

Improved electron injection in organic LED with lithium quinolate/aluminium cathode

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Abstract

Lithium quinolate (Liq), covered with aluminium, was used as an electron injection layer in a double layer organic light emitting diode consisting of NPD as the hole transport layer and Alq as the emitting layer resulting in lower turn on voltage and increased power efficiency. The driving voltage required to achieve a luminance of 100 cd/m² decreased from 5.8 V for the Ca/Al to 4.2 V when Liq/Al was used, improving device power efficiency from 2.3 to 4.1 lm/W. The performance tolerance to layer thickness of Liq devices is also better than that of the devices with lithium fluoride (LiF). Due to the highly insulating nature of LiF, it can only be used when deposited as an ultra-thin layer, while the Liq can be deposited into layers as thick as 5 nm without significantly affecting the EL properties. An Liq electron injecting layer has also been tried in combination with Ca, Mg and Ag cathodes. Our experiments support the assumption that free lithium is released from lithium quinolate, as in the case of lithium fluoride, when Liq is over coated with active metals such as Al. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Organic LED; Improved electron injection; Lithium quinolate

1. Introduction

Organic–inorganic interfacial modification in organic light emitting diodes (OLEDs) has been widely investigated for improving the charge injection efficiency of the contacts. By lowering the charge carrier injection barriers and in turn increasing the hole and electron injection efficiency, a better balance of the opposite carrier concentration can be achieved resulting in increased electroluminescent (EL) efficiency, improved OLED stability and prolonged lifetime. Insertion of carrier injection assisting layers at either or both anode and cathode sides is one of such interfacial modification techniques.

Thin layers (10–30 nm) of PEDOT, MTDATA, CuPc, as well as ultra-thin (0.1–5 nm) layers of inorganic oxides are often used to improve hole injecting properties of ITO/hole transporting layer interface [1–4]. Low work function metals and their compounds have been widely used as a part of the cathode in order to improve electron injection. A widely used example of such a low work function metal is Li. There are numerous works where either Li itself [5] or its inorganic compound LiF [6] is placed between an organic electron

transport layer (ETL) and an Al cathode. LiF/Al cathode is often used as a more stable alternative to silver capped calcium [7] and magnesium [8] cathodes.

In addition to lithium metal and LiF, lithium complexes [9,10] with organic ligands and lithium doped organic materials [11,12] have also been used as electron injection layers in combination with Al cathode. Lithium organic complexes or lithium doped organic materials can be deposited into much thicker layers in OLEDs than LiF, which, due to its high electrical insulation, has a thickness restriction (less than 2 nm) and consequently its deposition can be difficult to control.

Lithium quinolate is one of the complexes shown to assist electron injection [9,10] that has not yet been widely investigated. This paper will report our results on OLEDs where a combination of lithium quinolate as an electron injection layer with Al or other metals resulted in improved electron injection.

2. Experimental

Lithium quinolate was synthesised by a reported procedure [9] and subjected to further purification by high-vacuum sublimation ($p < 10^{-6}$ mbar) at 300 °C. The device

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structure is ITO/NPD/Alq/Liq/metal, where NPD and Alq were chosen for their stability and EL efficiency of the device. The devices were fabricated on oxygen-plasma treated patterned-ITO substrates. All layers were deposited by resistive thermal evaporation at a pressure of 10^{-6} – 10^{-7} mbar. The thickness of NPD and Alq are both 50 nm if not specifically indicated elsewhere. The thickness of Liq was varied between 0.2 and 10 nm. Layer thicknesses were controlled using a quartz crystal thickness monitor. Finally, 100 nm of Al were deposited on top of the organic layers through a shadow mask to form $2 \times 5 \text{ mm}^2$ pixels.

For comparison, some alkaline earth metals such as calcium and magnesium capped with silver were used to form multi-layer cathodes. In addition, lithium fluoride (LiF) and calcium (Ca) have been deposited instead of Liq between Alq and Al. Due to the limited number of evaporator sources, the chamber had to be open for changing sources after depositing organic layers. To minimize the exposure of the organic layers to the air while changing evaporation sources, the chamber was filled with dry nitrogen. The substrate coated with the organic layers was kept under a flow of nitrogen, while the source changing was carried out in as short as possible time ($<1 \text{ min}$).

All control devices used in this paper for comparison of EL characteristics were manufactured simultaneously with the Liq containing devices. Both investigated and control devices were tested in air at room temperature immediately after fabrication.

3. Results and discussion

First, we will compare EL properties of devices with Liq/Al to the control devices with Ca/Al or LiF/Al as a cathode. Fig. 1 shows the current density–voltage (I – V) and luminance–voltage (L – V) characteristics of double layer devices consisting of 40 nm of NPD and 60 nm of Alq. Either Liq or

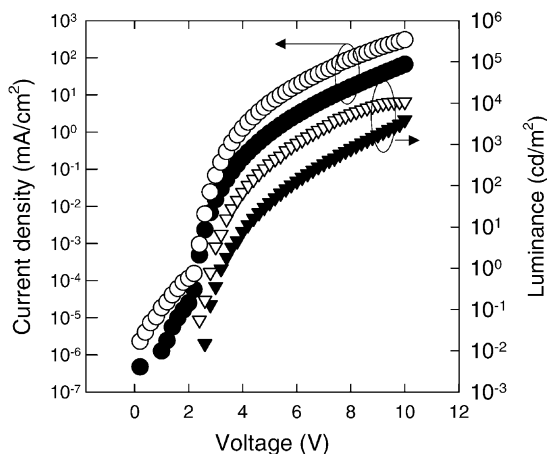


Fig. 1. Current density (circles) and luminance (triangles) of device NPD(40 nm)/Alq(60 nm)/Liq(1.0 nm)/Al(100 nm) (open symbols) and device NPD(40 nm)/Alq(60 nm)/Ca(10 nm)/Al(100 nm) (solid ones).

Ca is sandwiched between the Alq and Al. As seen from the graph, the device with lithium quinolate has lower driving voltage for a given luminance, as well as a faster increase in luminance with the increase in the driving voltage. With Liq, a luminance of 100 cd/m^2 is achieved at 4.2 V (compared with 5.8 V for the control device with calcium), and 1000 cd/m^2 is reached at 6.0 V (8.4 V for the control). At 100 cd/m^2 , the power efficiency is as high as 4.1 lm/W (5.5 cd/A), compared with 2.4 lm/W (4.4 cd/A) for the control calcium device. One can also see that the turn on voltage (at the minimum luminance of 10^{-2} cd/m^2) of the Liq device is 0.2 V lower than that of the control device with calcium. We should note that at a higher driving voltage range, the luminance of the Liq device does not increase as quickly as its current density. So we observed the efficiency decrease when the voltage reaches 9 V, and the mechanism is not very clear.

Fig. 2 shows the I – V and L – V curves for the two double layer NPD (50 nm)/Alq (50 nm) devices with either Liq or LiF as the electron injection layer. The EL performance of the device with Liq/Al is almost identical to that of the control device with LiF/Al.

When Fig. 2 with Fig. 1 are compared, one can notice two differences, one is that the luminance of Liq device is still increased quickly at higher voltage, and another is that the efficiency of two Liq devices are different. The thicker emissive layer gives higher efficiency.

We found that the Liq layer can be as thick as 5 nm without compromising the EL characteristics significantly, which is higher than the 2 nm, which we got for LiF in our experiment. Fig. 3 shows the variation of power efficiencies at a luminance of 100 cd/m^2 of devices with different thickness of lithium quinolate. We can see that the efficiency is still increasing when the thickness of Liq reaches 1.6 nm. We found that even when the thickness of Liq is as high as 5 nm, the EL performance is still acceptable (the power efficiency is about 1.4 lm/W). Our results for LiF show that

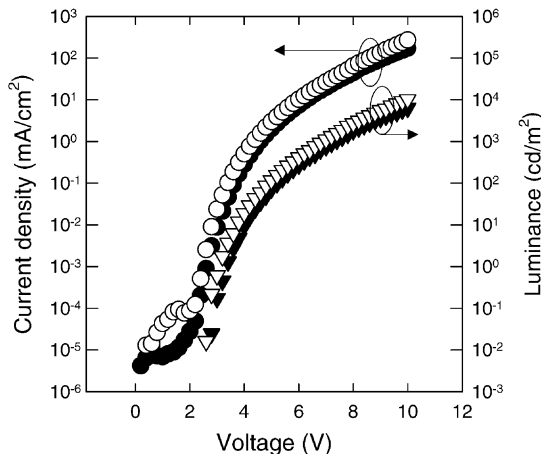


Fig. 2. Current density (circles) and luminance (triangles) of device NPD(50 nm)/Alq(50 nm)/Liq(1.0 nm)/Al(100 nm) (open symbols) and device NPD(50 nm)/Alq(50 nm)/LiF(0.2 nm)/Al(100 nm) (solid symbols).

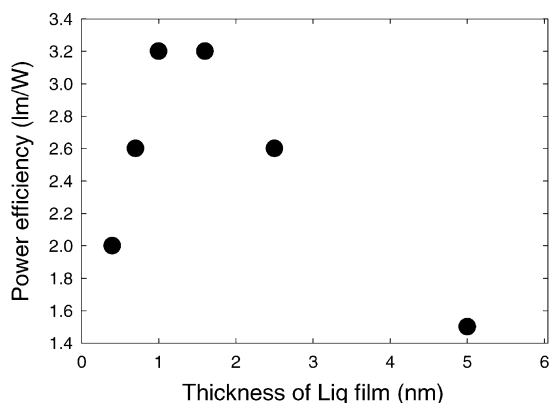


Fig. 3. Power efficiency variation with thickness of lithium quinolate. The structure of the device is ITO/NPD(50 nm)/Alq(50 nm)/Liq(x nm)/Al(100 nm).

the best device performance corresponds to the optimum thickness of between 0.2 and 0.5 nm (about 2.7 lm/W at 100 cd/m²). When the LiF thickness is increased to 1.0 nm, the EL efficiency deteriorates. When the thickness of LiF is 5 nm, the device is very unstable, and when it reaches 10 nm, the device does not give emission at all. According to Schmitz et al. [9], Liq is an electron transporting material. In this case, the extra thickness of Liq should not cause as much problem for the electron transport as the extra thickness of insulating LiF, which blocks electron injection.

We noticed that Brown et al. showed quite different results for polymer device with LiF. In their experiments the lowest turn on voltage and the highest maximum efficiency is reached for the thickness of LiF film of 7.2 nm [19]. The difference in the results may be due to the fact that a polymer rather than Alq₃ has been used in their devices. Alternatively, different test conditions may be responsible: our devices are measured in air, while theirs are encapsulated under dry nitrogen.

What is the mechanism responsible for the improved electron injection? In the case of LiF, Hung et al. [13] has suggested that it is the band bending in the organic layer that lowers the electron injection barrier height, while Fujikawa et al. [14] suggest that it is the presence of a dipole at the LiF/metal interface that shifts the work function of the metal cathode to lower energies. But more and more authors now agree [15–18] that it is free lithium metal released at the LiF/metal interface and doped into the organic layer that improves electron injection. Heil et al. [17] found that lithium liberated during the deposition of Al on LiF ended up in the Alq layer acting as a dopant. It was also suggested [16] that Alq anion states produced by the interaction of Alq and liberated Li was responsible for the EL performance improvement. Other authors [18] believe that lithium doping in the organic films increases the transparency of the barrier to electron injection from the contact.

The concept of Li doping was also put forward in the case of Liq [9]. To clarify this issue, we made Liq devices with different metal cathodes (Ca, Mg, and Ag). Devices with

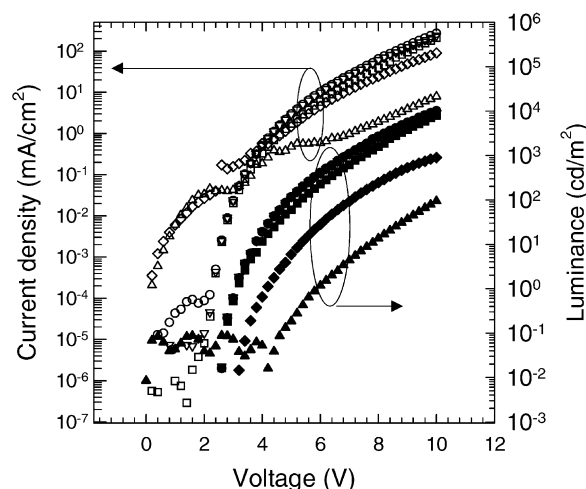


Fig. 4. Current density (left axis) and luminance (right axis) voltage characteristics of devices with different cathode metals: ITO/NPD(50 nm)/Alq(50 nm)/Liq(1.0 nm)/M(2.0 nm)/Al(100 nm), where M is Al (circles), Mg (down triangles), Ca (squares), and Ag (diamonds), compare with ITO/NPD/Alq/Ag (up triangles).

Liq/Al were used as a control device. EL characteristics of these devices are shown in Fig. 4. There are no significant changes in I - V , L - V or efficiency when Liq is coated with Al, Ca or Mg, though we can notice both the current density and the luminance decreased slightly from Al to Mg and Ca. While in LiF case, the tendency is same but the differences are bigger. This is also different from Brown's work [20], where for polymer device, LiF/Ca device gives much high current density and luminance. We can only attribute this difference to the different material and the measurement condition. When silver is used as a cathode, the Liq device shows a higher turn on voltage (3.2 V rather than 2.6 V for the control device), lower current beyond the turn on voltage and a much-reduced level of luminance. One can speculate that silver is not as chemically active as calcium, magnesium or aluminium and hardly reacts with lithium quinolate to yield free Li metal. We also noticed that the a thin layer of Liq with silver as a cathode gives much higher current density and the luminance than silver cathode, though it is still lower than for Liq/Al cathode. It is interesting to note that the value of the device current for the voltages below the turn on voltage are related to the activity of the metal used to release lithium. The more active the metal is, the lower the value of this current.

However, the fairly small difference in turn on voltages of Liq/Ag and Liq/Al devices supports the hypothesis that lithium quinolate reacts partially with Ag, to give free lithium that improves electron injection. Otherwise, the turn on voltage of the device with silver cathode should have been much higher.

To summarise, a thin layer of Liq combined with Al, Ca or Mg lowers the turn on voltage and increases the efficiency of an organic LED. It is twice as efficient as Ca and matches LiF/Al. Furthermore, a wider range of Liq thicknesses can

be used without compromising device performance. The performance tolerance of Liq devices to the layer thickness is better than that of the devices with LiF. Due to the highly insulating nature of LiF, it can only be used when deposited as an ultra-thin layer, while Liq can be deposited into layers as thick as 5 nm without significantly affecting the EL properties. Our experimental results for Ca, Mg and Ag cathodes support the assumption that free lithium released from lithium quinolate is responsible for the improved device performance, and that this release is more effective than that observed in devices with LiF.

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