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Effect of Potassium Citrate as Electron Injection Material on Organic Light Emitting Diodes

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Abstract: The multilayer organic light-emitting diodes (OLEDs) using potassium citrate ($C_6H_5K_3O_7$) as the electron-injection material have been fabricated. The electroluminescence (EL) efficiency of 3.6 cd/A was obtained by inserting 0.5-nm-thick $C_6H_5K_3O_7$ as electron injecting layer, which is higher than that of 2.5 cd/A in reference device with 0.5-nm-thick LiF. The turn-on voltage was decreased 0.5 V compared with the reference device with 0.5-nm-thick LiF. The results demonstrated that $C_6H_5K_3O_7$ is a promising electron injection material.

Key words: organic light-emitting diodes; potassium citrate; electron injection layer

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柠檬酸钾电子注入层对有机电致发光器件的影响

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摘要：使用柠檬酸钾($C_6H_5K_3O_7$)作为电子注入材料，制备了多层有机电致发光器件。当柠檬酸钾阴极修饰层厚度为0.5 nm时，得到3.6 cd/A的发光效率，高于0.5 nm LiF作阴极修饰层时的发光效率(2.5 cd/A)。器件的开启电压相比0.5 nm LiF作阴极修饰的器件降低了0.5 V。实验结果表明，柠檬酸钾($C_6H_5K_3O_7$)是一种良好的电子注入材料。

关 键 词：有机发光二极管；柠檬酸钾；电子注入层

1 Introduction

High efficiency is still a crucial factor for the commercialization of organic light emitting diodes (OLEDs), although many efforts have been made since the 1980s[1-4]. Interposing a buffer layer between organic layer and Al cathode is a common method to improve the efficiency. Several approaches have been adopted, such as, doping with active metal, *e.g.*, Li, Cs, Ca and Sr[5-8] in the electron transporting layer (ETL). But these approaches have their own demerits because these materials are easy to be oxidized and diffuse into the emitting layer (EML), and cause excitons quenching in the EML.

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For more practical applications, thin chemical compound films such as LiF, NaCl, and alkaline earth fluorides have been selected to improve the electron injection by inserting them between Al cathode and the ETL[9-10]. Some organic metal complexes such as 8-hydroxyquinolinolato lithium (Liq)[11], and Sodium stearate (NaSt)[12] have also been reported as electron injecting layers (EILs). Potassium citrate is a potassium salt of citric acid with the molecular formula $C_6H_5K_3O_7$, which is no toxic, low cost and with low melt temperature.

In this letter, organic salt potassium citrate film was prepared as the electron injection layer. Then the effect of $C_6H_5K_3O_7$ on the device performance has been investigated.

2 Experiments

The device structure is shown in Fig. 1. ITO-coated glass (20 Ω/□) was used as the substrate. N, N′-Di (naphth-2-yl)-N, N′-diphenyl-benzidine (NPB), and tris (8-hydroxyquinoline) aluminum (Alq_3) were used as the hole transport layer and the electron transport layer, $C_6H_5K_3O_7$ was deposited as the electron injection layer, respectively. The thickness of $C_6H_5K_3O_7$ layer varied from 0.5 to 1.5 nm, and the thickness of NPB, Alq_3, and Al were 40, 60, and 150 nm, respectively. The current-voltage and luminance characteristics of these devices (the emitting area was defined with a shadow mask to be 3 mm × 3 mm) were recorded simultaneously by combining a silicon photodiode calibrated by a PR-650 spectrometer with a programmable voltage-current source Keithley 2410. The emission spectra of devices were measured by a CCD spectrometer. All the measurements were carried out at room temperature under ambient atmosphere without encapsulation.

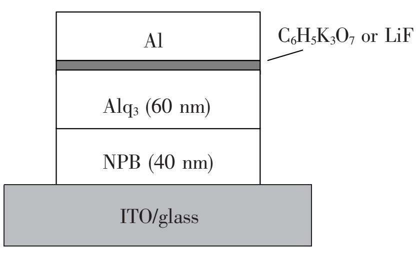

Fig. 1　Configuration of OLEDs in our experiment

3 Results and Discussion

Fig. 2 shows current density-voltage (*J-V*) characteristics of the devices. The current density-voltage (*J-V*) behavior of OLEDs with thin $C_6H_5K_3O_7$ layers is superior to that of the Al-only device in terms of low-voltage operation. It can be seen that the current density is 450, 419, 349, 316 and 164 mA/cm^2 at 15 V for the five devices: with 0.5, 1.0, and 1.5 nm $C_6H_5K_3O_7$ interlayer, LiF/Al cathode, and Al-only cathode, respectively. That is, the current density of the device decreases as the thickness of $C_6H_5K_3O_7$ increases. But it shows that the bias voltage is obviously lower for the OLEDs with $C_6H_5K_3O_7$ layer than without $C_6H_5K_3O_7$ and LiF/Al cathode under the same current density. In the present work, the optimum thickness was determined to be 0.5 nm. This indicates that the $C_6H_5K_3O_7$ can improve electron injection and the performance of OLEDs. The effect of $C_6H_5K_3O_7$ on the improvement of electron injection is better than LiF.

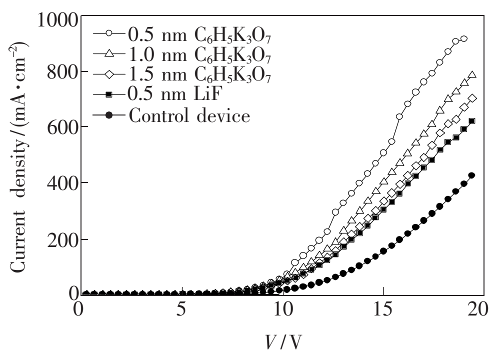

Fig. 2　The current density versus voltage (*J-V*) curves of OLEDs with $C_6H_5K_3O_7$ (0.5, 1.0, 1.5) nm/Al, LiF(0.5 nm)/Al, and Al-only cathodes, respectively.

Fig. 3 shows the luminance-voltage (*L-V*) characteristics of the devices. The luminance at a certain voltage decreases as the $C_6H_5K_3O_7$ thickness increases from 0.5 to 1.5 nm. For instance, the luminance is 17 716, 15 421, 11 973, 9 250, and 2 296 cd/m^2 at 17 V for the devices: with 0.5, 1.0, and 1.5 nm $C_6H_5K_3O_7$ interlayer, LiF/Al cathode, and Al-only cathode, respectively. In terms of low-voltage operation, the luminance-voltage (*L-V*) behavior of the devices with $C_6H_5K_3O_7$ interlayer is superior to that of LiF/Al and the Al-only devices. The turn-on voltage (the voltage as luminance is 1 cd/m^2) of Al cathode based device is 5.1 V, which is higher than those of the other devices. The turn-on voltages are 3.1, 3.3, 3.5, and 3.6 V for the four devices: with 0.5, 1.0, and 1.5 nm $C_6H_5K_3O_7$ interlayer and LiF/Al cathode, respectively. It is clearly shown in the Fig. 3 that the performance of $C_6H_5K_3O_7$/Al devices is improved over the Al-only device and the LiF/Al device in terms of luminance and turn-on voltage. And the $C_6H_5K_3O_7$(0.5 nm)/Al device shows the best performance among $C_6H_5K_3O_7$/Al devices.

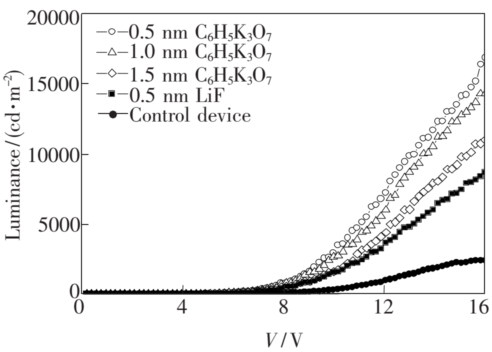

Fig. 3　The luminance versus voltage (L-V) curves of OLEDs with $C_6H_5K_3O_7$(0.5, 1.0, 1.5) nm/Al, LiF(0.5 nm)/Al, and Al-only cathodes, respectively.

Fig. 4 shows the electroluminescent (EL) efficiency-current density characteristics of the devices. The OLED with the 0.5-nm-thick $C_6H_5K_3O_7$ turned out to be the most efficient and the one with Al-only cathode is far less efficient than the others with inserted layers. Fig. 4 reveals that the OLEDs of

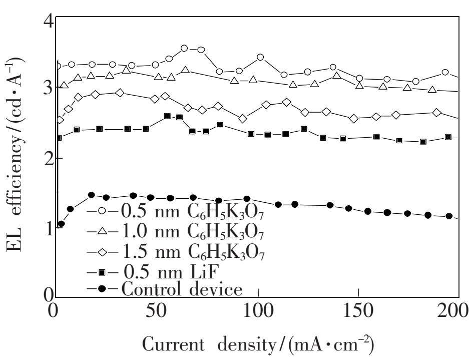

Fig. 4　The EL efficiency versus current density curves of OLEDs with $C_6H_5K_3O_7$(0.5, 1.0, 1.5) nm/Al, LiF(0.5 nm)/Al, and Al-only cathodes, respectively.

$C_6H_5K_3O_7$(0.5, 1.0, 1.5 nm) exceed the device of LiF in the range of overall current density. The EL efficiencies at 80 mA/cm^2 are 1.4, 3.6, 3.3, 2.8, and 2.5 cd/A for the five devices: with 0, 0.5, 1.0, and 1.5 nm $C_6H_5K_3O_7$ layer and LiF/Al, respectively. The efficiency of the device with 0.5 nm $C_6H_5K_3O_7$ layer, which is 2.6 times of that of Al-only device, is the highest among the five devices and even higher than that of LiF/Al-cathode device. These analytical results mean that inserting the $C_6H_5K_3O_7$ of an optimum thickness as an injection-supporting medium advantageous over using the LiF.

The enhancement in EL efficiency can be attributed to an improved hole-electron current balance[13-15]. As we know, electrons possess a much lower mobility than holes in the organic materials. Efficient electron injection from cathode to emitting layer improves hole and electron balance. And Alq_3/Al interface were attributed to the interface reaction between the organic EIL and the Al cathode. When we employed $C_6H_5K_3O_7$ as the electron injection layer in Alq_3 based devices, the enhancement of the electron injection is very similar to that obtained by inserting ultrathin film of organic salt[11,16].

Another mechanism of ion dissociation and doping was proposed to interpret the improvement of electron injection. The strong n-doping by a low-work-function metal is responsible for the electron injection enhancement[17-18]. The low-work-function metal combine with the Al cathode can lower the energy barriers when electron injecting. In our devices, the potassium citrate contains active metal potassium(K); it may also decompose on the Alq_3 surface, and facilitate the electron injecting[19-21]. Therefore, the thermal decomposition model may be used to explain the decrease of the effective barrier for electron injection by using $C_6H_5K_3O_7$.

4　Conclusion

$C_6H_5K_3O_7$ electron injection layer was utilized to fabricate OLEDs. The devices showed enhanced electron-injection efficiency and improved EL efficiency. An EL efficiency of 3.6 cd/A was obtained by inserting 0.5-nm-thick $C_6H_5K_3O_7$ as the EIL, which was higher than the EL efficiency of 2.5 cd/A for the reference device with 0.5-nm-thick LiF. The turn-on voltage was lowered by 0.5 and 2 V compared with the LiF/Al and Al-only cathode device, respectively. Therefore, $C_6H_5K_3O_7$ is an alternative efficient electron injecting material.

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