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# Effects of Ca/Al/Mg Alloy as Cathode on The Performance of White Organic Light-emitting Devices

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**Abstract:** Based on the red and green/blue light emitting layer, six white phosphorescent OLEDs are fabricated by using Ca/Al/Mg alloy as cathode, and the effects of different proportion of Ca/Al/Mg alloy on OLEDs are researched by changing the doping ratio of Mg. The device structures are as follows: ITO/MoO<sub>3</sub> (30 nm)/NPB(40 nm)/mCP: Firpic(8%)(40 nm)/CBP: R-4B(2%): Ir(ppy)<sub>3</sub>(14%)(5 nm)/TPBi(10 nm)/Alq<sub>3</sub>(40 nm)/Ca: Al: Mg(x%)(100 nm)(x=0, 5, 10, 15, 20, 25). The experiment results show that the cathode with Mg mass fraction of 15% has good electron injection characteristics which can effectively improve the light-emitting characteristics of the device. The maximum brightness is 1 504 cd/m<sup>2</sup>, the maximum current efficiency is 14.3 cd/A, and the color coordinates is close to (0.46, 0.42).

**Key words:** Ca: Al: Mg alloy; cathode; electron injection

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## 钙铝镁合金阴极对 WOLED 器件性能的影响

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**摘要:** 采用 Ca/Al/Mg 合金作为器件的阴极, 基于红绿/蓝双发光层制作了 6 种白色磷光 OLED 器件, 器件结构为 ITO/MoO<sub>3</sub> (30 nm)/NPB (40 nm)/mCP: Firpic (8%, 40 nm)/CBP: R-4B (2%): Ir(ppy)<sub>3</sub> (14%, 5 nm)/TPBi (10 nm)/Alq<sub>3</sub> (40 nm)/Ca: Al: Mg (x%, 100 nm) (x=0, 5, 10, 15, 20, 25)。通过改变 Mg 的掺杂比例, 研究了不同比例的 Ca/Al/Mg 合金阴极对器件性能的影响。结果表明: Mg 质量分数为 15% 的 Ca/Al/Mg 阴极具有良好的电子注入特性, 有效改善了器件的发光特性, 最大发光亮度可达 1 504 cd/m<sup>2</sup>, 效率达到最大值 14.3 cd/A, 色坐标接近(0.46, 0.42)。

**关键词:** 钙铝镁合金; 阴极; 电子注入

### 1 Introduction

Currently, the majority of materials used for the organic light emitting device belong to hole transport

type, injection and transport of the holes are relatively easy by ITO and the hole transport layer<sup>[1-2]</sup>. Alq<sub>3</sub> is the most commonly used electron-transporting material at present, its electron mobility is two

orders of magnitude smaller than the hole mobility of NPB which is commonly used as the hole transport material, injection and transport of the electrons are more difficult, therefore, electrons belong to the minority carriers in the most of the organic light emitting device<sup>[3]</sup>. To improve the performance of the device, it is bound to increase the electron injection. In order to make electrons easy to inject from a metal cathode, the cathode material requires the metal at a low work function should be adopted as possible, Ca(2.9 eV), Mg(3.7 eV) and so on, but the low work function metal is sensitive to water and oxygen, anti-corrosion property is poor, and the plated film is easily oxidized and peeled<sup>[4]</sup>. This requires should use better stability of the metal, Al(4.3 eV), Ag(4.3 eV) and so on. However, the better stability of the metal has high work function, electron injection barrier is large, which could affect the performance of the device.

In order to overcome the shortcomings of the single metal cathode, the low work function metal with very active chemical character is combined with high work function metal whose chemical character is relatively stable to form the alloy cathode<sup>[5]</sup>. The alloy cathode can not only improve the stability of the material in the air, but also reduce the electron injection barrier, which greatly improves the device performance. As early as 1987, Kodak first proposed a double-layer structure of OLED which significantly reduced the driving voltage by using Mg: Ag alloy cathode, and it also reported for the first time that the alloy cathode was applied to OLED. In addition, the alloy is widely used as cathode material in the transparent and top-emitting devices, such as Yb: Ag, Yb: Au, Sm: Ag alloy and so on, and results in the devices having a high transmittance<sup>[6]</sup>.

In this paper, Ca: Al: Mg alloy was used as the cathode of the device. Through the production of different cathode structure devices and the measurement of the devices performance, Ca: Al: Mg alloys as cathode for optimal proportion can be derived.

## 2 Experiments

First, the cleanliness of the ITO glass is sent

into the preparation chamber through plasma bombardment. After 10 minutes, the ITO substrate is transported to the evaporation chamber. When the evaporation chamber pressure reaches  $7 \times 10^{-4}$  Pa, the organic and metal layers are evaporated onto the ITO substrate in turn. The device structures are as follows: ITO/MoO<sub>3</sub>(30 nm)/NPB(40 nm)/mCP: Firpic(8%, 40 nm)/CBP: R-4B(2%): Ir(ppy)<sub>3</sub>(14%, 5 nm)/TPBi(10 nm)/Alq<sub>3</sub>(40 nm)/Ca: Al: Mg(*x*%, 100 nm) (*x* = 0, 5, 10, 15, 20, 25), respectively, represent the devices of A, B, C, D, E, and F. *x*% is the mass fraction of Mg. A is the contrast device. The mass fraction of Ca is 15%. In this structure, ITO and Ca: Al: Mg are used as the anode and the cathode, respectively. NPB is the hole transporting layer. Firpic is used as a dopant of blue light-emitting layer. R-4B is used as a dopant of red light-emitting layer. Ir(ppy)<sub>3</sub> is used as a dopant of green light-emitting layer. TPBi is the hole blocking layer. In addition, in order to verify the effect of Mg on the electronic injection capability of the device, two sets of electronic injection devices are made. The device structures are as follows: ITO/Alq<sub>3</sub>(40 nm)/Ca: Al: Mg(5%, 100 nm) (Device G) and ITO/Alq<sub>3</sub>(40 nm)/Ca: Al(100 nm) (Device H).

The materials used in the experiment are purchased from several companies except the alloy material which is formed in the laboratory. The synthesized procedure of Ca: Al: Mg alloy includes fusion in the quartz glass tube under vacuum and natural cooling.

The characteristics of devices are measured using a Photo Research PR-670 spectroradiometer and a Keithley source 2400.

## 3 Results and Discussion

Fig. 1 shows the brightness-voltage characteristics of the devices. It can be seen that the brightness of the devices increases firstly and then decreases with the increasing of Mg content. The increasing brightness of device A, B, C, and D is mainly due to the lower work function of the metal cathode and the better electron injection with the increasing of

Mg content, which results in the bigger recombination probability of electrons and holes. The brightness of device E and F tends to decrease. The reason is the carriers distribute unreasonable causing the light-emitting concentration quenching. The maximum brightness is  $1\ 504\ \text{cd}/\text{m}^2$  at 12 V.

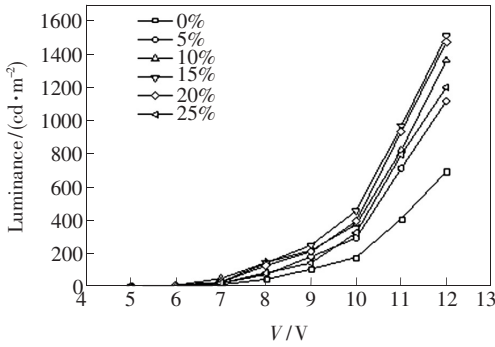


Fig. 1 Luminance-voltage characteristics of device A, B, C, D, E, and F, respectively.

Fig. 2 shows the current efficiency-current density characteristics of the devices. It can be seen from the figure, the trends of the six devices are identical and efficiency roll-off is relatively flat. This explains using Ca: Al: Mg alloy as cathode can improve the stability of the device. The current efficiency of device A, B, C, and D tends to increase and device E and F tends to decrease. Device D has the maximum current efficiency of  $14.3\ \text{cd}/\text{A}$  at  $6.9\ \text{mA}/\text{cm}^2$ . The main reason of the high efficiency is that the lower work function of the metal and the stronger electron injection capacity result in the electron and hole injection into balance for this device. For device E, the work function of the cathode is the lowest, but the efficiency is falling. This is because the electrons inject too much, and a part of the electrons

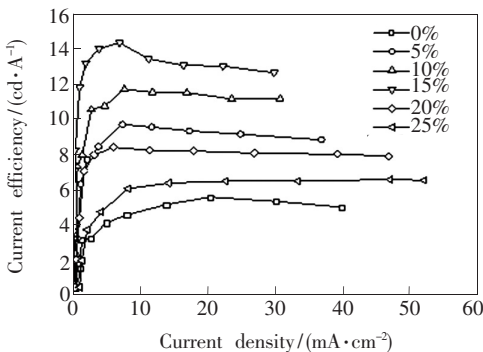


Fig. 2 Current efficiency-current density characteristics of device A, B, C, D, E, and F, respectively.

and holes can not recombine and release out in other forms<sup>[7]</sup>.

Fig. 3 shows the current density-voltage characteristics of the devices. It can be seen from the figure, the trends of the six devices are similar, that is, the current density of the devices increases along with the voltage. The current density of the devices increases slowly along with the voltage at low voltage, while current density increases rapidly beyond a certain voltage. For device A, B, C, and D, the curves change little, the current density is smaller. The current density of device D is the smallest. The reason is that the electron injection can completely meet the hole carriers in the light emitting layer and the electrons and holes form an effective recombination luminescence, which results in a decrease in current density and a significant increase in efficiency. For device E and F, the curves show a clear change and tend to increase. At the same voltage, the current density of device F is larger than other devices.

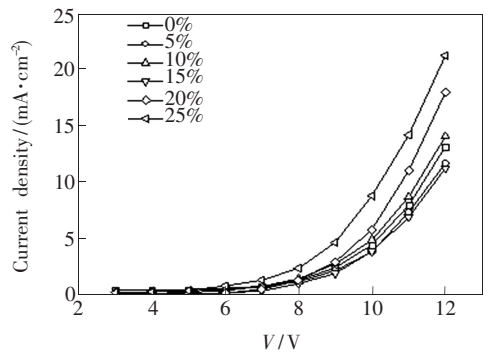


Fig. 3 Current density-voltage characteristics of device A, B, C, D, E, and F, respectively.

Fig. 4 shows the curve of current density-voltage of device G and H. It can be seen that the current density of device G is higher than that of device H at the same voltage. The current density of device G is enhanced 6.1 times as compared to that of device H at 8 V driven voltage. This shows that the introduction of Mg can effectively improve the injection of electrons from the cathode to the organic layer.

Fig. 5 shows EL spectra at 10 V driving voltage of the devices. It can be seen that EL spectra of the devices completely cover the total visible region ranging from 380 to 780 nm. The spectra consist of three

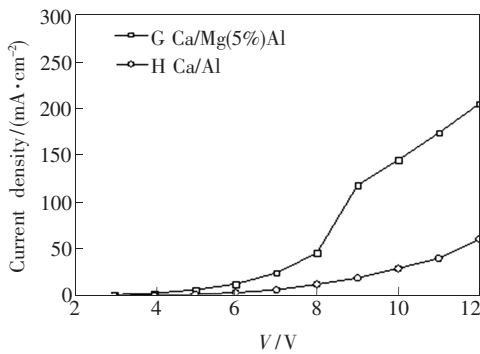


Fig. 4 Current density-voltage characteristics of device G and H

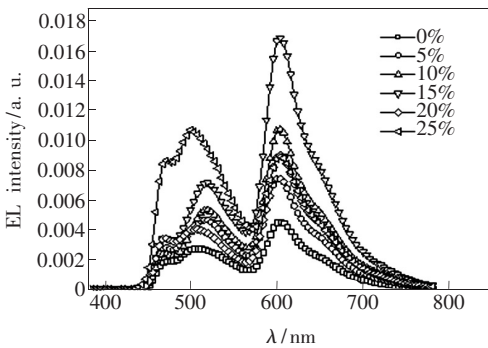


Fig. 5 EL spectra of device A, B, C, D, E, and F at 10 V, respectively.

primary peaks at 468, 512, and 556 nm. The peak at 468 nm is the characteristic luminescence of Firpic. The luminous peak of  $\text{Ir}(\text{ppy})_3$  is located at 512 nm. The luminous peak of R-4B is located at 604 nm. The peak intensities of device B, C, D, and E differ bigger. The intensity of red emission is large, followed by the green emission, and the blue emission is weak. The intensity of red emission of device D is the largest. The RGB spectra of device A and F are relatively balanced.

Fig. 6 shows the normalized EL spectra of device D at different driving voltage. It can be seen that the luminous peak of red has no bias shift, but the luminous peak of blue and green gets a slight deviation at different driven voltage. The intensity of red emission is similar, but the intensities of blue and green emission tend to increase with the increasing of driving voltage. The reason is probably due to the R-4B doping concentration of 2% is small. With the increasing of voltage, the number of carriers reaches the peak and the light reaches saturation. The doping concentrations of Firpic and  $\text{Ir}(\text{ppy})_3$  are

8% and 14% respectively, and the proportions of the two dopants are respectively large. More high-energy excitons are formed on Firpic and  $\text{Ir}(\text{ppy})_3$  with the increasing of voltage, which results in the increasing of the recombination probability of electrons and holes. Therefore, the number of carriers has not reached its peak and has been increasing.

Table 1 shows the color coordinate of device D at different voltage. It can be seen that the color coordinates are almost no change with the increasing of the bias voltage. The stability of color coordinate is better. The chroma is largely insensitive to the driven voltage. When the voltage ranges from 6 to 9 V, the color coordinates are (0.460 6, 0.427 9), (0.461 1, 0.428 3), (0.462 0, 0.428 8), and (0.462 8, 0.429 1), respectively. At different voltage, device D can emit white light which belongs to warm yellow color<sup>[8]</sup>.

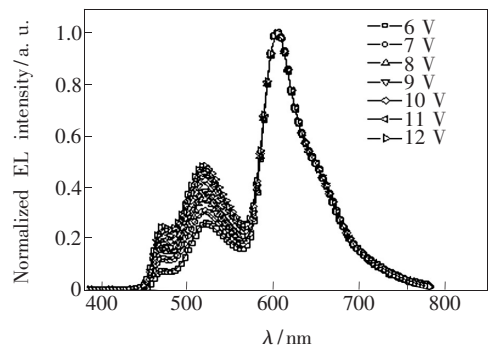


Fig. 6 Normalized EL spectra of device D at different driving voltage

**Table 1 Voltage-color coordinate of device D**

V/V	Color coordinate
6	(0.460 6, 0.427 9)
7	(0.461 1, 0.428 3)
8	(0.462 0, 0.428 8)
9	(0.462 8, 0.429 1)

## 4 Conclusion

Based on the red and green/blue light emitting layer, six white phosphorescent OLEDs are made by using Ca/Al/Mg alloy as cathode, and the effects of different proportion of Ca/Al/Mg alloy on OLEDs are researched by changing the doping ratio of Mg. The

experiment results show that Ca/Al/Mg alloy cathode can not only improve the brightness and efficiency of the device, but also improve the stability. When the mass fraction of Mg is 15%, the device has the best

performance: The maximum brightness is 1 504 cd/m<sup>2</sup>, the maximum current efficiency is 14.3 cd/A at 6.9 mA/cm<sup>2</sup>, and the emitting white light belongs to warm yellow color at different driving voltage.

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