¹⁵ ionic liquid,¹⁶ or a self-assembled dipole monolayer^{17,18} between contact layers can reduce the injection barrier, balance the charge carrier injection, and improve the device performance. However, there is still considerable room for optimizing contacts so as to yield high device performance.

Here, we present a straightforward strategy to reduce the charge injection barrier and enhance air stability and device

efficiency. This method relies on the mixing of mobile ionic liquid molecules (ILMs) into the fluorescent polymer layer in hybrid organic-inorganic polymeric light-emitting electrochemical cells (HyPLECs). The operating mechanism of the light-emitting electrochemical cells (LECs) is different from that of LEDs, as shown on Figs. 1(c)–1(e).^{19–22} The mobile anions and cations accumulated at each electrode/active layer interface under an applied bias form electric double layer and then a light-emitting p-n junction in emissive polymer layer. This p-n junction effectively reduces the charge injection barriers at the electrode/active layer interfaces, balanced charge injection, and high electroluminescence efficiency at relatively low operating voltages.

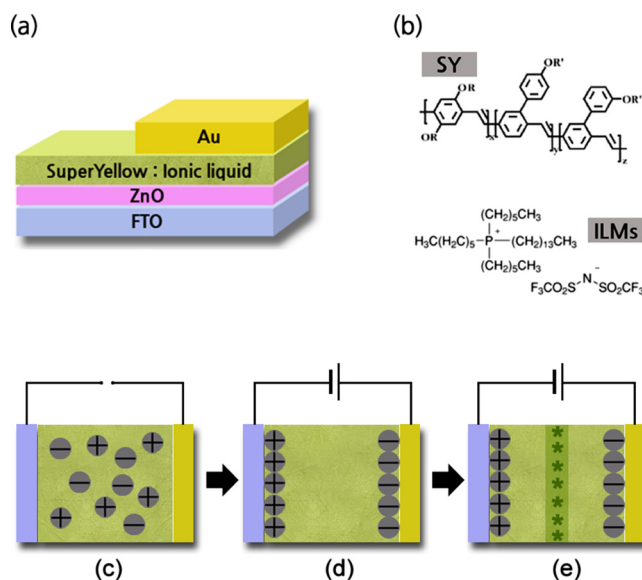


FIG. 1. (Color online) (a) Device configuration of HyPLECs using a blend of super yellow (SY) and ionic liquid molecules (ILMs). (b) Chemical structure of phenyl-substituted PPV copolymer, SY as a luminescent polymer and tetradecyltrihexylphosphonium bis(trifluoromethylsulfonyl)amide as mobile ILMs. Schematic representation of polymer LEC operation (c) before and (d) under an applied forward bias. (e) The recombination of injected electrons and holes in emissive layer caused by the redistribution of anions and cations.

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The performance of our HyPLECs was improved from a luminance of 0.11 cd/m², luminous efficiency of 0.002 cd/A, and turn-on voltage of 34.0 V for pure superyellow (SY) layer to a luminance of 3400 cd/m², luminous efficiency of 1.20 cd/A, and turn-on voltage of 2.1 V for blend films by optimizing the composition of SY and ILMs in HyPLECs.

Figure 1(a) shows the complete device architecture of HyPLECs. The hybrid devices were fabricated by successive deposition of SnO₂:F (FTO) as a transparent cathode, ZnO, a blended active layer, phenyl-substituted poly(para-phenylene vinylene) (PPV) copolymer [SY (Merck Co., Mw = 1 950 000 g/mol):tetradecyltriethylphosphonium bis(trifluoromethylsulfonyl)amide (hydrophobic ILMs, Aldrich), and Au as the anode. An 80-nm-thick ZnO film was deposited by spray pyrolysis method onto the precleaned FTO substrate using a ZnO precursor solution of zinc acetate dehydrate (Aldrich) in methanol at 400 °C.⁴ A single active layer is spin-coated (1500 rpm, 45 s) from a blend solution (9 mg/ml), which is composed of SY [Fig. 1(b)] as luminescent polymer and ILMs [Fig. 1(b)] as ion supply in chlorobenzene with different ILMs content, such as 0 (pure SY), 10, 20, 25, and 35 wt %. The blend films were annealed at temperature of 80 °C for 1 h in a nitrogen atmosphere glove-box. A 70-nm-thick Au layer is thermally evaporated on the active layer to complete device fabrication under vacuum at 10⁻⁶ Torr.

The SY:ILMs blend films were observed by atomic force microscopy as shown in Fig. S1.²⁵ As the ILMs weight percent was increased in fluorescent SY polymer, the root mean square roughness slightly increased. However, polymer blend film containing large ion portion (35 wt %) still had low roughness (~0.7 nm), and we could not find a significant phase separation in the blend film of SY and ILMs because hydrophobic ILMs show excellent compatibility with SY. We confirmed that the system is thermodynamically stable and that device stability, which is one of the important characteristic in applicable LEDs, is also likely to be excellent.

As mentioned before, HyPLECs and HyPLEDs show different operating mechanism. When a bias is initially applied, the electric field is equally distributed across the device, as shown in Fig. 1(c). An applied bias causes the motion of anions and cations toward the Au anode and the FTO/ZnO or FTO cathode, respectively, and the movement of the ions creates double layers, giving rise to then a light-emitting p-n junction in emissive polymer layer at each electrode/active layer interface until steady-state is reached, as shown in Fig. 1(d). This p-n junction enhances the charge carrier injection, thereby eliminating the restrictions on the work function of each electrode. Therefore, the HyPLECs exhibit

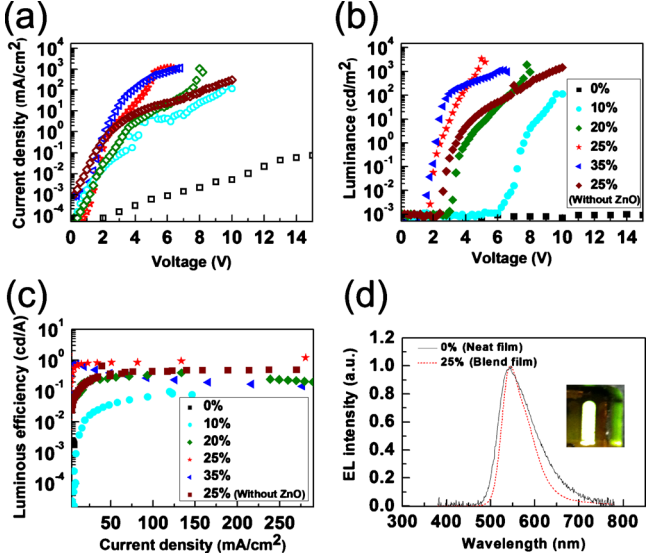


FIG. 2. (Color online) Device characteristics of (a) current density vs applied voltage (J - V), (b) luminance vs applied voltage (L - V) and (c) luminous efficiency vs current density (LE - J) curves with SY:ILMs blend films using different ILMs weight percent after initial forward bias of 5.0 V for 30 s for ion redistribution in polymer LECs with and without ZnO layers. (d) Electroluminescence spectra for pure SY and SY:ILMs (25%) blend film.

extremely low turn-on, and high luminance efficiency at low operating voltage without matching the work functions between each electrode and active layer.^{23,24}

The device performances of FTO/ZnO/SY:ILMs blend/Au device with different ILMs content and FTO/SY:ILMs blend (25 wt %)/Au device are presented in Fig. 2. The device performances were measured using a Keithley 2400 source measurement unit and a Konica Minolta spectroradiometer (CS-2000) in atmospheric conditions without any encapsulation after initial forward bias of 5.0 V for 30 s for ion redistribution. Compared to the device without any ILMs, those mixed with ILMs in the SY layer showed remarkably enhanced current density. Moreover, the current density of devices using SY:ILMs blends as active layers was enhanced with increasing ILMs content due to the reduced charge injection barriers between each electrode and active layer. The much lower current density for a device using pure SY was attributed to the large energy barriers that bring low device performance. The turn-on voltage of the device made using pure SY was 41.8 V, the maximum luminance was 0.11 cd/m² at 44.8 V, and the maximum luminous efficiency was 0.002 cd/A. The devices using SY:ILMs blends showed much lower turn-on voltages, higher luminance and higher luminous efficiencies.

Table I summarizes the detailed device characteristics

TABLE I. Summarized polymer LECs performance of the different ILMs content.

Device configuration	Turn on (V)	L _{max} @ bias (cd/m ²)	LE _{max} @ bias (cd/A)
FTO/ZnO/SY:IL (0 wt %)/Au	41.8	0.11@44.8 V	0.002@42.0 V
FTO/ZnO/SY:IL (10 wt %)/Au	7.1	110@10.0 V	0.09@10.0 V
FTO/ZnO/SY:IL (20 wt %)/Au	3.5	1900@7.8 V	0.63@7.8 V
FTO/ZnO/SY:IL (25 wt %)/Au	2.1	3400 @5.0 V	1.20@5.0 V
FTO/SY:IL (25 wt %)/Au (without ZnO layer)	2.9	1500@10.0 V	0.65@7.0 V
FTO/ZnO/SY:IL (35 wt %)/Au	1.8	1100@6.2 V	0.74@2.8 V

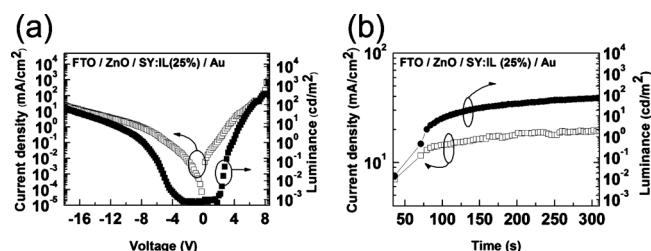


FIG. 3. (a) Current density-applied voltage-luminance (J - V - L) characteristics under forward and reverse bias of the HyPLECs fabricated with SY:ILMs (25%) blend film. (b) Time response of current density (open symbol) and luminance (closed symbol) for FTO/ZnO/SY:ILMs (25%)/Au configuration under a forward bias of 3.2 V.

including luminance, luminous efficiency, and turn-on voltage. Although the device performance was improved with increasing ILMs content, there was an optimum condition for the highest luminous efficiency of HyPLECs. Especially, the device with 25 wt % of ILMs in SY and ZnO layer showed the highest device performance with a turn-on voltage of 2.1 V, a luminance of 3400 cd/m^2 at 5.0 V, and a luminous efficiency of 1.2 cd/A at 5.0 V, which correspond to approximately a 600-fold increase compared to the electroluminescence efficiency of pure SY. We also confirmed that the device with ZnO layer showed enhanced device performance (approximately a twofold increase for luminous efficiency) than the polymer LEC without ZnO layer, as shown in Fig. 2(a)–2(c). Moreover, we measured the luminance and luminous efficiency of polymer LECs with and without the ZnO layer by applying voltage up to 3 V as a function of time in air atmosphere. The luminance and luminous efficiency of polymer LEC without ZnO layer rapidly degrades, whereas the polymer LEC with ZnO layer shows robust air-stability even after 55 h exposure to air, as shown in Fig. S2.²⁵ We note that all the devices exhibited original green emission of SY regardless of using the SY:ILMs blend film, as shown in Fig. 2(d).

Figure 3(a) shows the current density-voltage-luminance (J - V - L) characteristics of the device under forward and reverse bias. In contrast to the device with the pure SY active layer, electroluminescence of the device with the SY:ILMs (25 wt % of ILMs) blend was also observed under reverse bias (0 ~ -18 V). The turn-on voltage is around -3.0 V, which is not quite different from the turn-on voltage in forward bias (0 ~ 8 V). Maximum luminance is around (260 cd/m^2) for a reverse bias scan. Figure 3(b) shows the time response of the (J) and (L) under a constant bias of 3.2 V in HyPLECs with SY:ILMs (25 wt % of ILMs) blend. It took a few seconds to redistribute the mobile anions near the Au anodes and to redistribute the cations near the transparent FTO/ZnO cathode; charge carriers were injected after building the electric fields. These results, including high luminance, high luminous efficiency, low turn-on voltage, the ability to emit light under applied reverse bias, and time response behavior confirmed the LEC behavior in the FTO/ZnO/SY:ILMs blend film/Au structure.

In conclusion, we demonstrated a straightforward way to enhance the device performance by using a blended film of fluorescent SY polymer and mobile ILMs in HyPLECs using ZnO layer. After the redistribution of cations and anions at

each electrode/active layer boundary, the charge injection barriers between each electrode and the active blend layer were reduced and the charge injection and transfer were remarkably enhanced in the corresponding device performance when using pure SY. The modified HyPLECs using ZnO layer with an ILMs (25%) blended into the SY as an active layer exhibited good device performance with low turn-on voltage of 2.1 V, excellent air stability, improved luminance of 3400 cd/m^2 , high efficiency of 1.2 cd/A , which is approximately sixfold higher than the electroluminescence efficiency of LECs without ZnO layer. Furthermore, our HyPLECs with SY:ILMs (25 wt % of ILMs) blend showed electroluminescence under reverse bias. This strategy offers a design scheme for improved carrier injection, low turn-on voltage, and high device performance at low operating voltage in air stable hybrid light-emitting devices.

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