Enhanced Performance of Polymer Light-Emitting Device via Optimization of Processing Conditions and Device Configuration

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ABSTRACT: The improved performance of polyalkylfluorene light-emitting device has been achieved through the optimization of processing conditions and device configuration. The current density, brightness, power efficiency, and operation lifetime of polymer light-emitting device (PLED) were strongly dependent on the surface treatment of anode, the film thickness of light-emitting polymer (LEP), and the cathode configuration. The anode surface treated with O_2 plasma exhibited a higher current density and brightness than the CF_4 plasma treated device. However, better operation stability was obtained for the CF_4 plasma treated device than for the O_2 plasma treated device. The maximum of brightness and power efficiency has been achieved for the PLED with an LEP thickness of 80 nm. The PLED with LiF/Ca/Al cathode possesses a better power efficiency and operation stability than does the Ca/Al or LiF/Al based PLED. The influences of device fabrication conditions and device configuration on the performance of a polyalkylfluorene-based PLED are discussed in detail. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 133–141, 2006

Key words: light emitting polymer; polyalhylfluroene; hole-transporting material; electroluminesence; polymer light emitting device

INTRODUCTION

Recently, polymer light-emitting diodes (PLEDs) fabricated from the semiconducting polymer, such as polyalkylfluorene, have been extensively studied because of their potential use in the flat panel display.[1,2] The electro-optical properties of PLEDs were determined by the intrinsic character of light-emitting polymer (LEP),[3,4] device processing parameters,[5–12] and device configuration.[13–18] How to fabricate the PLED with excellent electroluminescence properties, such as high brightness, high efficiency, and high operation stability, is an important issue for the application of LEP in the flat panel display.

To fabricate the PLED with excellent electroluminescence properties, different device-processing conditions, such as surface treatment of anode and thin film processing condition, have been studied previously.[5–12] The indium-tin oxide (ITO) surface treatments included the chemical, mechanical, UV irradiation, and plasma treatments.[5–9] The treatment of the ITO surface is important for the improvement of PLED performance because of the reduction of hole injection energy barrier and the enhancement of hole injection at the interface of ITO and hole-transporting layer. This improvement will lead to the reduction of turn-on voltage, and the enhancement of luminescence efficiency and operation stability of PLEDs, as widely investigated in the literature.[5–9] However, the difference between the oxygen- and CF_4-plasma treatment effects has not been thoroughly examined. In addition, the electroluminescence properties of PLEDs are also influenced significantly by the morphology of LEP films. The correlation between the morphology and the electroluminescence properties of MEH-PPV-based device has been reported by Yang and coworkers.[10–12] However, LEPs with different chemical structures would display different thin film morphologies even under similar processing conditions. Therefore, an optimized thin film processing condition is also strongly dependent on the chemical structure of LEP.

In addition to the device-processing condition, the device configuration also plays an important role in the electroluminescence properties of PLED. The device performance strongly depends on the balanced injection of holes and electrons into the emitting layer from the anode and cathode, respectively. However,

the majority of carriers reaching the emitting layer are generally holes, because of their higher mobility and typically smaller injection barrier, especially for the semiconducting polymers. Therefore, lowering the barrier height and enhancing the electron injection will lead to a better balance of electron and hole currents. For this purpose, the lower work function cathodes, such as calcium/aluminum (Ca/Al), LiF/Al, and LiF/Ca/Al, have been used as the electron injectors in the PLED.[13–18] Among these, Ca/Al and LiF/Al are the most commonly used cathodes for the PLED because of the lower work functions of Ca and Li, respectively.[13] The dissociation of LiF would liberate Li, which will lead to the reduction of barrier height between light-emitting layer and cathode of LiF/Al.[14–17] Moreover, the dissociation of LiF is related to the reactivity of the metal. Compared to the Al electrode, Ca would react with LiF more readily to liberate Li, thus resulting in the lower work function of LiF/Ca/Al.[18] For these cathodes, the energy barrier and the mechanism of electron injection have been extensively studied. Despite all that, the lowest unoccupied molecular orbital value and interface morphology of polymer/metal would be different for the LEP depending on the variation of chemical structure. As a result, different electron-injection conditions would be obtained for the different LEPs even with the same cathode.

In this study, the influences of device fabrication conditions and device configuration on the performance of a polyalkylfluorene-based PLED were investigated. The effect of ITO surface treatment on the device performance was studied for the PLEDs treated with oxygen- and CF_4-plasma, respectively. The optimized thin film processing condition was determined by the performance evaluation of PLEDs containing different thin film thicknesses. PLEDs with different cathode configurations, such as Ca/Al, LiF/Al, and LiF/Ca/Al cathodes, have been investigated for the cathode effect on the electroluminescence behavior. The performance of polyalkylfluorene-based devices would be enhanced through the aforementioned optimization of processing conditions and device configuration.

EXPERIMENTAL

The green emission PLED structure in this study was ITO glass/PEDOT/PFG-B/Cathode. The green alkylfluorene copolymer was used as received (PFG-B; Dow Chemical Co.). Different chemical structures of the green alkylfluorene copolymer have been reported by Dow Chemical Co., including the copolymerization of alkylfluorene with the thiophene, bithiophene, or benzothiadiazole compounds. Chemical structure of PFG-B is shown in Figure 1.[19–23] Glass substrates with patterned ITO electrodes were washed well and
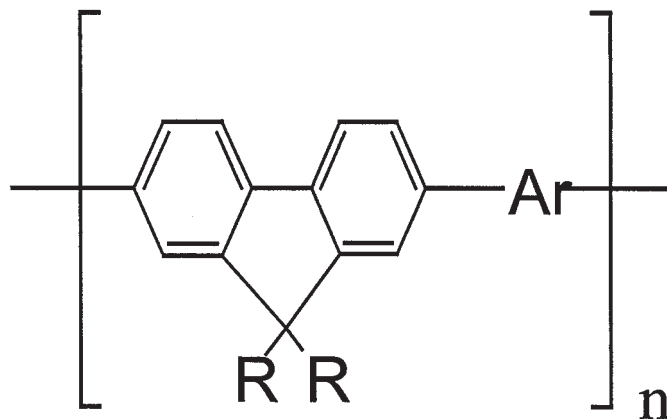

Figure 1 Chemical structure of alkylfluorene copolymer PFG-B.

cleaned by O_2 or CF_4 plasma treatment. A thin film (600 Å) of hole-transporting material PEDOT (Baytron P, Bayer) was formed on the ITO layer of a glass substrate by the spin-casting method. The green emission LEP thin film was then spin-coated from the 8 mg/mL xylene solution onto the PEDOT layer, and was dried at 70°C for 1 h in a glove box. A high purity Ca or LiF cathode was thermally deposited onto the green LEP thin film, and this was followed by the deposition of silver (Ag) or Al metals as the top layer in a high vacuum chamber. The device was then encapsulated by glass covers, which were sealed with UV-cured epoxy glue. The deposition rate of cathode was determined with a quartz thickness monitor (STM-100/MF, Sycon). Thickness of the thin film was determined with a surface texture analysis system (3030ST, Dektak). Current-voltage characteristics were measured on a programmable electrometer with current and voltage sources (Keithley 2400). Luminance was measured with a BM-8 luminance meter (Topcon).

RESULTS AND DISCUSSION

The influences of device-fabrication conditions and device configuration on the performance of a polyalkylfluorene-based PLED are discussed here.

Plasma treatment effect on anode surface

The plasma effect on the electroluminescence properties of the PLEDs is shown in Figure 2. As compared to the device with CF_4-plasma treatment, the PLED pretreated with oxygen plasma exhibited a higher current density and brightness. This result implies that the plasma effect on the enhancement of the work function of ITO or the reduction of energy barrier height between ITO and PEDOT interface was more pronounced for the oxygen plasma in comparison with
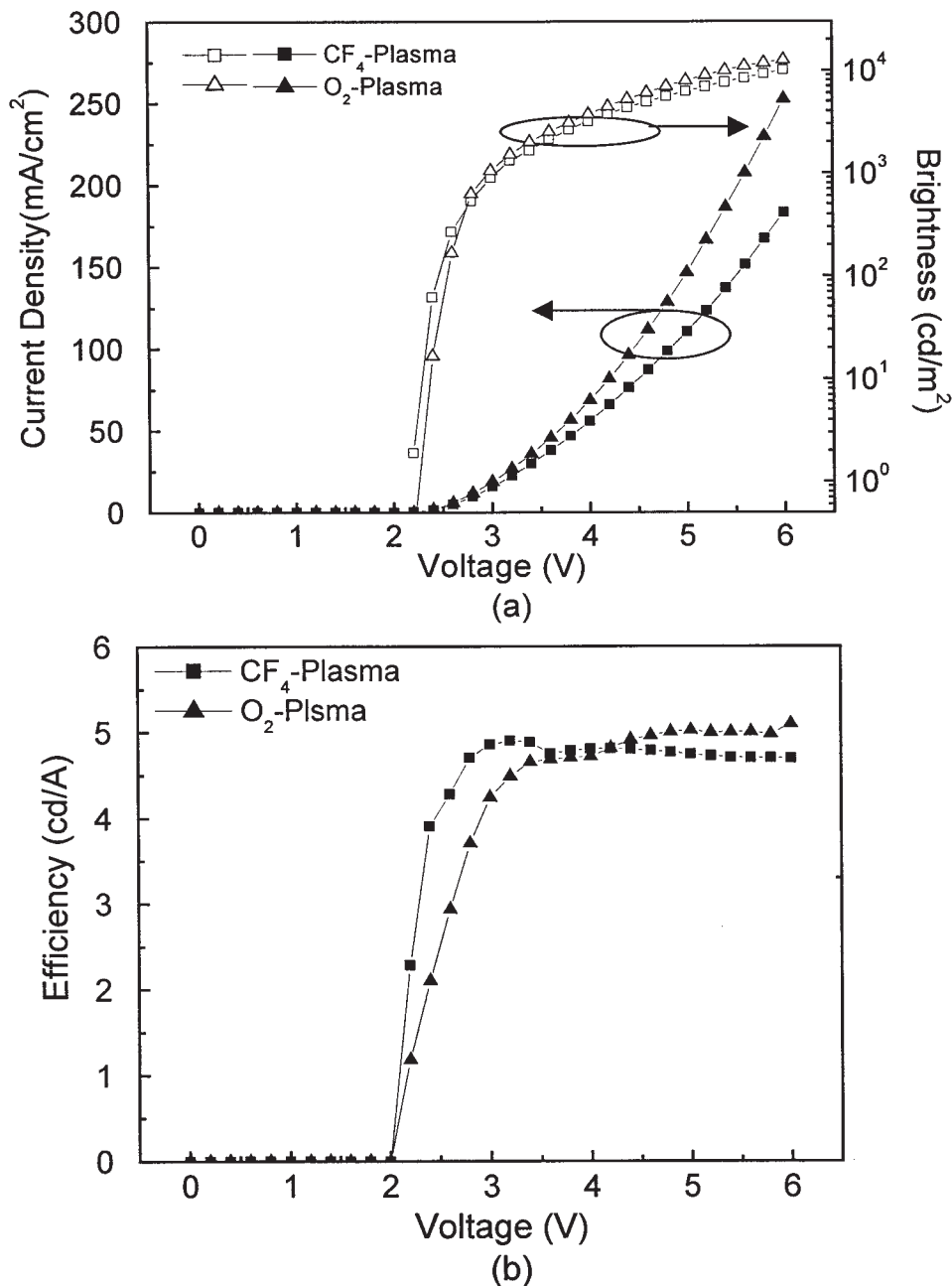
Figure 2 The current density, brightness, and efficiency versus voltage for PLEDs: ITO (O_2 or CF_4 plasma)/PEDOT (60 nm)/PFG (60 nm)/Ca (10 nm)/Ag (120 nm).

the CF_4-plasma treatment. However, the power efficiency did not vary significantly for these two different plasma treatments. The power efficiency was related to the balance of carriers and the carrier recombination efficiency, which was not dominantly determined by the ITO work function.[18] This is because the hole was the majority carrier. The charge balance was determined by the injection of minority carrier, the electron. Lowering the cathodic barrier height and enhancing the electron injection capacity lead to a better balance of carrier currents.[18]

Plasma effect on the lifetime of PLED is shown in Figure 3. The result indicates that the PLED treated

with CF_4-plasma exhibits a half-life of 350 h with an initial brightness ($L\phi$) of 660 nits. Starting at the initial brightness of 1200 nits, the PLED treated with O_2-plasma shows a half-life of 100 h. Despite that the initial driving current was not the same for these two devices, the initial driving current was not large enough to result a current effect to accelerate the degradation of the PLED device. Therefore, the scaling law was applicable for translating the lifetime of the PLED with a low driving current density (13.5 or 24 mA/cm^2).[24–26] Using the scaling law established by Van Slyke and Tang, $L_{initial} \times t_{1/2} = $ constant, where, $L_{initial}$ is the initial brightness and $t_{1/2}$ is the half-
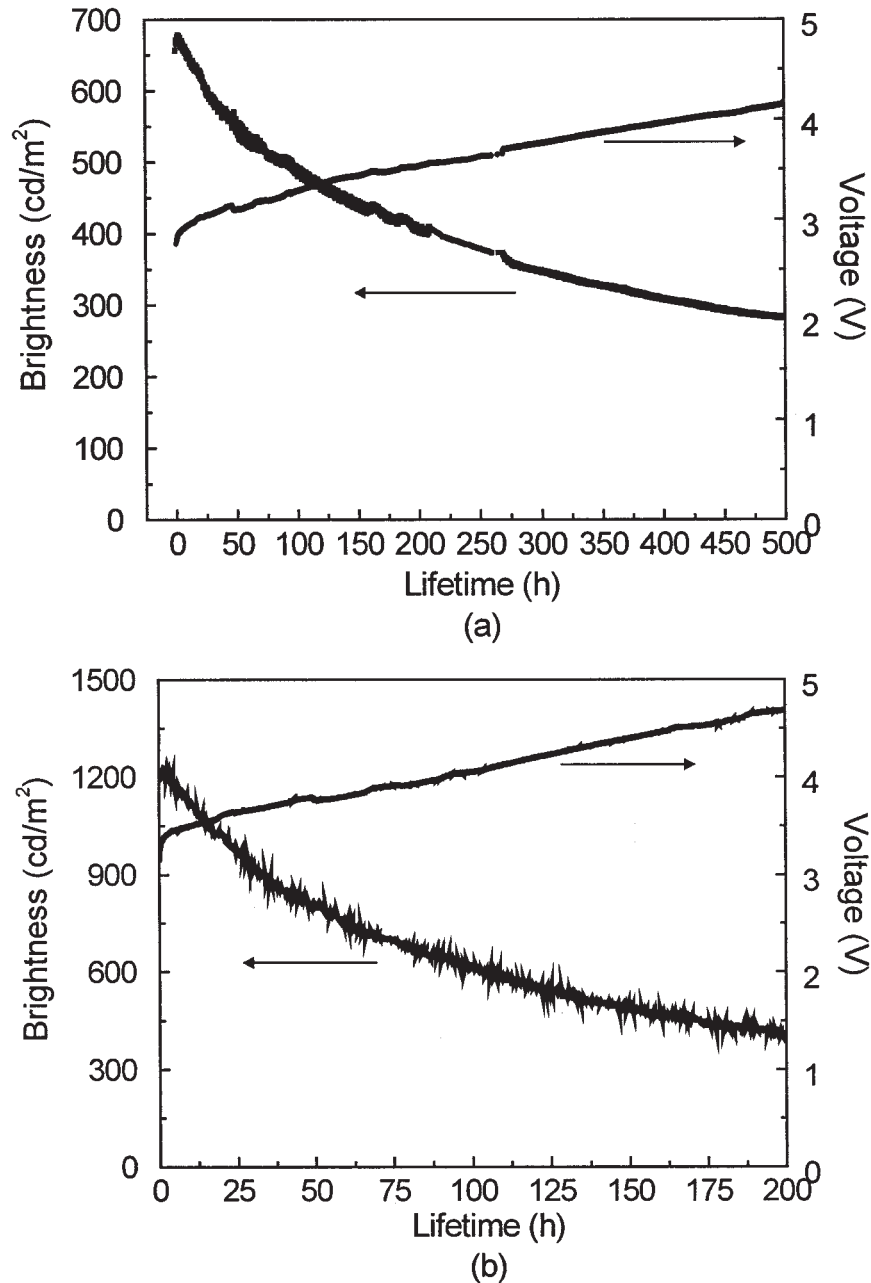
Figure 3 Operation lifetime of PLEDs: (a) device treated with CF_4-plasma (drive current, 13.5 mA/cm^2; $L\phi$ = 660 nits) and (b) device treated with O_2-plasma (drive current, 24.0 mA/cm^2; $L\phi$ = 1200 nits).

life,[24–26] it can be stated that the half-life of PLED treated with CF_4-plasma would translate to 2310 h for the initial brightness of 100 nits. The half-life of PLED treated with O_2-plasma would be 1200 h for the initial brightness of 100 nits. Therefore, the PLED treated with CF_4-plasma exhibits a longer operation lifetime as compared to the device with the O_2-plasma treatment. Some researchers have reported that the oxygen fills the vacancies in the surface of ITO glass during the oxygen-plasma treatment process, and partially vacates from ITO surface during device operation. The released oxygen provides the source of photo-oxida-

tion in the LEP film and subsequently results in the formation of quench center for the electroluminescence.[27,28] As a result, the CF_4-plasma treated PLED exhibits higher operation stability as compared with the O_2-plasma treated device.

Thickness effect of LEP film

The influence of LEP film thickness on the electroluminescence properties of PLED is shown in Figure 4. The current density increased with decrease in the thin film thickness. Moreover, the brightness in-
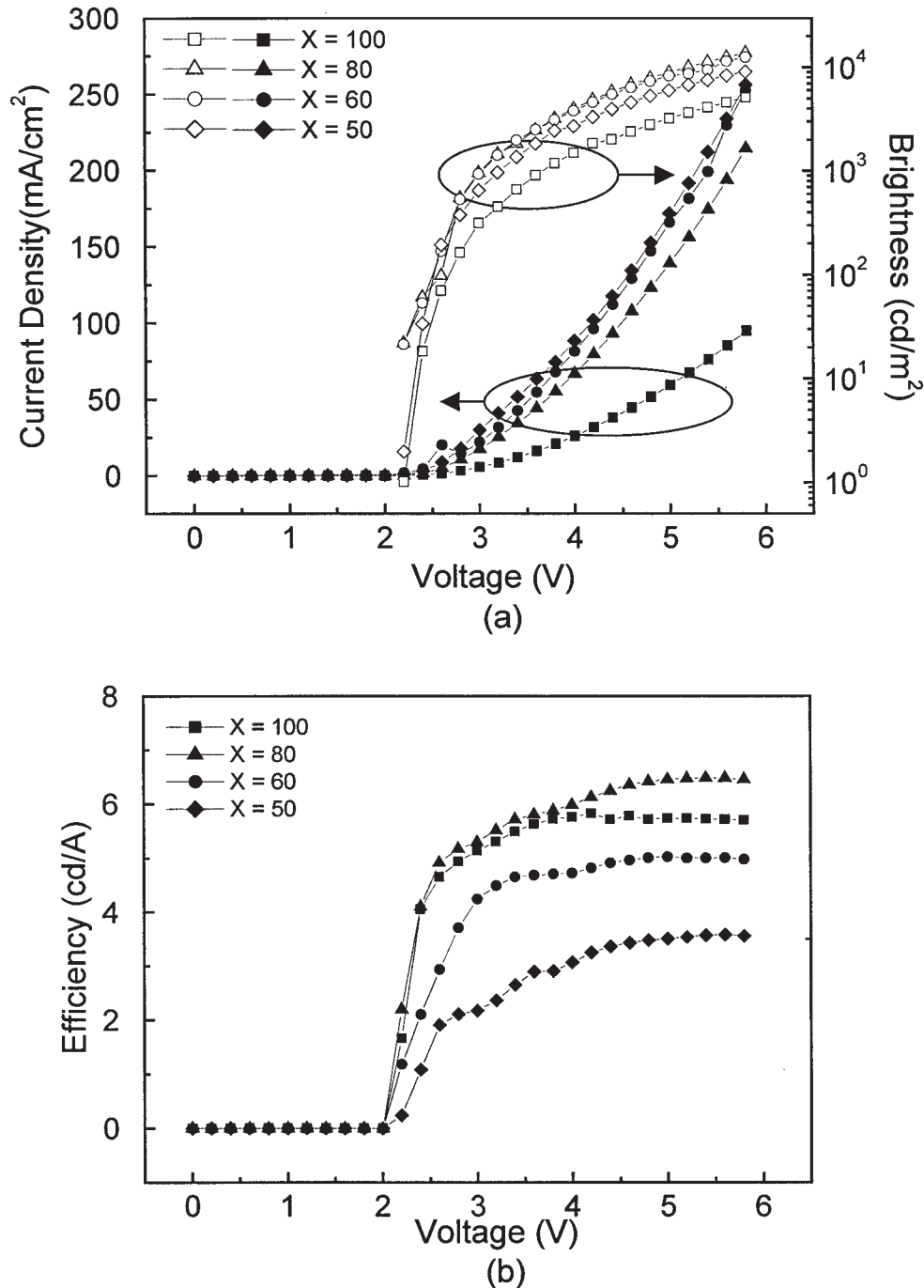
Figure 4 The current density, brightness, and efficiency versus voltage for PLEDs: ITO (O_2 plasma)/PEDOT (60 nm)/PFG (X nm)/Ca (10 nm)/Ag (120 nm).

creased with decrease in LEP thickness. A maximal brightness was obtained with a thickness of 80 nm. The brightness decreased further with decrease in the LEP thickness. In addition, a maximal power efficiency was obtained for the PLED with an LEP thickness of 80 nm. For the PLED with a thick light-emitting layer, the polymer chains could not extend thoroughly because of the low spin rate of coating process. This is not favorable for the carrier transporting and

recombination within the polymer chains.[10,11] Therefore, low brightness and power efficiency were obtained for the PLED with an LEP thickness of 100 nm. On the other hand, the presence of particles on the surface of ITO glass and the roughness of the ITO surface could not be smoothed down by a thin polymer film. As a result, electric leakage could have occurred during the operation processes for PLED because of the presence of defects.[29,30] Consequently,
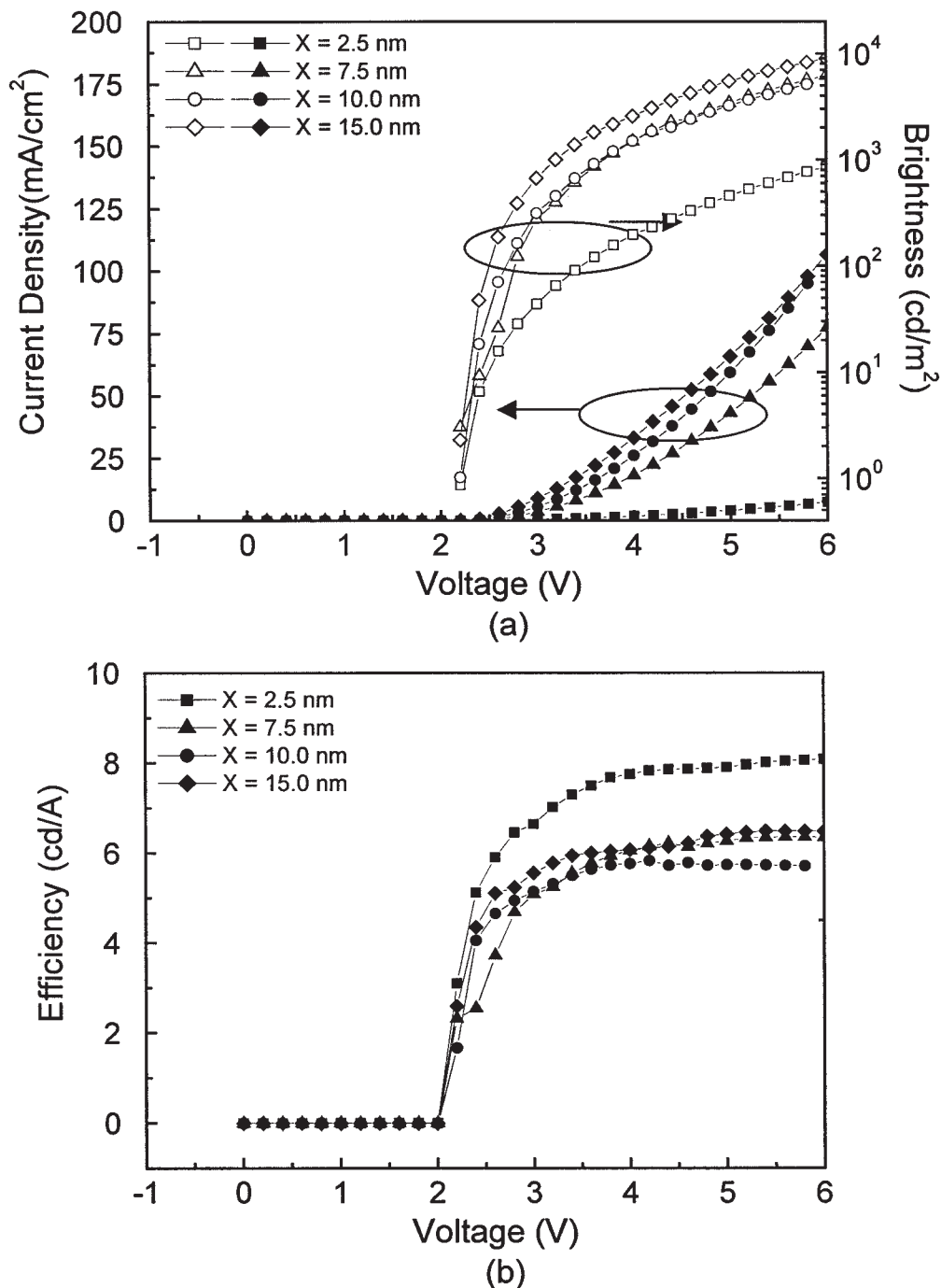
Figure 5 The current density, brightness, and efficiency versus voltage for PLEDs: ITO/PEDOT (60 nm)/PFG (100 nm)/Ca (X nm)/Ag (120 nm).

low brightness and power efficiency were obtained for the PLED with a thickness less than 80 nm.

Cathode configuration effect

Calcium thickness effect

The Ca thickness effect on the electroluminescence properties of PLED is shown in Figure 5. Current density and brightness increased with increase in Ca thickness. A lower current density and brightness were obtained for the PLED with a thin Ca thickness of 2.5 nm. This is because electrical conductivity is related to the thickness of the metal thin film. Moreover, the power efficiency was dependent on the Ca thickness of PLED. The PLED with Ca thickness of 2.5 nm exhibits a higher efficiency as compared to the one with the Ca thickness of more than 7.5 nm.
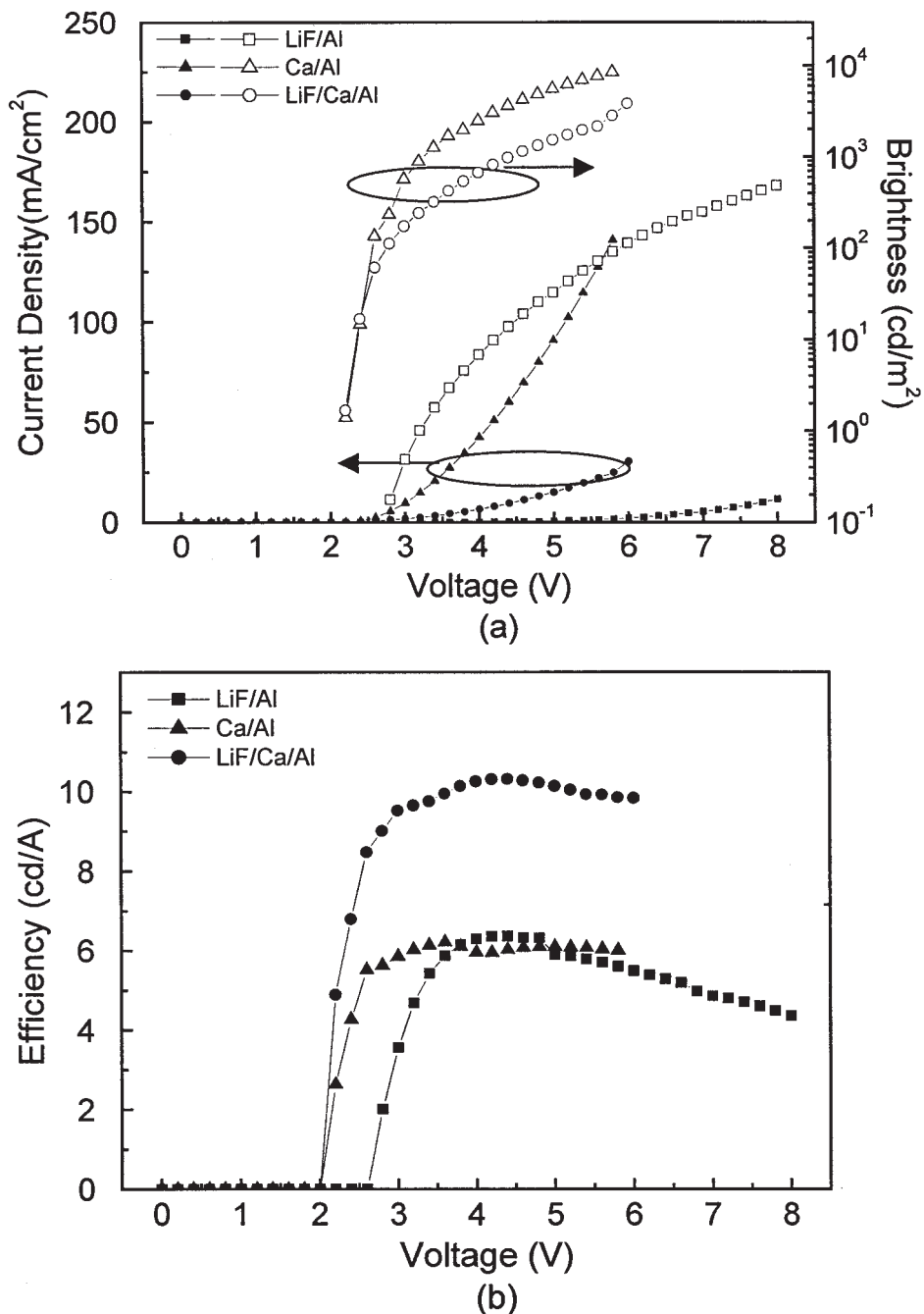
Figure 6 The current density, brightness, and efficiency versus voltage for PLEDs with different cathodes: ITO (O_2 plasma)/PEDOT (60 nm)/PFG (100 nm)/cathode.

This implies that the thin Ca layer with low conductivity was favorable for the charge balance between electron and hole of the PFG-B based PLED. Consequently, higher power efficiency was obtained for the PLED with a thinner layer of calcium. On the other hand, high electron conductivity of the thick Ca layer would enhance the electron injection, and resulted in the high current density and brightness. However, the excess of electrons was not favorable

for the charge balance of the carriers, and led to low power efficiency. In addition, the Ca-induced luminescence quenching also played a role in the decrease of power efficiency when increasing the Ca thickness.[22,31,32] Stoessel et al. have reported that the electroluminescence efficiency was reduced significantly when the Ca layer thickness was increased, especially in the case of the thick Ca layer.[22] The brightness decreased drastically as the Ca thickness
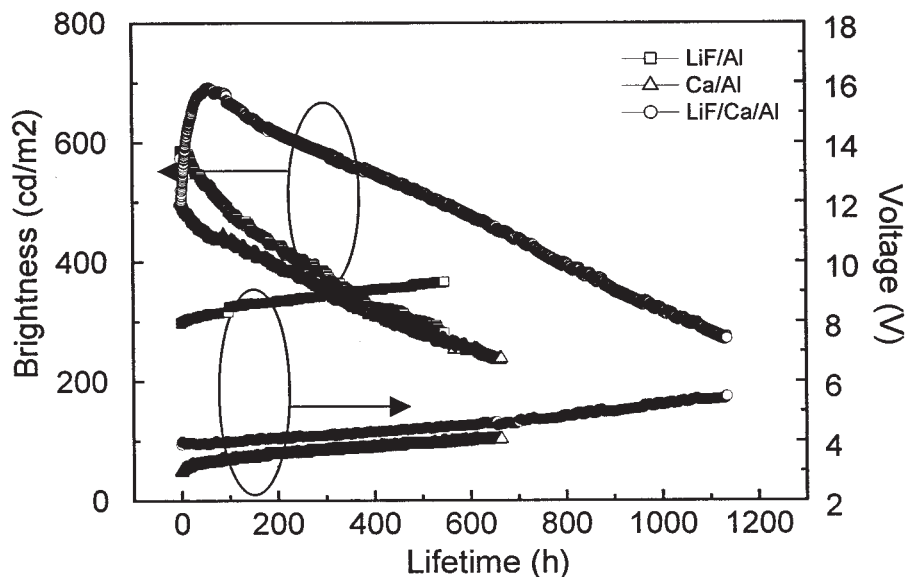
Figure 7 The operation stability of PLEDs with different cathodes: ITO (O_2 plasma)/PEDOT (60 nm)/PFG (100 nm)/cathode; driving current and initial brightness: LiF/Al (13.6 mA/cm^2, 580 nits), Ca/Al (8.7 mA/cm^2, 500 nits), and LiF/Ca/Al (5.5 mA/cm^2, 574 nits).

increased up to 30 nm for the polyalkylfluorene-based device.[22]

Lithium fluoride effect

In addition to calcium, LiF also plays an important role in influencing the electroluminescence properties of PLED. The electroluminescence properties of PLEDs with various cathodes are shown in Figure 6. The PLEDs with Ca/Al cathode exhibited a higher current density and brightness than the one with LiF/Al cathode. This implies that the Ca/Al cathode is more efficient for the electron injection into the light-emitting layer than the LiF/Al cathode is.[18] The electron-injection capacity is reduced when the LiF layer is inserted between Ca and light-emitting layer. Consequently, the values of current density and brightness of PLED with LiF/Ca/Al cathode are between those of the PLEDs with Ca/Al and LiF/Al cathodes. In addition, the PLED with LiF/Ca/Al would exhibit higher power efficiency than the Ca/Al and LiF/Al cathodes based PLEDs. This implies that the insertion of LiF layer between Ca and light-emitting layer is efficient for promoting charge balance. In addition to the factor of charge balance, the quenching effect of Ca is also part of the reason for the lower power efficiency of Ca/Al cathode based PLED.[22] The insertion of LiF layer between Ca and light-emitting layer would deter the diffusion and contamination of Ca into the polymer layer. This leads to the reduction in luminescence quenching of PLED.[33] As a result, high power efficiency was obtained for the PLED with LiF/Ca/Al cathode.

The insertion of LiF layer not only affects the power efficiency but the operation lifetime of PLED as well. The operation stability of PLED with different cathode configurations is shown in Figure 7. The measurement of operation stability was carried out under constant DC current. The brightness decreased with increase in the applied voltage during aging measurement for the PLEDs with Ca/Al and LiF/AL cathodes, whereas the PLED with LiF/Ca/Al cathode behaved differently. The brightness increased with increase in operation time at initial stage for the PLED with LiF/Ca/Al cathode. The improvement of polymer/LiF contact results in the better charge balance and power efficiency under an applied driving voltage, which leads to the increase in brightness during the early stage of lifetime.[34] Moreover, the result indicates that the PLEDs with LiF/Al and Ca/Al cathodes exhibit half-life of 530 and 600 h with initial brightness of 580 and 500 nits, respectively. Starting at the initial brightness of 574 nits, the PLED with LiF/Ca/Al cathode possesses a half-life of 1100 h. The half-life of the PLEDs with LiF/Al and Ca/Al cathodes could be translated to 3074 and 3000 h for the initial brightness of 100 nits, whereas the half-life of the PLED with LiF/Ca/Al cathode would be 6314 h for the initial brightness of 100 nits. Obviously, the operation stability of PLED with LiF/Ca/Al cathode was much more than those of the Ca/Al and LiF/Al cathodes based PLEDs. In addition to the higher power efficiency, the LiF layer hinders the Ca-induced electroluminescence quench, and also acts as an excellent buffer layer that limits oxygen diffusion through an Al layer into polymer lay-

er.[14,33] This results in the better operation stability of LiF/Ca/Al cathode based PLED in comparison with those of the Ca/Al and LiF/Al cathodes based devices.

CONCLUSIONS

The influences of device fabrication conditions and device configuration on the performance of the poly-alkylfluorene-based PLEDs were investigated. The PLED performance, such as current density, brightness, power efficiency, and operation stability, directly related to the injection and balance of electrons and holes, was strongly dependent on the treatment of ITO surface, the thickness of LEP film, and the cathode configuration. Excellent electroluminescence properties of PLEDs could be achieved through the optimization of the surface treatment of anode, the film thickness of LEP, and the cathode configuration.

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