



Enhanced Emission Using Thin Li-Halide Cathodic Interlayers for Improved Injection into Poly(p-phenylene vinylene) Derivative PLEDs

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In this study, the effects of thin Li-halide cathodic interlayers on electron injection were examined for electroluminescent layers of polymer light-emitting diodes (PLEDs). An order of magnitude increase in current density is observed as Li-halide salts are varied down the group VII column of the periodic table. When considering luminance, devices with a LiCl interlayer were $2.3\times$ greater than those with LiF, whereas devices with LiBr were $2.8\times$ greater, while concurrently lowering the turn-on voltage. This resulting enhanced current density and subsequent luminance could be due to a lowered work-function difference at the cathode created by either the Li-halides dissociation-induced doping of the polymer surface or an interfacial dipole of ionic Li-halide compound, leading to band bending.

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One of the important rate-limiting steps for high-efficiency polymer light-emitting diodes (PLEDs) is charge injection into the polymer semiconductor. It has been known that the interface, and subsequent potential barrier, between the active light-emitting conjugated polymer layer and the metal cathode plays an important role in controlling charge injection across this interface.¹ Because most light-emitting conjugated polymers are good hole transporters but poor electron transporters, electron injection becomes a critical issue for balanced current components. It has been shown by numerous groups that the insertion of a thin compound interlayer, such as alkaline earth metal fluorides (i.e., LiF and CsF), between the Al cathode and the electroluminescent polymer improves PLED device performance by enhancing electron injection.²⁻⁴ The physical mechanism behind this improved performance still remains a topic of some speculation.⁵⁻⁷ However, two competing mechanisms have been proposed: a metal-halide dissociation introducing a localized surface doping effect, thus creating a low work-function contact at the interface and an interfacial dipole created by the polar metal halides, leading to strong localized band bending.^{8,9}

Previous work has principally investigated fluoride-based chemistries, and this study extends that work by examining other halide-based chemistries (LiF, LiCl, and LiBr), which are considered salts. PLEDs using poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV) with various thin metal-halide interlayers between the electroluminescent layer and Al cathode were fabricated and tested. This study examined the effects of metal halides on the electron injection into the electroluminescent layers of PLEDs from their current density–voltage (*J-V*) and luminance–voltage (*L-V*) characteristics and electroluminescence (EL) emission spectra of the devices.

Patterning of the indium-tin-oxide (ITO) coatings was performed to define eight finger-shaped transparent anodes using conventional photolithography and HCl-based wet etching. The ITO film thickness and sheet resistance were ~ 1500 Å and 10Ω cm, respectively. After photolithographic patterning, the anodes were plasma treated using an inductively coupled plasma reactive ion etching system with oxygen at a radio frequency power of 80 W to modify the surface work function.¹⁰ Poly(styrenesulfonate)-doped poly(3,4-ethylenedioxythiophene) (PEDOT:PSS, Baytron P) layers were then added on top of the ITO anodes by spin coating, then annealed in an oven at 110°C for 10 min in ambient air. Thin films of the MEH-PPV were then spin-coated on top of the PEDOT:PSS layer

from a 0.5% MEH-PPV solution in 80% toluene and 20% tetrahydrofuran. The conjugated polymers used in this study were purchased commercially and did not undergo any chemical modification or purification other than modest filtration.

Lithium-halide compounds ($>99.99\%$) for the interlayer between the EL layer and Al cathode were commercially obtained from Aldrich, Inc. Lithium-halide interlayers were evaporated thermally at pressures below 10^{-6} Torr with thicknesses nominally 5 nm. The PLEDs were completed by shadowmask evaporation ($< \sim 10^{-6}$ Torr) of an Al cathode, about 100 nm thick. The final device structure is ITO/PEDOT:PSS/MEH-PPV/Li-halide/Al.

In order to investigate the role of thin Li-halide interlayers between the MEH-PPV and Al on the device performance of PLEDs, control devices were fabricated and tested. First, a control device without Li-halides (ITO/PEDOT:PSS/MEH-PPV/Al) was tested. Next, control devices incorporating metallic Li (ITO/PEDOT:PSS/MEH-PPV/Li/Al) were tested. All fabrication steps were performed in an inert glove box environment with ≤ 1 ppm level of oxygen and water.

Highly conductive leads were attached to each patterned ITO anode surface along an edge, and the device was encapsulated with a cover glass slide and an appropriate epoxy. *J-V* and *L-V* measurements were performed with a semiconductor characterization system (Keithley 4200), a switching matrix (Keithley 7002), and a black test box mounted with a calibrated large-area Si-photodiode (18×18 mm²) for a semiautomated test. The voltage was swept from -5 to 5 V with a zero biased photodiode monitoring. Encapsulated PLED *L-V* tests were performed at room temperature and in air. The EL emission spectra from PLEDs were evaluated using a spectrometer at room temperature under darkness by using a multimode optical fiber butt-coupled to a PLED pixel, while it was biased at about 5 V. The active area of the devices was 0.19 cm².

Figure 1 shows the forward-biased *J-V* characteristics of the devices incorporated with 5 nm thick interlayers between the MEH-PPV and Al. The control device with a plain Al cathode showed a current density of only 39 mA/cm² at 5 V. An approximately three times larger current density was observed for the same bias when inserting a thin LiF interlayer between the MEH-PPV and Al. This cathodic Li-halide interlayer was then varied down the group VII column. Devices with a LiBr interlayer show even higher current densities than both the LiF and the LiCl devices with a current density of 231 mA/cm² at 5 V. From the *J-V* curves, it is clear that as the cathode interlayer is varied down the group VII column of the periodic table, the current density increases due to the enhanced electron injection. Table I summarizes the *J-V* characteristics of the devices, illustrating the current density at 5 V.

Figure 2 shows the *L-V* characteristics of the devices. Comparing the luminance at 5 V, devices with LiF, LiCl, and LiBr interlayers

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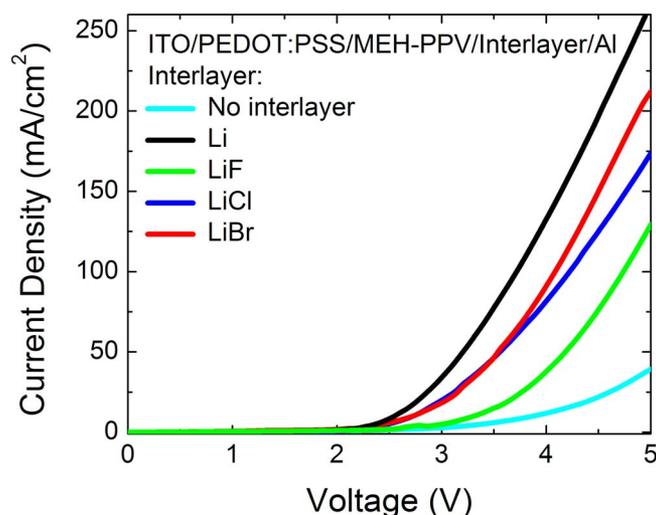


Figure 1. (Color online) J - V characteristics of PLEDs with 5 nm thick Li-halide interlayers between the MEH-PPV and Al cathode (ITO/PEDOT:PSS/MEH-PPV/Li-halide/Al). Two control devices were also tested, one without a Li-halide interlayer (ITO/PEDOT:PSS/MEH-PPV/Al) and the other with metallic Li (ITO/PEDOT:PSS/MEH-PPV/Li/Al).

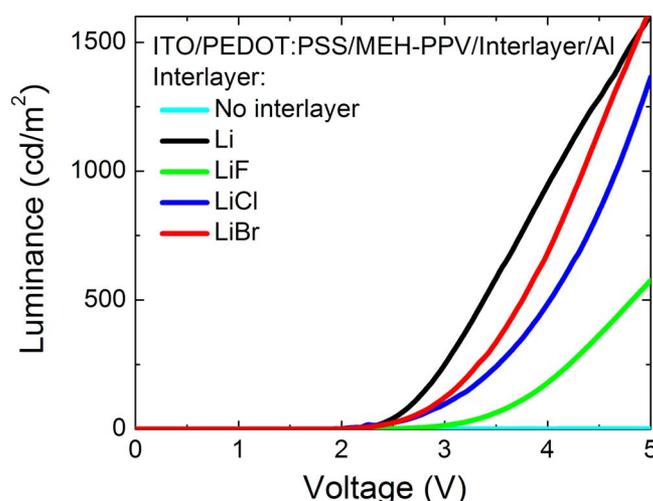


Figure 2. (Color online) L - V characteristics of PLEDs with 5 nm thick Li-halide interlayers between the MEH-PPV and Al cathode (ITO/PEDOT:PSS/MEH-PPV/Li-halide/Al). Two control devices were also tested, one without a Li-halide interlayer (ITO/PEDOT:PSS/MEH-PPV/Al) and the other with metallic Li (ITO/PEDOT:PSS/MEH-PPV/Li/Al).

show 583, 1363, and 1632 cd/m^2 , respectively. The luminance from the device with a LiBr interlayer at a 5 V bias is slightly smaller than the luminance of the device with Li-only interlayer, 1609 cd/m^2 at 5 V (Table I). The observed modest luminance of the Li/Al cathode devices can be interpreted as a greatly increased Li doping density penetrating deep into the MEH-PPV active layer and quenching luminescence efficiency. Considering the relation between the doping level and the depth of the doped region, increased Li doping into the MEH-PPV layer could lead to enhanced electron injection due to a low work-function contact at the interface, but meanwhile Li dopants can form quenching sites due to the long-range Li diffusion into the emission zone of MEH-PPV.¹¹ As the Li-halide interlayers between the MEH-PPV and Al are varied down the group VII column, a reduced turn-on voltage is also observed. Table I summarizes the L - V characteristics of the devices, illustrating the luminance at 5 V and the turn-on voltage.

Figure 3 shows normalized EL emission spectra of the devices at 5 V. The emission peak occurred at around 2.1 eV for all devices, independent of the interlayer and the current density. From the extracted full width at half-maximum (fwhm), the device with Al cathode only shows about 242 meV of fwhm of the spectra, which is slightly narrower than that of the device with Li/Al cathode (252 meV). For the devices with LiF, LiCl, and LiBr interlayers, each extracted fwhm was 245, 250, and 279 meV, respectively. As

Li-halide interlayers are varied down the group VII column, a small broadening of the EL emission spectra was observed, which might indicate an increase in electronic disorder and possible interfacial-chemical activity between MEH-PPV and the Li-halide interlayer. Similar effects have been reported in the literature.¹²

Among the various mechanisms used to explain enhanced electron injection with thin metal-halide interlayers between the electroactive polymer and metal cathode, it is possible that the metal-halide salts dissociate and the Li ions diffuse into the EL polymer layer, where they donate electrons to the π -system, thereby increasing the electron density near the electron injecting contact, or by lowering the electron injection barrier in the polymer/cathode interface by introducing gap states in the energy gap of the bulk polymer semiconductor.¹³ Thus, enhanced electron injection is observed, which also leads to higher EL external quantum efficiencies. Baldo

Table I. The current density (J) at 5 V, the luminance (L) at 5 V, and the turn-on voltage ($V_{\text{turn-on}}$), defined at which $L = 0.2 \text{ cd/m}^2$, are extracted from the J - V and L - V characteristics of PLEDs (ITO/PEDOT:PSS/MEH-PPV/Li-halide/Al) with various 5 nm nominally thick Li-halides and two control devices (ITO/PEDOT:PSS/MEH-PPV/Al and ITO/PEDOT:PSS/MEH-PPV/Li/Al). Results from the best devices are presented.

	Control device cathode ^a		Li-halide cathode ^a		
	Al	Li/Al	LiF/Al	LiCl/Al	LiBr/Al
J (mA/cm^2) at 5 V	39	291	129	173	231
L (cd/m^2) at 5 V	0.9	1609	583	1363	1632
$V_{\text{turn-on}}$ (V)	4.6	2.6	3.6	3.4	3.2

^a Device structure: ITO/PEDOT:PSS/MEH-PPV/Cathode.

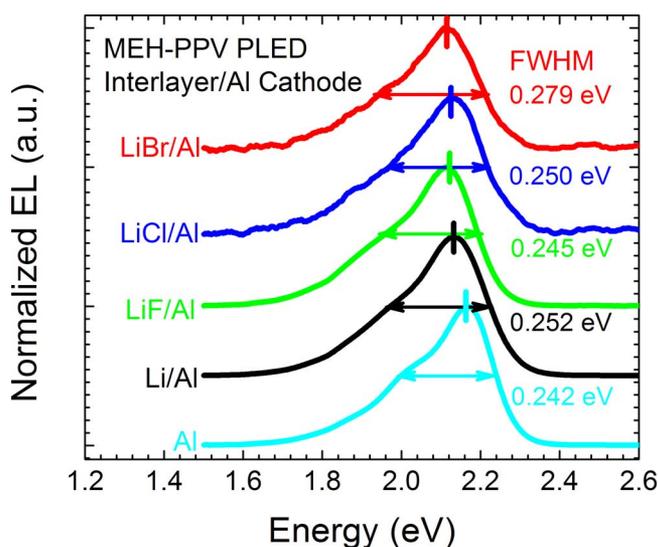


Figure 3. (Color online) The normalized EL spectra of PLEDs (ITO/PEDOT:PSS/MEH-PPV/Li-halide/Al) with 5 nm thick various Li-halide interlayer and two control devices at the drive voltage of 5 V. fwhm is extracted: Al (242 meV), Li/Al (252 meV), LiF/Al (245 meV), LiCl/Al (250 meV), and LiBr/Al (279 meV). The plots have been shifted vertically.

et al. reported that a thermally evaporated surface layer of metallic Li diffuses through, and subsequently dopes, the electron-transporting organic semiconducting thin film immediately below the cathode, forming an ohmic contact as evidenced by current-voltage and secondary ion mass spectrometry data.¹³ Furthermore, photoemission spectroscopy supports the claim that enhanced electron injection by Li metal doping occurs, suggesting that Li metal lowers the barrier to electron injection at the polymer/cathode interface by introducing gap states in the forbidden gap of the polymer semiconductor.^{13,14} Similar behavior was also observed in the case of Cs dissociating from CsF upon deposition of Al and diffusing into and doping the underlying polymer layer.¹⁵

Generally, the lattice energy of ionic solids can be defined as the energy per ion required to separate completely into ions in a crystal lattice at a temperature of absolute zero.¹⁶ There is a possible correlation between the lattice energy of the Li-halide compound and the current density. LiF has the highest lattice energy of 1030 kJ/mol and has the lowest device performance, followed in order of decreasing lattice energy (834 kJ/mol) by the LiCl devices. Finally, the LiBr devices have the lowest lattice energy (788 kJ/mol), concurrently with the highest current density.¹⁷ This result is possibly explained by the fact that Li-halide salts decompose, facilitating the diffusion of Li ions into the EL polymer. The electron mobility of the MEH-PPV is reported to be about 3 orders of magnitude lower than the hole mobility.¹⁸ In MEH-PPV PLED with various Li-halides interlayers, hole current dominates the current flow and the electrical properties of the devices are essentially the same as space-charge-limited hole-only devices. For such low electron mobility of the MEH-PPV, it is reported that the electron density can only be significant near the electron-injecting contact due to the low mobility of electron in the MEH-PPV.¹⁹ The resulting enhanced current densities, reduced turn-on voltages, and subsequent improved light output, as the lattice energy of the Li-halide compound decreases, could be due to a high surface charge density with increased Li-ion doping density at the cathode interface in the EL layers of PLEDs. It is well known that alkali metals, such as Li, Na, and Cs, are used as efficient donors, and often they are introduced through the decomposition of materials like metal halides. However, the alkali cation is mobile and can also diffuse through the polymer layer.^{20,21} Zhao et al. reported improved PLED performance by doping the EL polymer layer with LiBr, suggesting that doping with LiBr facilitates lowering charge-injection barriers at one or both electrode-polymer interfaces.²² A possible explanation is that the metal halides with higher atomic mass and radius are less diffusive and therefore create a greater concentrated effect at the hybrid interface, promoting better electron injection.

In this study, the PLED with a LiBr interlayer shows a similar performance to the PLED with a Li interlayer. However, the amount of free Li metal dissociated from the LiBr interlayer should be significantly less than the pure Li metal interlayer due to the lattice energy of LiBr compound and the creation of Li ions instead. Therefore, it is unlikely that Li-halide's dissociation-induced doping could be the only mechanism for the enhanced electron injection upon inserting Li-halides. As the lattice energy decreases, the dipole moment also increases for the Li-halide compounds as follows: LiF (6.3D), LiCl (7.1D), and LiBr (7.3D).²³ An alternative mechanism, which could account for the increase in both *J* and *L* upon insertion

of Li-halides, could be that an interfacial dipole is formed by the Li-halides at the interface.²⁴ The strong interfacial dipole of Li-halides at the interface could promote better band bending and enhanced electron injection.

In conclusion, the effects of Li-halides on electron injection were examined for EL layers of PLEDs by monitoring their *J-V* and *L-V*. An order of magnitude increase in the current density was observed as halides were varied down the group VII column of the periodic table. When considering the light-output intensity, LiCl was 2.3× greater than LiF, whereas LiBr was 2.8× greater, while lowering the turn-on voltage. This resulting enhanced current density, and subsequent luminance, could be due to a low work-function contact created by Li-halide dissociation-induced doping or an interfacial dipole of Li-halides at the interface as the lattice energy of the Li-halide compound decreased, leading to band bending.

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