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Effects of Organic Lithium Salt Ultrathin Films on the Electron Injection Efficiency in OLED

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We investigated the effects of the ultrathin film of a new cathode underlayer material, lithium tert-butyl cyclopentadienide (Li-TBCPD), on the electron injection efficiency and performance of the Alq3-based OLED. The current density-voltage-luminance (I-V-L) and the luminous efficiency characteristics of the [ITO/ α -NPB (40 nm)/Alq3 (60 nm)/Li-TBCPD (1.0 nm)/Al] device were examined. The device with the Li-TBCPD/Al bilayer cathode demonstrated the current density of $360 \, \text{A/m}^2$ at 12 V and the maximum luminance of $8,100 \, \text{cd/m}^2$, while the device with the LiF/Al cathode showed $70 \, \text{A/m}^2$ and $5,800 \, \text{cd/m}^2$, respectively. This improvement seems to originate from the relatively lower bond dissociation energy of Li-TBCPD and hence the easiness of lithium layer formation beneath the aluminum cathode.

Keywords: cathode modification; electron injection; lithium tert-butyl cyclopentadienide; OLEDs

INTRODUCTION

Balanced injection and transport of the positive and negative charge carriers into the recombination zone is essential for obtaining high efficiency and luminance output from organic light-emitting diodes (OLEDs) [1]. In most OLEDs, the efficient electron injection from cathode to organic layers is particularly a key issue for achieving high electroluminescence (EL) efficiency. The use of low-work-function

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metals or alloys is effective in enhancing electron injection [2,3]; however, low-work-function metals such as Li, Ca, and Mg easily react with oxygen and moisture. Thus bilayer cathodes with a ultrathin cathode underlayer, such as metal fluorides (LiF, NaF, CsF), metal oxides (MgO, Al_2O_3), organic metal complexes (Ca(acac)₂), NaSt), and alkali metal carboxylates (lithium acetate, lithium benzoate) have been used to enhance the electron injection in OLEDs [4–10].

In this work, we interposed the ultra-thin layer of a new organic lithium salt, lithium tert-butyl cyclopentadienide (Li-TBCPD), between the emitting layer of Alq3 and the Al cathode, and investigated the effect of the cathode underlayer on the electron injection efficiency and luminance of the Alq3-based OLED. Also, we compared the effects of the three kinds of cathode underlayers, LiF, lithium acetate (Li acetate), and Li-TBCPD on the OLED device performance.

EXPERIMENTAL

Patterned indium-tin oxide (ITO)-coated glass substrates with a surface resistance of $10\,\Omega/\mathrm{sq}$ were sequentially cleaned with trichlor-oethylene, acetone, deionized water, and isopropyl alcohol in an ultrasonic bath. A 40 nm-thick hole-transporting layer of N,N'-bis(1-naphthyl)-N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (α -NPB) and a 60 nm-thick emitting/electron-transporting layer of tris-(8-hydroxy-quinoline) aluminum (Alq3) were successively vacuum-deposited by thermal evaporation onto the cleaned ITO substrates under 3×10^{-6} torr. And then, an ultra-thin (1.0 nm) layer of the LiF, Li acetate, or Li-TBCPD was also vacuum-deposited, followed by the Al deposition to complete the device preparation. The deposition rates were 0.9–1.1, 0.1, 0.1–0.2, and 5–6 Å/s for the α -NPB and Alq3 layers, the LiF layer, the Li acetate or Li-TBCPD layer, and the Al cathode, respectively.

Figure 1 shows the schematic diagram of the device structure and the chemical structures of the materials studied. All layer thicknesses were determined by a quartz crystal microbalance. The emitting area was defined to be $3\times3\,\mathrm{mm}^2$ by using a shadow mask during the vacuum evaporation process. The electroluminescence (EL) characteristics of the devices were measured using a JBS IVL-300 EL characterization system under ambient condition.

RESULTS AND DISCUSSION

We investigated the effects of the ultra-thin cathode underlayer (1.0 nm) of Li-TBCPD on the performance of the device with

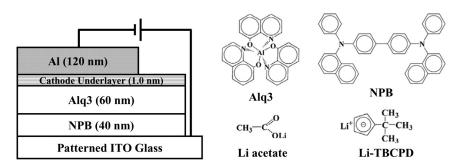


FIGURE 1 Schematic diagram of the device structure and the chemical structures of the materials studied.

a structure of [ITO/ α -NPB (40 nm)/Alq3 (60 nm)/Li-TBCPD (1.0 nm)/Al]. Also, the control devices with the LiF or Li acetate layer (1.0 nm) were tested for comparison.

The current density-voltage (I-V) characteristics of the devices with a 1.0 nm-thick cathode underlayer of LiF, Li acetate, or Li-TBCPD are shown in Figure 2. It was very interesting to observe that the device with the Li-TBCPD layer displayed more enhanced electron injection than the device with the LiF or Li acetate layer. In addition, the device with the Li-TBCPD layer showed lower driving voltage than the other

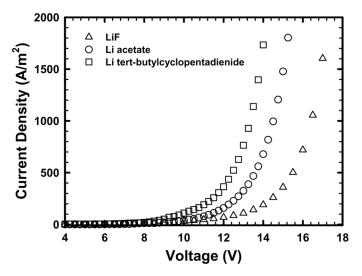


FIGURE 2 Current density-voltage (I-V) characteristics of the OLEDs with a 1.0 nm-thick cathode underlayer of LiF, Li acetate, or Li-TBCPD.

devices at a given current density. The current density for the device with the Li-TBCPD layer reached $360\,A/m^2$ at 12 V, while that for the device with the LiF or Li acetate layer was 70 or $160\,A/m^2$, respectively.

Figure 3 shows the luminance-current density (L-J) characteristics of the devices with the cathode underlayer of LiF, Li acetate, or Li-TBCPD. At all the current densities, the luminance of the Li-TBCPD device was as high as that of the Li acetate device, and much higher than that of the LiF device. Maximum luminance was 5,800,7,800, and $8,100\,\mathrm{cd/m^2}$ for the devices with the LiF, Li acetate, and Li-TBCPD layers, respectively.

Interposing a LiF layer between the Alq3 emitting layer and the Al cathode has long been known to much enhance the electron injection and EL performance of the Alq3-based OLED device [4]. Ganzorig et al. [10] also demonstrated that the devices with an organic lithium carboxylate layer, such as lithium acetate and lithium benzoate, showed even better electron injection and luminance than that with the LiF layer. It has been suggested that free lithium atoms are easily produced by the reaction of the organic lithium salts with hot Al atoms due to the high reactivity of the anions of the organic lithium salts. The free lithium atoms may form a layer to lower the work function of the cathode or dope the Alq3 layer to facilitate

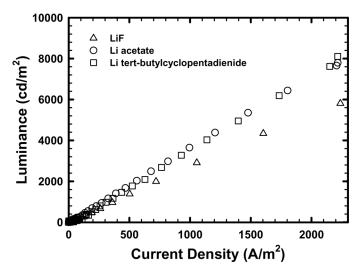


FIGURE 3 Luminance-current density (L-J) characteristics of the OLEDs with a 1.0 nm-thick cathode underlayer of LiF, Li acetate, or Li-TBCPD.

electron injection [10,11]. Therefore we consider the enhancement of the current density and EL performance of the device with the Li-TBCPD layer results from the lowering of the electron injection barrier via the formation of the lithium metal layer during the deposition of hot aluminum atoms [10]. Bond dissociation energy of Li-TBCPD is considered to be lower than that of LiF or Li acetate. However, the location and role of the anions released from Li-TBCPD should be further investigated.

CONCLUDING REMARKS

We investigated the effects of the ultra-thin cathode underlayer $(1.0\,\text{nm})$ of Li-TBCPD on the performance of the device with a structure of [ITO/ $\alpha\text{-NPB}$ (40 nm)/Alq3 (60 nm)/Li-TBCPD (1.0 nm)/Al]. The device demonstrated the current density of $360\,\text{A/m}^2$ at $12\,\text{V}$ and the maximum luminance of $8,100\,\text{cd/m}^2$. This improvement seems to originate from the free lithium atoms released by the reaction of the organic lithium salt with hot aluminum atoms. The free lithium atoms may form a layer to lower the work function of the cathode or dope the Alq3 layer to facilitate electron injection. However, the location and role of the anions released from the organic lithium salts has not yet been clearly understood.

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