High-performance polymer light-emitting diodes utilizing modified AI cathode

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We report an increase of electroluminescence (EL) efficiency by two orders of magnitude for poly(2-methoxy-5-(2′-ethyloxyloxy)-1,4-phenylene vinylene) (MEH-PPV) based polymer light-emitting diodes (PLED) while employing Al as the cathode with an ultrathin layer of poly(ethylene oxide) (PEO). EL efficiencies of MEH-PPV PLEDs biased at 10 mA were found to be 0.017 cd/A at 31 cd/m², 1.50 cd/A at 2515 cd/m², and 4.96 cd/A at 8416 cd/m² for applying Al, PEO/Al, and PEO/LiF/Al as the device cathodes, respectively. The significant improvement in the device performance is attributed to the promotion of minority carrier injection (electrons), where the threshold of the injection can be characterized through the deviation of Fowler–Nordhiem tunneling prediction. © 2005 American Institute of Physics. [DOI: 10.1063/1.1984101]

The electroluminescence (EL) efficiencies of organic or polymer light-emitting diodes (OLED/PLED) can be promoted with better charge injection as well as the balance of the opposite charge carriers. 1–3 The barrier heights for carrier injection were usually determined by the difference between the work functions of the applied electrodes with the corresponding energy levels of EL layers. 4 Therefore, low work function metal materials, such as Ca, Ba, Mg, etc., which have lower injection barriers for electrons, are the commonly used cathode materials. However, low work function metals are highly reactive in the atmosphere. 5 For application to flat display devices, OLEDs/PLEDs have to be strictly encapsulated inside a glass lid with desiccants to prevent degradation generated by the existing oxygen and moisture. 6

It has been reported that the presence of an ultrathin alkali metal fluoride, such as LiF, between Al cathode and the emissive layer can make significant improvement of the device performance. 7–9 Recent studies also revealed that an environmentally stable, high work function metal cathode, such as Al, can be used in EL devices to improve efficiencies through interfacial modifications. 10–14 The device performance was enhanced by placing a nanolayer of polystyrene (PS) at the contact interface between EL layer and the cathode, 15 or blending the poly(ethylene glycol) (PEG) into the EL polymer layer. 16 In spite that the bulk resistance and the injection barrier height of PEG and PS are considered to be much higher than that of the EL layer, the higher luminescence intensity and efficiency of devices suggest the injection of minority carriers (electrons) is enhanced in their device configurations. We presume the formation of specific interactions or reactions in the organic buffering materials (PEG or PS) during cathode deposition, lowering the injection barrier height or creating a tunneling path for minority carriers. Consequently, we introduce an ultrathin layer of poly(ethylene oxide) (PEO) as a buffering interface between the EL layer and the metal electrode. An increase in the luminescence intensity and efficiency with two orders of magnitude is reported for the devices with Al cathode. The efficiencies are doubly increased for the devices with Ca/Al and LiF/Al as the cathodes. The injection of electrons is significantly enhanced by the nano-scale, polymer buffering layer and such phenomenon could be characterized by the deviation of Fowler–Nordhiem tunneling prediction.

This study involves the use of a device configuration having a poly(2-methoxy-5-(2′-ethyloxyloxy)-1,4-phenylene vinylene) (MEH-PPV) polymer film sandwiched between the transparent anode [indium tin oxide (ITO) pre-deposited on glass substrate] and the metal cathode. A thin layer of poly(3,4-ethylenedioxythiophene): polystyrenesulfonate (PEDOT:PSS Bayer Corp. 4083) was spin cast on ITO/glass substrate as the hole transport layer. The ultrathin poly(ethylene oxide) (PEO) (Aldrich, Mr ~400,000) layer is prepared from 0.01 wt% PEO/Acetonitrile anhydrous solution and cast on the surface of MEH-PPV at a spinning speed of 6000 rpm. The thickness of PEO layer is about ~5 nm. The active pixel area of the device is 0.06 cm². The current-brightness-voltage (I-L-V) measurements were carried out by keithley 2400 source measure units and keithley 2000 digital multimeter along with a silicon photodiode, calibrated by Minolta LS-100 luminous meter. All the procedures are carried out inside a nitrogen-filled glovebox except for casting the PEDOT:PSS layer. The detailed fabrication procedures can be found elsewhere. 15

Figure 1 shows the I-L-V curves of devices using Al and PEO/Al as the device cathode. For ITO/PEDOT: PSS/MEH-PPV/Al based PLED, the injection barrier

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height of holes is small, around 0.1–0.2 eV. Holes can be injected into the device at the threshold of charge injection (1.02 V) and are the dominant charge carriers. For the injection of electrons, the injection barrier height is 1.2–1.3 eV, which is much higher than that of holes. Therefore, the devices with Al cathode have to be biased at a higher voltage in order to accomplish the injection of minority carriers as well as the recombination of opposite charge carriers. Light emission for the Al cathode device cannot be detected until 3.82 V. The poor EL efficiency, 0.017 cd/A (at 10 mA, 28.9 cd/m²), is attributable to the unbalanced injection of holes and electrons.

When an ultrathin PEO layer was introduced as the interface between Al cathode and the top surface of the MEH-PPV layer, as shown in Fig. 1, the turn-on voltage of the PEO/Al cathode device was brought forward to the lower biased voltage, 2.40 V, and the light intensity was increased by two orders. A luminescence efficiency of 1.50 cd/A is achieved as presented in Fig. 4, which is at the same level of the device applying Ca as the cathode. The forward shift of device turn-on voltage as well as the higher luminescence efficiency infers the enhanced injection of electrons for the device by introducing the PEO interfacial layer. In addition, the threshold voltage of charge injection is 1.02 V and 1.20 V for the Al and PEO/Al cathode devices, respectively. The higher charge injection voltage is due to the increase of the device built-in potential, which implies a reduction of the injection barrier for electrons.11,12,14 Several blank experiments were performed to confirm the enhanced performance not coming from the solvent washing effect. Also, there is no obvious variation in the EL spectra.

The processes for the injection of charge carriers are examined by Fowler–Nordheim (FN) tunneling theory, \( I \propto F^2 \exp(-\kappa/F) \), where \( I \) is the device current, \( F \) is the electric field under bias, and \( \kappa \) is a parameter which is related to the shape of the injection barrier height.4,16 Figure 2 presents the plots of \( \ln(I/F^2) \) vs \( 1/F \) for the devices with Al and PEO/Al cathodes. For MEH-PPV based device applying Al cathode, the curve follows the FN prediction at the threshold of charge injection, which is a straight line for \( \ln(I/F^2) \) vs \( 1/F \) plot. Due to the much smaller injection barrier height of holes than that of electrons, the straight-line FN curve indicates the holes are injected into the MEH-PPV layer through the tunneling process at the beginning of charge injection and are the dominant charge carriers. As the electric field (biased voltage) is increased, the FN curve deviated negatively from the predicted line, suggesting the accumulation of space charge at the polymer/Al interface. The considerably low mobility of charge carriers in MEH-PPV restricts the tunneling of holes in this bias regime.17–19 The space charge limited condition can be analyzed by the log \( J \) vs \( \log V \) curve as presented in the inset of Fig. 2. The log \( J \) vs \( \log V \) curve deviated positively from the predicted line as the bias voltage was increased. When we examined the \( I-L-V \) curve in Fig. 1 and converted the light turn-on voltage (2.40 V) into \( 1/F \), the turn-on point of light emission was found at this bias regime. The deviation of predicted FN tunneling, therefore, can be contributed to the threshold of minority carrier injection as well as the carrier recombination. The FN prediction for the single carrier is invalid under these conditions. This assumption is fortified by inspecting the log \( J \) vs \( \log V \) plot for the device with PEO/Al cathode as shown in the inset of Fig. 2. Since the injection of electrons (minority carriers) was brought forward to the lower biased voltage, the recombination of opposite charge carriers (holes and electrons) compensates the space charge limited effect. The log \( J \) vs \( \log V \) plot for MEH-PPV device with PEO/Al cathode did not follow SCLC prediction as a straight line.

In order to reduce the injection barrier height for promoting electron injection, low work function metals, such as...
Ca, or an ultrathin alkali metal fluoride placed between the Al and emissive layer, such as LiF/Al, are commonly used as cathode materials. The Ca/Al (Ca:600 Å, Al:1200 Å, Al was used as the passivated layer) and LiF/Al(LiF:5 Å, Al:1200 Å) cathodes were applied to the devices in this work to investigate the correlation for cathodes of different work functions with the PEO layer on the device performance. Unlike the Al and PEO/Al cathode devices where holes are the dominant charge carriers, for the devices applying Ca/Al or LiF/Al cathodes, both the holes and electrons can be injected into MEH-PPV layer at the low bias voltage regime. In Fig. 3, there is no difference at the threshold voltages of charge injection for the devices using Ca/Al with PEO/Ca/Al and the LiF/Al with PEO/LiF/Al cathodes, respectively. The devices applying the ultrathin PEO layer even perform higher injected current while biased in the high voltage regime and lower device light turn-on voltage as shown in the inset of Fig. 3. Although the low work function metal cathode was already used to elevate the injection of electrons as well as to balance the injected charge carriers, the increase in the injected current and the move forward of device turn-on voltage, therefore, are considered to be the enhanced injection of electrons from the cathode part, because of the same anode part for all devices.

In Fig. 4, the EL efficiency for the device with PEO/Al cathode was 1.50 cd/A, which is two orders of magnitude higher than that of the Al cathode device, 0.017 cd/A, and was doubly increased from 1.34 cd/A (Ca/Al cathode) to 2.48 cd/A (PEO/Ca/Al cathode). The luminescence efficiency is 2.01 cd/A for the device applying LiF/Al cathode. The efficiency is achieved as high as 4.96 cd/A with the PEO/LiF/Al cathode. Besides, the luminescence efficiencies are sustained at the high level while the devices are biased under the high current, high brightness regime. The CIE coordinate numbers of the emission spectra for the above devices are calculated, (0.54, 0.45). We did not observe an obvious difference in the EL spectra or the CIE coordinates. Therefore, the increases in the EL efficiencies for the above devices are due to the improvement in the device performance, but not the color change of the emissions.

In summary, we report a nano-scale, interfacial, and solution processible modification at the cathode part for high performance PLEDs utilizing environmentally stable metal materials. By introducing an ultrathin PEO layer placed at the cathode interface, even MEH-PPV devices fabricated with a high work function metal cathode, such as Al, the EL efficiency can reach the same or higher levels in comparison to that of devices with Ca as the cathode. The function of the PEO layer also works with other EL polymer materials. We regard the formation of specific interaction and reaction at the PEO layer during the cathode deposition, which results in the enhanced injection of electrons.

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