Mechanisms of injection enhancement in organic light-emitting diodes through insulating buffer


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Three types of organic light-emitting diodes are fabricated. Tris-8-hydroxyquinoline aluminum (Alq3) is used as an electron-transporting layer (ETL) and sodium stearate (NaSt) as an electron-injecting buffer. The optimal thickness of NaSt for electron injection is different for cathodes of different metals, such as Mg, Al, and Ag. This is attributed to the different work functions of cathodes, which result in different initial barrier heights for electron injection from cathodes into ETL, and explained based on tunneling theory. © 2004 American Institute of Physics.

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Highly efficient injection of carriers from electrodes is needed for the development of high-performance organic light-emitting diodes (OLEDs). In 1997, the introduction of LiF into OLEDs was proved to be an effective way for improving electron injection from Al into tris-8-hydroxyquinoline aluminum (Alq3). Thereafter, it has been found that many insulators with proper thicknesses, including MgF2, NaCl, CsF, and Al2O3, have similar effects on electron injection into a variety of organic semiconductors. Meanwhile it has been shown that besides electron, hole injection could also be enhanced by introducing insulating buffers at some interfaces.

In general, it is believed that the similar characteristics of devices with different insulating buffers should result from similar mechanism. The debate on the mechanism has mainly focused on two models. One is tunneling mechanism. The other is the chemical reaction model, showing that various parameters, such as the electronic conductivity ratio of buffer to organic layer, position of the conduction band minimum of the buffer relative to the lowest unoccupied molecular orbital (LUMO) of the organic layer and the thicknesses of both layers, may affect the electron injection in the system of cathode/buffer/organic layer. More recently, it was demonstrated that the introduction of LiF between indium-tin-oxide (ITO) and N,N′-bis(1-naphthyl)-N,N′-diphenyl-1,1′-biphenyl 4,4′-diamine (NPB) can enhance hole injection or not is dependent on the initial barrier height (IBH) for hole injection from ITO into NPB. For large IBH (the ITO used is treated by H2-plasma and hence has low work function resulting in large IBH for hole injection), LiF greatly enhances the hole injection; for small one (the ITO is treated by UV ozone and hence has high work function resulting in small IBH for hole injection), LiF will weaken the hole injection. Additionally, it has also been found that in the case of LiF-induced hole injection the optimal thickness of the buffer layer is dependent on the values of IBHs. The larger the IBH is, the larger the optimal thickness will be. Such behaviors have been explained based on the tunneling model.

In this letter, it is demonstrated experimentally that the optimal thickness of sodium stearate (NaSt) as an electron-injecting buffer at cathode side also depends on the IBH at the interface of the cathode/electron-transporting layer (ETL). The optimal thickness of NaSt increases with IBH. These phenomena indicate that the mechanism of NaSt-induced electron injection enhancement in OLEDs is not a chemical reaction but energy level alignment and tunneling.

Three types of OLEDs with the same structure, i.e., cathode/NaSt (with varied thickness)/Alq3 (65 nm)/NPB (65 nm)/ITO, were fabricated, named, respectively, Mg-OLEDs, Al-OLEDs, and Ag-OLEDs corresponding to the use of Mg, Ag, Al and Ag as cathode. The details of sample fabrication and measurement of current density–voltage (I–V) characteristics are shown elsewhere.
Zhan et al.\textsuperscript{12} at this laboratory have shown the effect of NaSt on electron injection in OLEDs and an optimal thickness of 3.0 nm for NaSt-enhanced electron injection was obtained. For the integrality of the experimental data in this study, we repeated the experiments with the device structure of ITO\textbackslash NPB\textbackslash Alq3 NaSt\textbackslash Al and obtained the same results. Figure 1 shows the $I$\textendash $V$ and $L$\textendash $V$ curves of Al-OLEDs. It can be seen that a thin (1.0 nm) layer of NaSt enhances not only the current injection but also the brightness. A 3.0 nm NaSt shows the optimal effects and a 5.0 nm one shows the degradation of current injection and EL output. So, the NaSt optimal thickness of 3.0 nm is also obtained for Al-OLEDs here.

Figure 2 shows the $I$\textendash $V$ and $L$\textendash $V$ curves of Mg-OLEDs, in which the electron is injected through Mg because Mg contacts directly with NaSt (or Alq3) for Mg\textbackslash Ag composite cathode. As can be seen, such type of device is different from Al-OLEDs. The current injection is slightly enhanced by the layers of 0.5 and 1.0 nm NaSt (the 1.0 nm layer even looks better) but evidently deteriorated by 2.0 nm layer. From Fig. 2 it is considered that the optimal thickness of NaSt for electron injection from Mg to Alq3 is about 1.0 nm.

Figure 3 shows the $I$\textendash $V$ and $L$\textendash $V$ curves of Ag-OLEDs. Different from the above mentioned cases, with a 1.0 nm NaSt layer inserted between Alq3 and Ag, both $I$\textendash $V$ and $L$\textendash $V$ curves are shifted toward high voltage region compared with the device without NaSt. Further increasing the NaSt layer thickness (3.0 nm), current injection of the device is gradually enhanced. When the thickness of NaSt is increased to 5.0 nm, the device shows optimal current injection and EL output. The NaSt layer thickness over 5.0 nm shifts the $I$\textendash $V$ and $L$\textendash $V$ curves back to the higher voltage region. Similar phenomenon has also been observed in the case of Ag\textbackslash LiF\textbackslash Alq3 and a qualitative explanation on it was given.\textsuperscript{10} In short, compared with the cases of Al-OLEDs and Mg-OLEDs, a large optimal thickness of NaSt for electron injection from Ag to Alq3 is definitely observed.

The optimal thickness of NaSt for electron injection versus the IBH between Fermi level ($E_F$) of different cathode and LUMO of Alq3 are plotted in Fig. 4. The work functions of Mg, Al, and
Ag are about 3.7, 4.3, and 4.6 eV, respectively, and the LUMO of Alq3 is about 3.0 eV below the vacuum level. Therefore, the IBH of Mg:OLEDs, Al:OLEDs, and Ag-OLEDs are about 0.7, 1.3, and 1.6 eV, respectively. It can be clearly seen in Fig. 4 that the optimal thickness of NaSt increases with IBH. A tentative dashed line to guide the eye is drawn through the three experimental points. Noticeably, the line intersects the abscissa axis at (0.5,0), which might be an indication that for an IBH less than 0.5 eV no buffer will be needed for the optimal injection. Interestingly, as mentioned previously, it has been found that an insulating buffer (LiF) even with optimal thickness can hardly enhance the hole injection at ITO\NPB interface with about 0.5 eV IBH for hole injection; on the contrary, the hole injection can be greatly enhanced by introducing the same buffer at ITO\NPB interface with larger IBH.

The dependence of buffer thickness on IBH can be understood based on a simple tunneling model, which is schematically shown in Fig. 5. If no buffer layer is included, upon application of a forward voltage the electron must tunnel through the shaded triangle barrier, as shown in Fig. 5(a). The presence of a thin layer of buffer has two effects: (i) the voltage drop across it lifts the cathode $E_F$ by the same amount and hence reduces the triangle barrier in Alq3 layer, i.e., that the position of the electron injection is governed only magnitude of barrier observed. Therefore, the optimal thickness will increase with IBH, as given voltage, and hence the buffer layer should be thicker. (ii) the line intersects the abscissa axis at (0.5,0), which might be an indication that for an IBH less than 0.5 eV no buffer will be needed for the optimal injection. Interestingly, as mentioned previously, it has been found that an insulating buffer (LiF) even with optimal thickness can hardly enhance the hole injection at ITO\NPB interface with about 0.5 eV IBH for hole injection; on the contrary, the hole injection can be greatly enhanced by introducing the same buffer at ITO\NPB interface with larger IBH.

In conclusion, we have shown the dependence of optimal thickness of NaSt for electron injection on IBH between ETL and different cathodes. The larger the IBH is, the larger the optimal thickness will be. This is attributed to the different work functions of cathodes, which result in different initial barrier heights for electron injection from cathodes into ETL, and can be understood based on tunneling model.

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