Improved Electron Injection on Organic Light-emitting Diodes with an Organic Electron Injection Layer

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To overcome of poor electron injection in organic light-emitting diodes (OLEDs) with Al cathode, a thin layer of inorganic insulating materials, like as LiF, is inserted between an Al cathode and an organic electron transport layer. Though the device, mentioned above, improves both turn on voltage and luminescent properties, it has some problems like as thickness restriction, less than 2 nm, and difficulty of deposition control. On the other hand, Li organic complex, Liq, is less thickness restrictive and easy to deposit and it also enhances the performance of devices. This paper reports the improved electron injection on OLEDs with another I A group metal complex, Potassium quinolate (Kq), as an electron injection material. OLEDs with organic complexes showed improved turn-on voltage and luminous efficiency which are remarkably improved compared to OLEDs with Al cathode. Especially, OLEDs with Kq have longer life time than OLEDs with Liq.

Keywords: Organic light-emitting diodes, Organic electron injection material,
I A group metal complex, Dipole moment, Luminous efficiency, Lifetime

1. INTRODUCTION

After the discovery of efficient organic light emitting diodes (OLEDs), there has been considerable interest in developing OLEDs with high brightness, high efficiency, and long lifetime for applications[1-5]. Since an organic light-emitting device is operated by injected carriers, electrons and holes, it is important to balance the carrier concentration in an emitting organic material and supply sufficient carriers from both electrode metals to an organic material. Bilayer or multilayer structure has been used for the carrier balance in the emitting material. Surface modified indium-tin-oxide (ITO) is commonly used as the hole-injecting contact, while a low work function metal or metal alloy is required to form an effective electron-injecting contact[6]. However, OLEDs with a low work function metal cathode such as Li, Ca and Mg exhibit poor device reliability due to the reactive nature of these metals. The use of high work function metals, such as Al, though less reactivity, shows low efficiency due to less efficient electron injection[7]. Recently, it was reported that the introduction of a thin layer with an inorganic insulator such as LiF, CsF, MgO, Al2O3 between Al and the organic layer, significantly enhances electron injection and prolongs the device lifetime[8,9]. Though the device, mentioned above, improved both the drive voltage and luminescent properties, it has some problems like as thickness restriction, less than 2 nm, and difficulty of deposition control. On the other hand, Li organic complex, Liq, is less thickness restrictive and easy to deposit.

This paper will report the improved electron injection on OLEDs with I A group metal-quinolate complexes as an electron injection layer.
2. EXPERIMENTAL

OLEDs were fabricated by the high vacuum (~10^-6 torr) thermal deposition of organic materials onto the surface of an ITO (30 Ω/□, 80 nm) coated glass substrate chemically cleaned using acetone, methanol, distilled water and isopropyl alcohol. The organic materials were deposited in the following sequence: 40 nm of α-naphthylphenylbiphenyl (NPB) was used as a hole transporting layer, followed by a 50 nm thick tris-(8-hydroxyquinoline) aluminum (Alq3) used as an electron transporting and emitting layer. Finally, an organic electron injection material was deposited with the thickness of 2, 3 and 4 nm, as shown in Fig. 1. As references, the device without the electron injection layer and the device with 2 nm thick LiF layer were also fabricated. LiF thickness was decided through our previous works.

The chemical structures of the organic electron injection materials are also shown in Fig. 2. Organic deposition rate was 0.2 nm/sec. Finally the 150 nm of Al was deposited as a cathode. An active area of the OLED was typically 0.09 cm^2.

The electrical and optical properties of device were measured under ambient conditions in air without any encapsulation against degradation. Current - voltage - light intensity of the OLEDs were measured with programmable electrometer (keithley 617), source measure unit (keithley 236) and Roper Scientific photodiode (SI440-UV). Maximum luminance of each device was measured with a chromometer (Minolta CS-100). To study the stability of OLEDs, we measured the operational lifetime.

3. RESULTS AND DISCUSSION

First, we will compare electrical and optical characteristics of devices with various organic electron injection layers to the device with LiF/Al as a cathode. Devices with 3 nm thick organic electron injection layer showed better characteristics among the various thicknesses. Figure 3 and Fig. 4 show the current density - voltage (J-V) and luminance - voltage (L-V) characteristics of optimized devices fabricated in this study.

![Fig. 3. Current density – voltage characteristics of the OLEDs with various electron injection materials.](image)

![Fig. 4. Luminance – voltage characteristics of the OLEDs with various electron injection materials.](image)
Table 1. Characteristic data of the devices fabricated in this study.

<table>
<thead>
<tr>
<th>Material</th>
<th>No EIL</th>
<th>LiF</th>
<th>Liq</th>
<th>Naq</th>
<th>Kq</th>
</tr>
</thead>
<tbody>
<tr>
<td>Life-time [min.]</td>
<td>50</td>
<td>1500</td>
<td>1850</td>
<td>2000</td>
<td>2400</td>
</tr>
<tr>
<td>Efficiency [cd/A]</td>
<td>1.675</td>
<td>2.16</td>
<td>2.19</td>
<td>2.36</td>
<td>2.69</td>
</tr>
<tr>
<td>Dipole moment [D]</td>
<td>4.382</td>
<td>5.2832</td>
<td>8.263</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As shown in Fig. 3 and Fig. 4, devices with the electron injection layer turned on at 2 V which is 1 V lower than the device without the electron injection layer, and also show better J-V and L-V characteristics.

The devices with any organic electron injection layer exceed the device with LiF/Al as a cathode in both characteristics. The thickness of each electron injection layer was optimized in previous study, and the characteristics of devices with Naq and Kq were less dependent on the thickness variation from 2 nm to 5 nm. With the lower deposition temperature, than LIF, which reduces the damage of the organic material surface, it is supposed that the organic electron injection material has the good contact adhesion to Alq3. Thus the devices with an organic electron injection layer showed better characteristics because of the enhanced electron injection.

In luminous efficiency, the device with Kq was the best among the devices with and without an electron injection layer as shown in Fig. 5. Each luminous efficiency is 1.68 cd/A without an electron injection layer, 2.16 cd/A with LiF, 2.19 cd/A with Liq, 2.36 cd/A with Naq and 2.69 cd/A with Kq, respectively. Issued voltages of devices were under 10 V except the bare device.

Figure 6 shows the life-time characteristics for the devices measured with the initial luminance of 100 cd/m². Devices with the electron injection layer survived over 30 times than the bare device. The device with Kq also showed the best characteristics in the life-time measurement. Specific data are listed in Table 1.

Both organic and inorganic electron injection materials help the electron injection from cathode to Alq3, like as metal cathode with lower work function, which leads to higher density of electrons in Alq3 layer adjacent to the NPB/Alq3 interface. These electrons at the interface reduce numbers of Alq3 cations, which are generated by excess hole injection from the hole transport layer into Alq3 layer and act as fluorescent quenchers[9]. Consequently the stability of devices is enhanced with improved luminous efficiency according to the applied voltage and prolonged life-time.

There are several suggestions that explain the role of the electron injection layer[10-13]. One has suggested when the Alq3 surface is in contact with LiF, the energy band of Alq3 is bent down and consequently lowers the electronic barrier of the Alq3/Metal interfaces[10]. Free lithium metal was found in Alq3 by SIMS-depth profile after sequential deposition of LiF and Al on Alq3[11]. It

Fig. 5. Luminous efficiency – current density characteristics of the OLEDs with various electron injection materials.

Fig. 6. Life-time of the OLEDs with various electron injection materials at the luminance of 100 cd/m².
implies that I $\text{A}$ alkali metals can be transferred to form the $\text{Alq}_3^-$ anion\cite{12}. The vacuum level shift induced by transferred charge between fluoride and AI cathode might be the reason of the efficient electron injection\cite{13}. With the assumption that the formation of interface dipole changes the electronic structure of the interface, we calculated the relative dipole moments of organic electron injection materials using Gaussian computer simulation\cite{14}. According to the calculation, $K_q$ has the larger dipole moment than the others and this result agrees with other experimental data. Hence $K_q$ with the large dipole moment is a good candidate as an electron injection material even if the dipole moment is not the all of the reason of the efficient electron injection.

4. CONCLUSION

In this study, we showed the improved organic light-emitting diodes with various organic electron injection layers. With an electron injection layer, the turn-on voltage, luminous efficiency and life-time of the device were enhanced. Especially, $K_q$ showed better characteristics than the others and was less dependent on the deposited thickness. It might be caused by the large dipole moment of $K_q$ relatively calculated by Gaussian computer simulation. This large dipole moment causes the change of the electronic structure of the interface and consequently shifts the vacuum level to lower the energy barrier height of the $\text{Alq}_3$/AI interface. The use of an organic material as the electron injection layer has many merits like as an easy to control and less dependent on the thickness and the relatively low deposition temperature compared to the inorganic material, LiF.

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REFERENCES