Influence of driving mode on the operation stability of organic light-emitting diodes

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The influence of pulse current (PC) versus direct current (DC) driving mode on the operation stability of organic light-emitting diodes, which based on N,N'-di(naphthalene-1-yl)-N,N'-diphenylbenzidine (NPB) and tris(8-hydroxyquinoline) aluminum (Alq_3) without hole-injection layer (HIL) and with two different HILs, was investigated. The two HILs were copper phthalocyanine (CuPc) and 4,4',4''-tris(3-methylphenylphenylamino) triphenylamine (m-MDTATA) respectively. It was found that the lifetimes of devices without HIL and with CuPc, m-MTDATA as the HIL under PC driving mode were 2, 1.5 and 0.9 times longer than that under DC driving mode respectively. Analysis of electrical characteristics of corresponding hole-only devices showed that the injected holes into device were greatly reduced by inserting m-MTDATA layer compared to the two other devices, and indicated that different ratios of the injected electrons / holes were obtained in these devices, which play a dominant role in the influence of driving mode on the operation stability.

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1. Introduction

Organic light emitting diode(OLED), which was first reported by Tang *et al.* in 1980s, [1] has received great attention due to their potential application in flat panel display technology. The operation stability of OLEDs is a critical factor for commercial application. Hence, many research groups devoted themselves to improving it. For small molecule-based OLEDs, several factors have been assumed to cause the instability of devices, such as electrochemical or thermal instability of the materials, [2,3] the charge unbalance between the injected holes and electrons, [3,4] and instabilities of the interfaces [3,5]. The driving method (Direct Current or Pulse Current) is an important factor for the stability and lifetime of device. In the most previous literatures, [6-9] the lifetimes of OLEDs under pulse current (PC) operation were reported to be longer than that under direct current(DC) operation, which were attributed to reasons such as the slowed down migration of ionic impurities in the OLEDs, [10,11] reducing the hole injection into the Alq_3 layer by reverse electric field of PC driving mode [8]. As a result, the PC driving mode was adopted in many OLEDs applications for their long lifetime [6-9, 12-14]. Recently, however, Luo *et al.* [15] found PC driving mode did not always lead to the longer lifetime of devices, for instance, with low duty cycle (4%) and higher current densities (27 mA/cm^2), PC driving mode exhibited worse operation stability than that of DC driving mode, and they considered that the dependence of device stability on the driving mode correlates with the relative EL efficiency under PC and DC driving modes.

In this paper, we investigated the effect of PC versus DC driving mode on the operation stability for OLEDs with different structures. The one was a standard device based on N, N'-di (naphthalene-1-yl)-N, N'-diphenylbenzidine (NPB) and tris(8-hydroxyquinoline) aluminum (Alq_3). The other two were trilayer devices based on NPB/Alq_3 with copper phthalocyanine (CuPc) and 4,4',4''-tris(3-methylphenylphenylamino) triphenylamine (m-MDTATA) as the hole-injection layer (HIL), respectively. It was found that the influence of driving mode on the stability of our experimental devices was not identical. The lifetimes of devices without HIL and with CuPc as the HIL under PC operation were longer than that under DC operation, but the case was contrary for the device m-MDTATA as the HIL. We attribute the unidentical influence of driving mode on the operation stability to the different ratios of the injected electrons/ holes in these devices, which result in different electrons/holes balance in the recombination zone.

2. Experimental

Three kinds of organic light-emitting diodes with different HILs were fabricated. The structures of devices are as follows:

Device A:

ITO/ NPB (60 nm)/Alq_3 (60 nm)/LiF(0.5 nm)/Al(100 nm);

Device B:

ITO/m-MTDATA(50 nm)/NPB(10 nm)/Alq_3(60 nm)/LiF(0.5 nm)/Al(100 nm);

Device C:

ITO/CuPc (20 nm)/NPB (40 nm)/Alq_3 (60 nm)/LiF(0.5 nm)/Al(100 nm).

In all devices, ITO, NPB, Alq_3 and LiF/Al are used as the anode, hole-transport layer (HTL), emitting/electron-transport layer (EML/ETL) and bilayer cathode, respectively. The m-MTDATA layer of device B and CuPc layer of device C act as the HILs. All organic materials were deposited at a rate of 0.3 nm/s using vacuum deposition at a base pressure of about 1×10^{-3} Pa. The Al film was deposited at a rate of 0.5 nm/s. The thickness of films was determined *in situ* with a quartz-crystal sensor and *ex situ* by a profilometry(Nano-View MF-1000). These devices were encapsulated in a dry nitrogen grove box. For stability tests, a constant DC and a "home-built" asymmetric PC power source were used.

3. Results and discussion

Fig. 1 shows the current density versus voltage (J-V), luminance versus current density (L-J), and efficiency versus current density (E-J) characteristics of devices A-C. As seen in Fig. 1 (a), the device B has smaller current density compared to devices A and C. But device B shows the highest luminance and current efficiency among devices A-C, which is shown in Fig. 1 (b) and Fig. 1(c) The detailed characteristics of devices are listed in Table 1. It was indicated the current efficiency and luminance was effectively improved by inserting a HIL between the ITO anode and the HTL (NPB). Moreover, m-MTDATA (device B) demonstrated greater improvement than CuPc as the HIL.

Table 1. Performance of devices A-C.

Device No.	Turn-on Voltage(V)	Maximum Luminance (cd/m^2)	Maximum Current Efficiency(cd/A)
A	4.1	13547	2.45
B	2.8	28278	4.22
C	3.5	19801	3.21

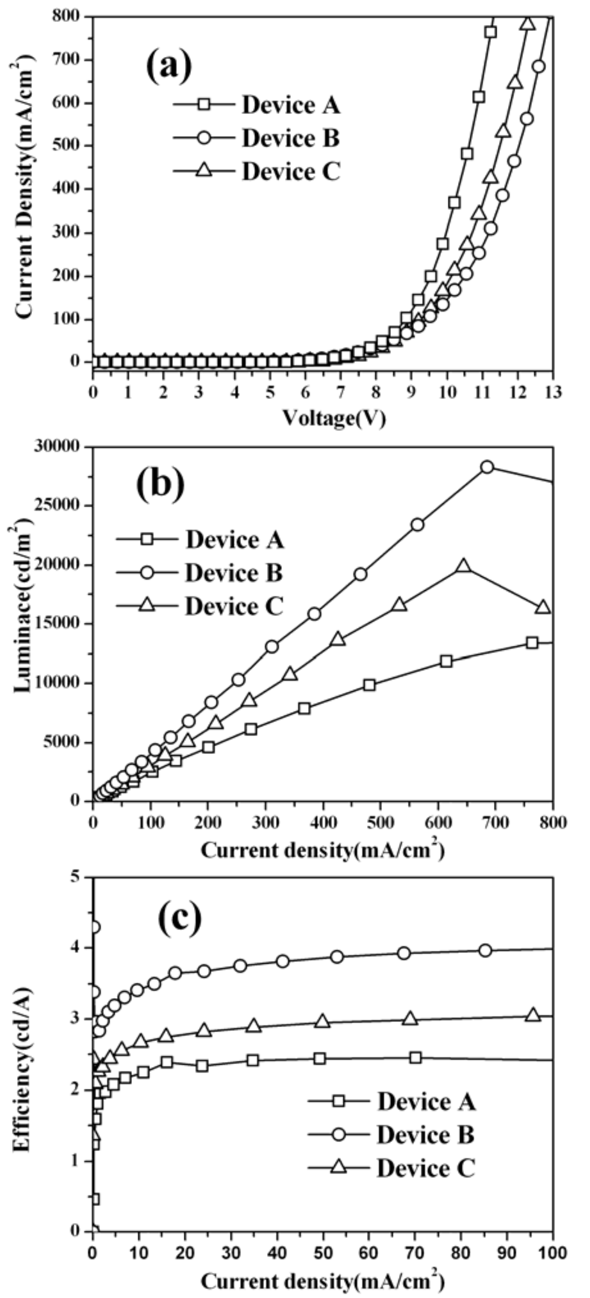

Fig. 1. (a) Current density - voltage, (b) current efficiency - current density, and (c) luminance - current density for devices A-C.

Fig. 2 shows the stability of devices A-C driven by DC and PC modes. In PC operation, a constant current density in the forward bias cycle and -5V in the reverse bias cycle, 50 Hz square wave , and 1:1 duty cycle. As the injected current in the reverse bias cycle is negligibly small, light emission is observed only in the forward bias cycle. The time-averaged injected current density is, therefore, half constant current density in the forward bias cycle. The following the constant current density of PC driving mode mentioned in the article is the time-averaged current density [6]. For device A, lifetime testing was carried out at constant current density of 35.65 mA/cm^2, corresponding to the initial luminance for DC and PC were 1013 cd/m^2 and 1025 cd/m^2, respectively. The lifetime under PC driving was almost twice as long as that under DC driving. Whereas for device C, the operation stability of device C was measured under constant current density of 71.30 mA/cm^2, corresponding to the initial luminance for DC and PC were 1851 cd/m^2 and 1874 cd/m^2, respectively. The lifetime under PC driving was 1.5 times less than that under DC driving. On the other hand, for device B, the test constant current density is 35.65 mA/cm^2, which produces initial luminance for DC and PC were 1076 cd/m^2 and 1123 cd/m^2, respectively. Both driving modes lead to approximately equivalent stability. The results reveal that operation stability under different driving mode depends on the device structure.

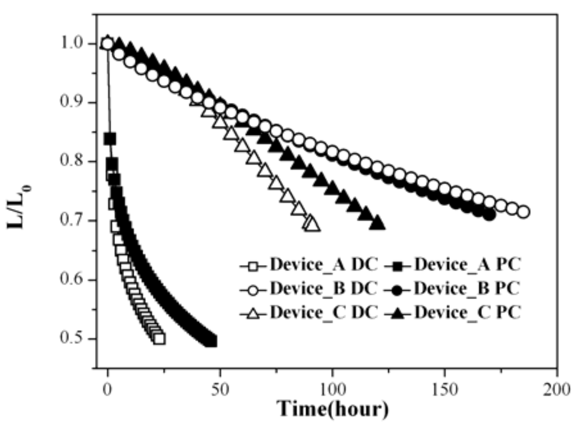

Fig. 2. Normalized luminance decay [luminance (L)/initial luminance (L_0)] of devices A-C as a function of operating time for DC and PC operation with 1:1 duty cycle, 50 Hz square wave and 5V reverse Voltage.

To investigate essential difference of device A-C, a series of the hole-only devices were fabricated, where the current density of electrons was reduced to negligible level by lowering the efficiency of the electron injecting contact. The structures of these hole-only devices are device D: ITO/NPB (120 nm)/Al (100 nm), device E: ITO/m-MTDATA (50 nm)/NPB (70 nm)/Al (100 nm) and device F: ITO/CuPc(20 nm)/NPB (100 nm)/Al (100 nm), their energy level are shown in Fig. 3. Al was used as cathode with Fermi energy of 4.6 eV, and NPB was used as HTL and electron blocking layer with a lowest unoccupied molecular orbital (LUMO) level of 2.6 eV. The great offset between the Fermi energy of the cathode and LUMO level of NPB was served to reduce the efficiency of the electron injection and guarantee that the holes injected from the anode would dominate in the device [16]. Fig. 4 shows the J-V characteristics of device D-F (hole-only devices). In previous reports, the CuPc layer as the HIL played the roles of improving or reducing the hole injection under different conditions or ITO treatments [17,18]. Device F had smaller hole current compared to device D, which indicated CuPc (20 nm) layer decreased hole injection efficiency in our devices. Device E had the smallest hole current because that the hole drift mobility of m-MTDATA is inferior to that of NPB and CuPc, [19] which results in the reduction of hole current. As a result, the injected holes into device are reduced by inserting the HIL, which indicates the different ratios of the injected electrons/holes into devices are obtained by inserting different HILs. In the standard bilayer NPB/Alq_3 device (device A), the hole mobility in NPB is almost two orders of magnitude higher than the electron mobility in Alq_3, [20] leading to unbalance of electrons/holes in the recombination zone, resulting in a number of holes injected into the Alq_3, creating unstable Alq_3 cationic species, and then leading to lower device performance. Therefore, the HIL can adjust the ratios of the injected electrons/holes in devices, impeding too many holes accumulating in the recombination zone, improving electrons/holes balance in the recombination zone, enhancing the device performance. The result is consistent with earlier research of other authors [21,22]. Moreover, better electrons/holes balance was expected since hole current was smaller when using m-MTDATA as the HIL compared to that when using CuPc as the HIL. So device C showed the higher current efficiency and luminance compared to device A, while these performances of device B excelled to that of device C. Based on the above discussion, the essential difference of device A-C is that the different ratios of the injected electrons /holes are obtained in these devices, which result in different electrons/holes balance in the recombination zone. In terms of the electrons/holes balance, device B is better than device C, and device C is better than device A.

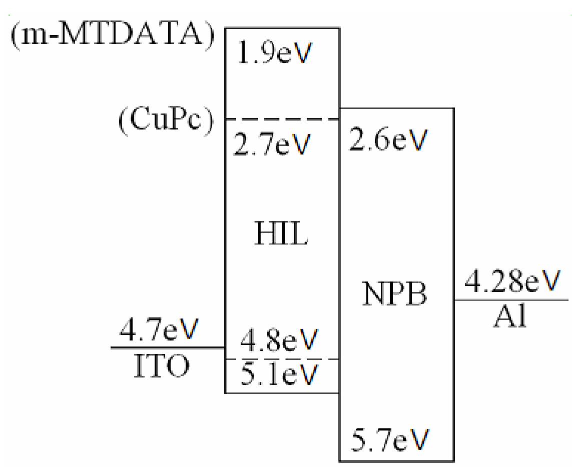

Fig. 3. Schematic energy level diagram for the hole-only devices.

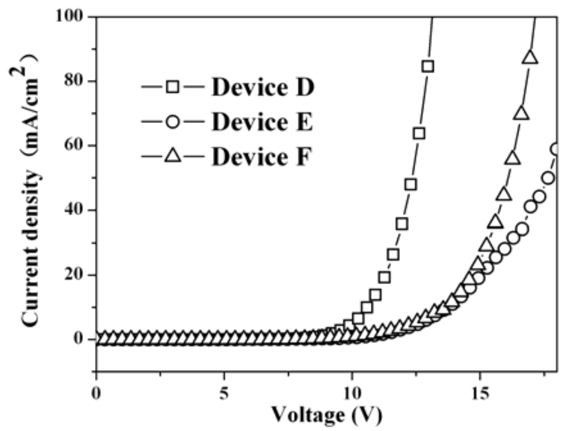

Fig. 4. Current density - voltage for the hole-only devices.

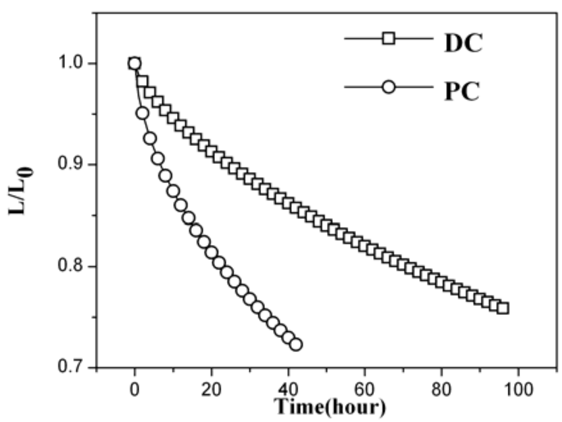

Fig. 5. Normalized luminance decay [luminance (L)/initial luminance (L_0)] vs. operating time for device B under DC and PC driving mode with 1:1 duty cycle, 50 Hz square wave and 5V reverse Voltage.

As mentioned above, for device A, the number of holes is lager than that of electrons in NPB/Alq3 interface. The holes can be injected into Alq3 layer and created the unstable Alq_3 cationic species under DC driving mode and forward bias of PC driving mode, [23] which is the main cause of device degradation. However, some holes may drift back to NPB layer because of the reverse bias of PC driving mode, so PC driving exhibits the higher operation stability compared to DC driving mode. For the device C, it has the better electrons/holes balance compared to device A because of inserting CuPc layer, it is expected the minor improvement on the stability by means of using PC driving is observed compare to device A. As for device B, it has the best electrons/holes balance in recombination zone among the three devices, even in DC driving mode, the leakage of hole into the Alq_3 layer is substantially reduced due to the lower total hole current. So, in the case of device B, the improvement on the stability with the reverse bias of PC driving mode is very limited. In contrast, the combination of Joule heating and electric field-induced disassociation of singlet states with higher forward current of PC driving mode gradually becomes a primary factor, which plays a negative role on the device stability. As a result, PC driving mode exhibits slight lower stability compared to DC driving mode. Fig. 6 shows the lifetime of device B under higher current condition is tested. The current density is 71.30 mA/cm^2, corresponding to the initial luminance for DC and PC were 2422 cd/m^2 and 2436 cd/m^2, respectively. It is found that the stability under PC driving mode is far smaller than that under DC driving mode, in agreement with this idea that Joule heating effect the degradation curve of device B. From these results and discussion, it is concluded that the different ratios of the injected electrons/holes into devices result in the different electrons/holes balance in the recombination zone, then result in the different influence of driving mode on the stability shown in Fig. 2.

4. Conclusions

In summary, the influence of PC versus DC driving mode on the operation stability of three various structures (without HIL, CuPc, m-MTDATA as the HIL, respectively) NPB/Alq_3-based organic light-emitting devices has been investigated. The influence of PC versus DC driving mode depends on the type of device. Devices without HIL showed expected improvement in the device lifetime under PC driving mode compared to DC driving mode. Device with the HIL, on the other hand, showed minor improvement, even deterioration in the device lifetime under PC driving mode compared to DC driving mode. These results are explained by different ratios of the injected electrons/holes in these devices. Because with the adjustment of the ratio of the injected electrons/holes into device by inserting different HTLs or other methods, which improves the electrons/holes balance, for the influence of PC driving mode on the stability, the positive role does diminish gradually, the negative role will inevitably be primary. For a given OLED, it is thus believed that the greater operation stability is achieved only with suitable driving mode.

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