

Organic Electroluminescent Devices Having Metal Complexes as Cathode Interface Layer

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We developed novel cathode systems, composed of metal complexes, for organic electroluminescent (EL) devices. Alkaline metal complexes, such as mono(8-quinolinolato) lithium (Liq), were used as a cathode interface layer in combination with metallic Al as a cathode material. Similarly, doping the organic electron-transporting layer with alkaline metal complexes was also effective in facilitating the electron injection from the cathode to the organic layer, which results in reducing the drive voltage. In both cases, we assume that alkaline metal ions in the complexes are reduced to free metal by thermally activated Al. Then, the free alkaline metal reacts with electron-transporting materials, forming the radical anions, which facilitate electron injection from the Al cathode. [DOI: 10.1143/JJAP.41.L800]

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In organic electroluminescent (EL) devices, organic thin layers are sandwiched between the anode and the cathode, and the organic emitting centers are excited by the recombination of holes and electrons injected from the electrodes. It is therefore important to balance the number of holes and electrons injected from the electrodes to the emitter layer to achieve high device performance. A typical material used for the anode is indium-tin oxide (ITO) which is transparent in the visible region and has a high work function of approximately 5.0 eV which is suitable for injecting holes into the typical hole-transporting organic materials with ionization potentials of approximately 5.2–5.4 eV. For the cathode material, Mg : Ag alloy (10 : 1) was first introduced by Tang and Vanslyke in 1987 and has been widely used.¹⁾ Later, Al : Li alloy was introduced to reduce the drive voltage.²⁾ Double-layer cathodes, such as Li/Ag,³⁾ Li₂O/Al,⁴⁾ and LiF/Al⁵⁾ were also developed and are now widely used. Very recently, we introduced a new type of cathode interface layer composed of metal complexes such as 8-quinolinolato lithium (Liq) and 8-quinolinolato sodium (Naq).^{6,7)} The details of the device characteristics using this type of cathode interface layer will be discussed here.

Figure 1 shows organic materials used in this study; a hole-transporting *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-benzidine (α -NPD), electron-transporting and light-emitting tris(8-quinolinolato) aluminum (III) (Alq₃), electron-transporting bathophenanthroline (Bphen) and several electron-injecting alkaline metal complexes. The ligands for the metal complexes are 8-quinolinolato (q), acetylacetonato (acac) and dipivaloylmethanato (dpm). Liq, for example, was synthesized from lithium hydroxide and 8-quinolinol, and was purified by the train sublimation method. Metal complexes with acac ligands and dpm ligands were purchased from Kojundo Chemical Laboratory Co., Ltd.

Figure 1 also illustrates the two types of device structures, (a) ITO (1100 Å)/ α -NPD (500 Å)/Alq₃ (700 Å)/alkaline metal complex (10 Å)/Al and (b) ITO (1100 Å)/ α -NPD (500 Å)/Alq₃ (*x* Å)/alkaline metal complex-doped layer (700 – *x* Å)/Al. The organic layers were successively deposited onto a precleaned ITO-coated glass substrate at 1.0×10^{-5} Torr. Alkaline metal complex-doped organic layers were deposited by coevaporation method and the molar ratio be-

tween the alkaline metal complex and electron-transporting material is fixed to be 1 : 1. Finally, the Al top electrode was deposited at 7.0×10^{-6} Torr using a metal shadow mask to define an emitting area of 0.5×0.5 cm². EL spectra were taken using an optical multichannel analyzer PMA 11 (Hamamatsu Photonics K.K.). Luminance measurements were carried out with a Topcon BM-8 luminance meter at room temperature.

EL devices having alkaline metal complexes, as a cathode interface layer, between Alq₃ and Al, exhibited high performance compared with a device without a cathode interface layer. Figures 2 and 3 show luminance–voltage (*L*–*V*) and current density–voltage (*I*–*V*) characteristics of EL devices having Liq, Naq, Liacac, or Lidpm as a cathode interface layer. The highest luminance values observed for each device were 27000 cd/m² at 12 V for Liq, 31500 cd/m² at 13 V for Naq, 23000 cd/m² at 12 V for Liacac, and 17000 cd/m² at 13 V for Lidpm. Current efficiencies were 7.3 cd/A at 11 V for Liq, 9.0 cd/A at 12 V for Naq, 6.7 cd/A at 11 V for Liacac, and 6.5 cd/A at 12 V for Lidpm. These results clearly demonstrate that the insertion of alkaline metal complexes between electron-transporting layer, Alq₃, and the cathode, Al, is effective in reducing the drive voltages and improving device efficiencies. Devices without the interface layer exhibited low efficiencies which are due to the low electron injection efficiency. Using the alkaline metal complexes as a cathode interface layer improves the electron injection efficiency, resulting in a balanced hole-electron injection and a higher carrier recombination efficiency.

Among the Li complexes, Liq exhibited the highest current efficiency, which may be due to the electron-transporting ability of Liq while other complexes such as Liacac are insulating materials. Comparing central metal ions of the complexes with the same ligand, we found that the current efficiency increases as atomic mass increases. For example, in the case of the devices using quinolinolato ligand, the current efficiency of the device using Naq was higher than that using Liq. Similarly, in the case of dipivaloylmethanato ligand, the device using Kdpm exhibited the highest current efficiency.

The lowest unoccupied molecular orbital (LUMO) level of Liq is –2.5 eV from the vacuum level while that of Alq₃ is –3.0 eV, making the barrier heights for electron injection from Al cathode, having a work function of –4.2 eV, to the organic layers lower for Alq₃. Therefore, the improvement of

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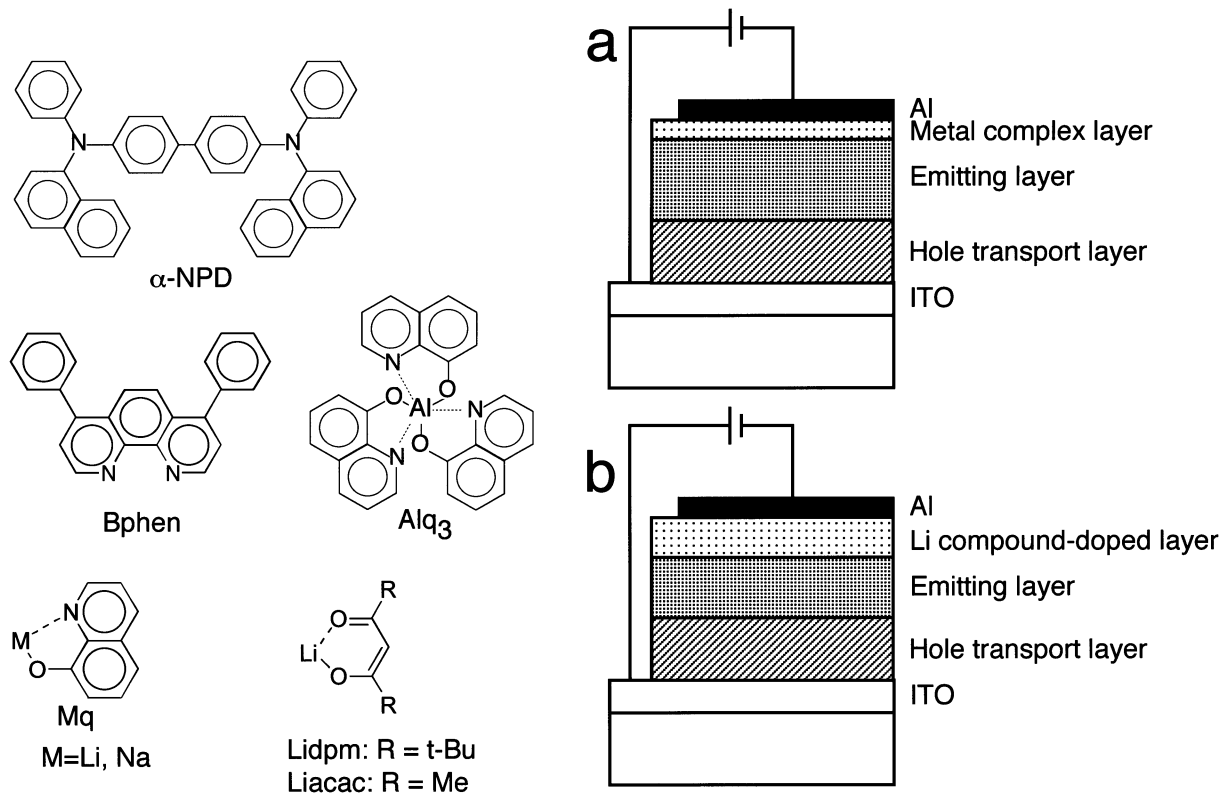
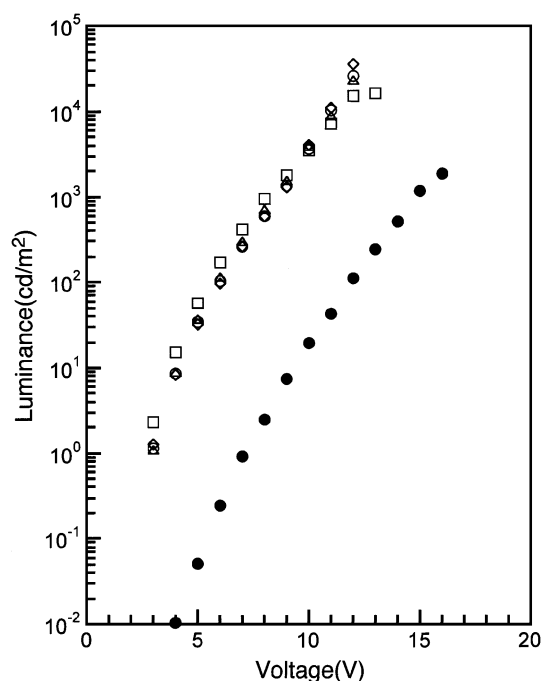
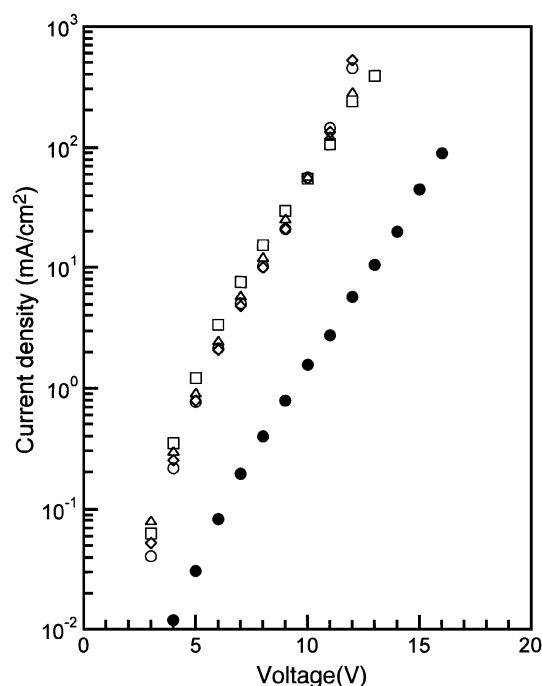


Fig. 1. Configuration of EL device and chemical structure of organic materials used.

Fig. 2. Luminance-voltage characteristics of ITO/ α -NPD (500 Å)/Alq₃ (700 Å)/alkaline metal complex (10 Å)/Al devices. Alkaline metal complex: [●] none, [○] Liq, [◇] Naq, [△] Liacac, [□] Lidpm.Fig. 3. Current density-voltage characteristics of ITO/ α -NPD (500 Å)/Alq₃ (700 Å)/alkaline metal complex (10 Å)/Al devices. Alkaline metal complex: [●] none, [○] Liq, [◇] Naq, [△] Liacac, [□] Lidpm.

electron injection from Al cathode to the organic layer cannot be explained by such simple energy diagrams. We proposed^{6,7)} that the central “metal ions” in these metal complexes are reduced to free metal by the reaction between the complexes and thermally activated aluminum in vacuum. Then the free alkaline metal liberated from the complexes re-

acts with Alq₃, forming the radical anions, which facilitate electron injection from the Al cathode. We call this an *in situ* chemical doping process. In fact, the reduction of alkaline metal compounds by thermally activated metals such as Al is often used in metallurgy.⁸⁾ In that field, high purity alkaline and alkaline-earth metals are obtained by such reactions. For

example, high purity calcium is obtained by the reaction of calcium oxide and Al in vacuum. Thus, it is reasonable to assume that thermal reduction of metal ions occurs in Liq when Al is deposited onto it. The reaction may also produce the byproducts derived from the Al ion and the organic ligands liberated from the alkaline metal complexes. Obviously, such byproducts do not affect the initial device performance, and we therefore investigate the effect of the byproducts on the device lifetime.

After our first report on the Liq cathode interface layer and assumption of the thermal reduction of Li ion in Li complexes, including LiF, Ganzorig and Fujihira reported lithium acetate as a cathode interface layer, supporting our assumption,⁹⁾ and, later, Le *et al.* proved *in situ* doping of Alq₃ by LiF through ultraviolet photoelectron spectroscopy and X-ray photoelectron spectroscopy.¹⁰⁾ As we reported previously, doping electron-transporting materials, such as Alq₃, with a highly reactive low work function metal, such as Li, facilitates electron injection from the cathode due to the gap states formed at the interface.⁷⁾ Thus, in the case of metal complexes, such chemical doping occurs *in situ*.¹¹⁾

We also developed a cathode interface layer which is doped with the metal complexes. A typical device structure is shown in Fig. 1. Host materials to be doped are Alq₃ and Bphen, and alkaline metal compounds as dopants are Liq, Lidpm and LiF for comparison. In devices with a structure of ITO (1100 Å)/α-NPD (500 Å)/Alq₃ (650 Å)/alkaline metal complex-doped Alq₃ (50 Å)/Al, the drive voltages were lower than those of the devices without the doped layer. Figures 4 and 5 show *L-V* and *I-V* characteristics of these devices. The highest luminance value was observed for the device using Liq, exhibiting the maximum luminance of 26000 cd/m² at 11 V. However, with increasing the thickness of the doped

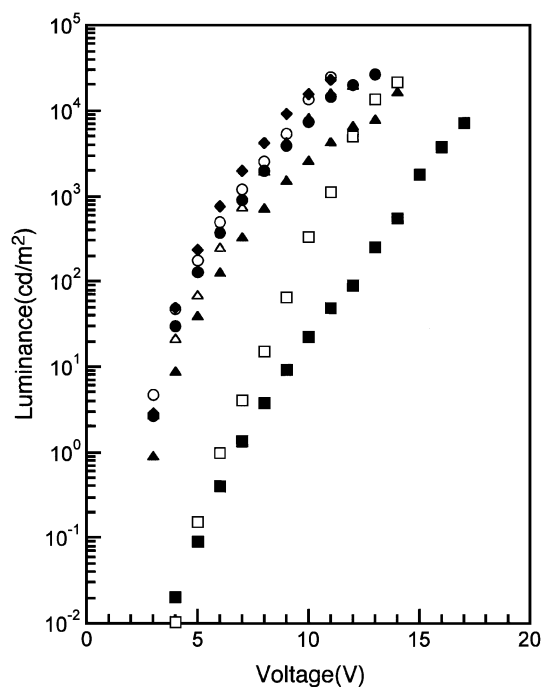


Fig. 4. Luminance-voltage characteristics of ITO/α-NPD (500 Å)/Alq₃ (700 - *x* Å)/Alq₃: Li compound (*x* Å)/Al devices, *x* = 50: [○] Liq, [△] Lidpm, [□] LiF, *x* = 300: [●] Liq, [▲] Lidpm, [■] LiF, and of the device having *x* = 300 Å of Bphen doped with Liq [◆].

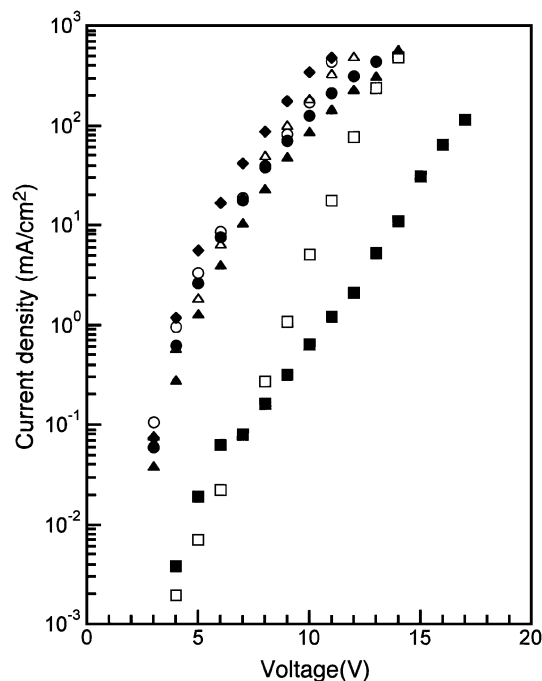


Fig. 5. Current density-voltage characteristics of ITO/α-NPD (500 Å)/Alq₃ (700 - *x* Å)/Alq₃: Li compound (*x* Å)/Al devices, *x* = 50: [○] Liq, [△] Lidpm, [□] LiF, *x* = 300: [●] Liq, [▲] Lidpm, [■] LiF, and of the device having *x* = 300 Å of Bphen doped with Liq [◆].

layer from 50 Å to 300 Å and keeping the total thickness of the Alq₃ layer and doped Alq₃ layer constant, 700 Å the drive voltages shift to the higher side. For example, the highest luminance values observed are 27000 cd/m² at 13 V for Liq, 17000 cd/m² at 14 V for Lidpm and 7300 cd/m² at 13 V for LiF. Although the increased thickness leads to the lower drive voltage in metal-doped devices,¹¹⁾ the results observed for metal complex-doped devices are the opposite. We presume that, in the case of Li compound dopants, thermal reduction by aluminum occurs to the thickness of approximately 50 Å from the Al interface and unreacted Li compounds cause lower electron mobility of the electron transport layer due to trapping electrons or stabilizing polarons by their dipole. The best results are obtained for the device with Liq-doped Bphen as a cathode interface layer. The device structure was ITO (1100 Å)/α-NPD (500 Å)/Alq₃ (400 Å)/Liq-doped Bphen (300 Å)/Al. *L-V* and *I-V* characteristics of this device are plotted in Figs. 4 and 5. Luminous efficiency of 4.0 lm/W and luminance value of 23000 cd/m² were observed at 11 V.

In conclusion, we developed novel cathode interface layers composed of alkaline metal complex. The devices exhibited lower drive voltages and higher luminance compared with devices without the cathode interface layer. In the case of the alkaline complex layer, the device using Naq exhibited the highest luminance value of 31500 cd/m² at 13 V and the highest current efficiency of 9.0 cd/A. In the case of the alkaline metal complex-doped layer, the device using Liq-doped Bphen maintains low drive voltages even at increased thickness, which makes the performance of the organic EL device much less sensitive to the thickness of the cathode interface layer.

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