

Efficient electron injection in organic light-emitting diodes using lithium quinolate/Ca/Al cathodes

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Device performances of green devices with cathode structure of lithium quinolate (Liq)/Ca/Al were investigated and electron injection mechanism was studied using ultraviolet photoelectron spectroscopy. Power efficiency could be improved by 70% by using Liq/Ca/Al cathode structure due to efficient electron injection, and interfacial energy barrier lowering by Liq/Ca/Al metal cathode was observed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2779105]

Organic light-emitting diodes (OLEDs) have been known for more than 20 years and they are promising as next generation displays for mobile appliances and television applications. They have several merits of wide viewing angle, wide color gamut, and short response time for various applications. However, their lifetime and power consumptions need to be improved further to compete liquid crystal display.

Power consumption is determined by driving voltage and current efficiency of OLEDs and many studies have been devoted to develop cathode structures because electron is a minor carrier in organic devices. LiF/Al has been typically used as a cathode for OLEDs and it was useful to get low driving voltage.¹⁻⁴ Similar cathode structures of CsF/Al, MgF₂/Al, and BaF₂/Al have been reported and it was found that those cathode structures were effective to facilitate electron injection to organic layers.^{5,6} Li₂O and Cs₂CO₃ have also been studied and it gave low driving voltage and high current efficiency.^{7,8} In particular, Cs₂CO₃ was very effective as an electron injection layer in polymer OLEDs. Another class of electron injection material is organometallic complexes with reactive alkali metals such as Li. Several Li containing electron injection materials have been developed and one of the most well known Li complexes is 2-hydroxyquinoline lithium (Liq) which was reported by Schmitz *et al.*⁹ Its performance as an electron injection layer was comparable to LiF/Al and the device performance was not so sensitive to electron injection layer thickness and it could be deposited at low temperature.

One efficient way to reduce the driving voltage is to use reactive metals such as Ca between LiF and Al. Brown *et al.* reported LiF/Ca/Al, and CsF/Ca/Al, and electron injection from cathode to organic layer was enhanced by incorporating reactive Ca, resulting in high efficiency in OLEDs.¹⁰ LiF dissociation by reactive Ca was proposed in their works. Assuming LiF dissociation by Ca, dissociation of Li complexes can be activated easily because bond energy in organometallic complexes is generally lower than that of ionic compounds such as LiF. Therefore, reactive metals can be very

effective in organometallic based cathode system as an interlayer and can facilitate electron injection from cathode to organic layer.

In this work, a cathode system of Liq/Ca/Al was developed and its device performances were compared with those of Liq/Al cathode. Current injection in the device was studied and electron injection in Liq/Ca/Al was investigated with ultraviolet photoelectron spectroscopy (UPS) according to thickness of each layer.

A device configuration of indium tin oxide (ITO)/N,N'-diphenyl-N,N'-bis-[4-(phenyl-*m*-tolyl-amino)-phenyl]-biphenyl-4,4'-diamine (60 nm)/N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (30 nm)/Alq₃ (50 nm)/Liq (1 nm)/Ca (1 nm)/Al (100 nm) was used to study the effect of Ca interlayer on device performances. The thicknesses of Ca were 0 and 1 nm. Deposition rate of Ca was 0.2 Å/s and Al was evaporated at a deposition rate of 2 Å/s. Current-voltage-luminance characteristics of devices were measured with Keithley 2400 source measurement unit and PR650 SpectraScan® colorimeter (Photoresearch, Inc.). UPS spectra were obtained on a PHI 5700 spectrometer using standard He I (21.2 eV) sources.

Liq is an organometallic compound with low deposition temperature and it can be useful as an electron injection material due to low binding energy between Li and hydroxyquinoline ligand.⁹ Assuming dissociation of Liq by metal deposition as reported in other studies,¹⁻⁵ low binding energy of Liq indicates easy liberation of Li during cathode deposition in Liq system. In addition, the dissociation of Li can be facilitated by reactive metals such as Ca and it is expected that Liq/Ca/Al cathode system can give low driving voltage due to efficient electron injection.

To correlate the cathode structure with device performances, current density and luminance of Liq/Ca/Al were compared with those of Liq/Al. Figure 1 shows current density and luminance of Liq devices with and without Ca interlayer between Liq and Al. Current density and luminance were increased by more than twice by introducing a Ca interlayer between Liq and Al. The high current density in Liq/Ca/Al indicates efficient electron injection from cathode to Alq₃ because the only difference between the two devices is electron injection structure.

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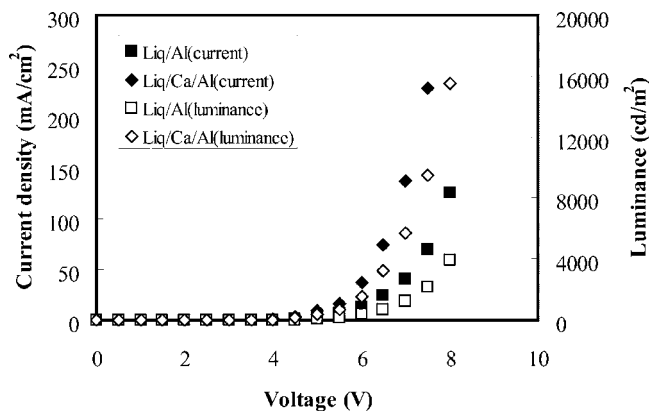


FIG. 1. Current density–voltage and luminance–voltage curves of Liq/Al and Liq/Ca/Al devices.

To study the change of interfacial energy barrier in Liq/Ca/Al, *in situ* measurement of the highest occupied molecular orbital (HOMO) shift during deposition of Ca and Al was carried out. Figure 2 shows UPS spectra of Liq/Al and Liq/Ca/Al according to the thicknesses of Liq, Ca, and Al. The binding energy was relative to the Fermi level and the onset of UPS spectra corresponds to HOMO or valence band. Assuming that the HOMO level shift induces the lowest unoccupied molecular orbital level lowering, the HOMO level lowering indicates reduced energy barrier for electron injection. It can be clearly seen that the HOMO level of Alq₃ was

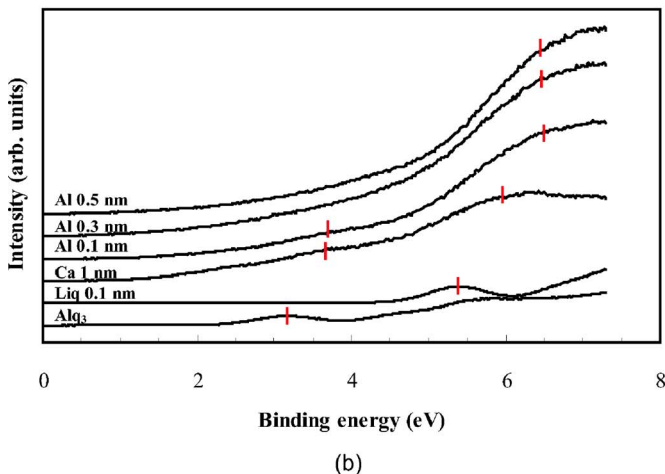
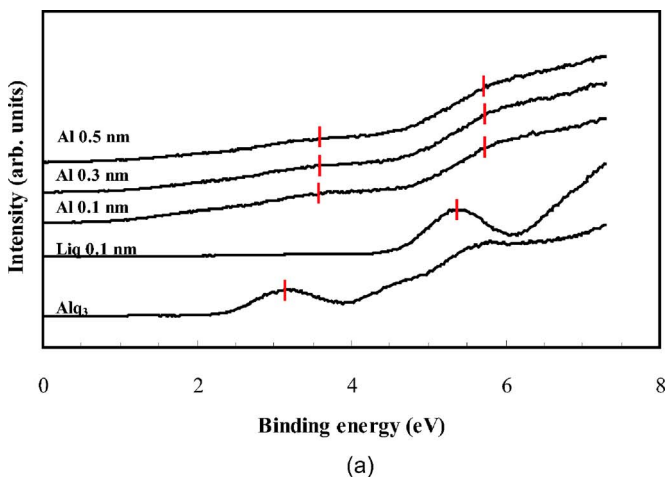


FIG. 2. (Color online) UPS spectra of Liq/Al and Liq/Ca/Al according to thickness of metal layers; (a) Liq/Al and (b) Liq/Ca/Al.

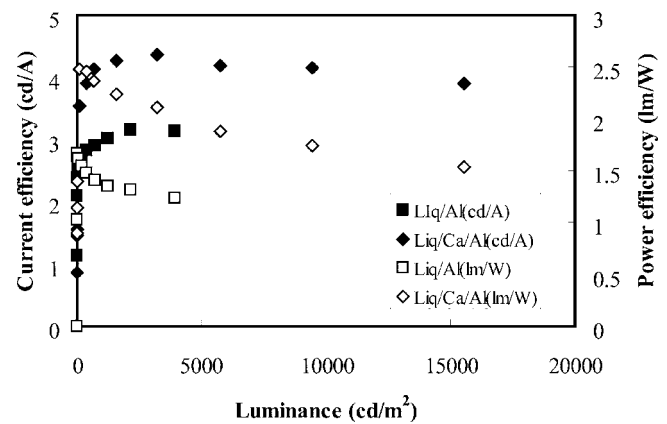


FIG. 3. Plot of current efficiency and power efficiency of Liq/Al and Liq/Ca/Al devices.

shifted from 3.2 to 5.4 eV by depositing Liq on Alq₃ at a thickness of 1 nm. Additional HOMO level shift and gap state formation were observed during deposition of Al on Alq₃/Liq film and the HOMO level was lowered up to 5.6 eV. Compared with Liq/Al devices, the HOMO level of Liq/Ca/Al was further lowered by Ca interlayer. Additional interfacial energy lowering by Ca was 0.5 eV and it was shifted by 0.6 eV after Al deposition. Total HOMO level change in Liq/Ca/Al was 3.3 eV compared with 2.4 eV of Liq/Al. This indicates that the electron injection barrier between cathode and Alq₃ is lowered by using Liq/Ca/Al cathode structure and the high current density in Liq/Ca/Al device can be explained by efficient electron injection from Al to Alq₃ by lowered interfacial energy barrier.¹¹ Gap state formation was similarly observed both in Liq/Al and Liq/Ca/Al, and it can be concluded that the interfacial energy barrier lowering by Liq/Ca/Al is mainly responsible for the high current density in Liq/Ca/Al devices. The origin of the low interfacial energy barrier in Liq/Ca/Al devices is not clear from UPS measurement, but it might be related with high chemical reactivity of Ca. Even though there is no direct evidence for the efficient dissociation of Liq by Ca, it can be indirectly postulated that Liq reaction with Ca can be effective considering Gibbs free energy formation for Li–CaF₂ and Li–AlF₃. Calculated Gibbs free energy for Li–CaF₂ formation from LiF–Ca is –0.2 kJ/mol, while it is 332.1 kJ/mol for Li–AlF₃, implying that Ca is more reactive than Al for the dissociation of Li compounds.¹²

Figure 3 shows current efficiency and power efficiency of Liq/Ca/Al devices compared with those of Liq/Al. Current efficiency and power efficiency of Liq devices were enhanced by Ca interlayer and high current efficiency of Liq/Ca/Al devices can be explained by efficient hole and electron recombination in light-emitting layer. In general, hole is a majority carrier in organic devices and more electron injection from cathode to emitting layer or less hole injection can improve charge balance in the light-emitting layer. In case of Liq/Ca/Al, electron injection was greatly improved by a metal interlayer and hole–electron balance in Alq₃ can be better after introduction of Ca interlayer. High current efficiency in Liq/Ca/Al devices with high current density supports the explanation. Current efficiency of Liq devices was enhanced from 3.1 to 4.3 cd/A by Ca interlayer. Power efficiency was even more improved than current efficiency and power efficiency of 2.3 lm/W could be obtained in Liq/Ca/Al device compared with 1.37 lm/W of standard Liq/Al device.

device. 70% improvement of power efficiency was observed in Liq/Ca/Al devices and high power efficiency of Ca devices is due to high current efficiency and low driving voltage of Liq/Ca/Al devices.

In summary, introduction of metal interlayer of Ca was effective to improve electron injection from cathode to Alq₃ and high current efficiency could be obtained. Power efficiency of Liq/Ca/Al devices was improved by 70% due to efficient electron injection, and low electron injection barrier in Liq/Ca/Al device was responsible for efficient electron injection.

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