

## Phosphorescent light-emitting electrochemical cell

Fang-Chung Chen and Yang Yang<sup>a)</sup>

*Department of Materials Science and Engineering, University of California, Los Angeles, Los Angeles, California 90095*

Qibing Pei

*SRI International, 333 Ravenswood Avenue, Menlo Park, California 94025*

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Due to the harvest of singlet and triplet excitons, highly-efficient phosphorescent polymer light-emitting diodes have been demonstrated. However, the driving voltage of these devices remains high because of the carrier trapping at the dopant sites. To achieve high power efficiency, a phosphorescent light-emitting electrochemical cell, which consists of bis[2-(2'-benzothienyl)-pyridinato-N,C<sup>3'</sup>]iridium(acetylacetonate) as the dopant, poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] as the host polymer, and lithium trifluoromethane sulfonate has been demonstrated in this letter. The turn-on voltage for light emission was as low as the band gap of the host material (2.8 eV). Compared with the light-emitting diode with a similar device structure, a sixfold enhancement in power efficiency has been achieved. © 2002 American Institute of Physics. [DOI: 10.1063/1.1525881]

Polymer light-emitting diodes (PLEDs) have attracted much attention because of their unique properties, such as light weight, flexibility, and low cost fabrication processes.<sup>1</sup> Due to the harvest of both singlet and triplet excitons, high quantum efficiency has been achieved in phosphorescent PLEDs.<sup>2-6</sup> However, in doped PLEDs, the driving voltage usually increases because of the carrier trapping at the dopants.<sup>4,7,8</sup> The electronic properties of the host polymer are perturbed by the present of the dopants.<sup>7</sup> The buildup of space charges further hinders the injection of carriers and, subsequently, increases the turn-on voltage and device operating voltage.<sup>4,8</sup> Therefore, power efficiencies of phosphorescent PLEDs are still low, despite the high quantum efficiencies that have been demonstrated. For portable electronic devices, high power efficiency of PLEDs is crucial, since it is directly related to the efficient usage of the battery.

Light-emitting electrochemical cells (LECs) provide an alternative way to achieve luminescent organic devices.<sup>9-16</sup> The active polymer layer of LECs consists both electronic and ionic conductors sandwiched between two electrodes.<sup>10</sup> When a sufficient potential difference is applied onto the electrodes, cations and anions dope the polymer into *p*-type near the anode and *n*-type near the cathode, respectively. Because both *p*- and *n*-type doped polymers have low electrical resistance and form ohmic contacts with the metal electrodes, low electroluminescent (EL) onset voltages, as well as low device driving voltages, have been obtained.<sup>10</sup> Ideally, an LEC should turn on at the polymer band gap energy, hence, it is ideal to use this approach to lower the device operating voltage of dye-doped PLED. In this manuscript, a phosphorescent-dye-doped LEC is demonstrated. The light turn-on voltage was as low as the optical band gap of the host material. In addition to describing the high power efficiency, this manuscript demonstrates the successful introduction of (phosphorescent) dopants into the LEC devices.

Conventional LECs are usually made by blending semiconductor polymers with an ionic conducting polymer, such as poly(ethylene oxide) (PEO). However, because of differences in polarities, phase separation, which may degrade the device performance, in the blending polymer films usually occurs.<sup>12</sup> To avoid this phase separation problem, poly[9,9-bis(3,6-dioxaheptyl)-fluorene-2,7-diyl] (BDOH-PF)<sup>13,14</sup> was synthesized as the host material in this study due to its PEO-like side groups. The amount of PEO can be reduced or eliminated completely in LECs. In addition, the wide band gap (2.8 eV) of BDOH-PF can facilitate the energy transfer from the host to the dopants and confine the triplet excitons on the dopants.<sup>17</sup>

Phosphorescent LECs were fabricated by spin-coating of a polymer blend, consisting of BDOH-PF, lithium triflate (LiCF<sub>3</sub>SO<sub>3</sub>) and a phosphorescent dopant, bis[2-(2'-benzothienyl)-pyridinato-N,C<sup>3'</sup>] iridium (acetylacetonate) (BtpIr),<sup>18</sup> from cyclohexanone onto a precleaned indium-tin-oxide (ITO) substrate. The weight ratio of the polymer thin films was BDOH-PF:LiCF<sub>3</sub>SO<sub>3</sub>:BtpIr = 1:0.1:0.05 (defined as device A). For device B, PEO was added to the polymer blend to enhance the ionic conductivity. The thicknesses of the polymer films were 1500–2000 Å. Next, a 100-nm-thick Al layer was thermally deposited on the top on the film as the cathode at ~10<sup>-6</sup> Torr vacuum. Typical LECs exhibit asymmetric current–voltage characteristics about the origin (0-voltage); it is convenient to define ITO as the positive electrode (anode) and Al as negative electrode (cathode). All devices were fabricated and tested under nitrogen environment. The photoluminescence (PL) spectra were obtained by Spex Fluorolog-3 double-grating spectrofluorometer.

Figure 1 shows the time-dependent current-brightness curves of the device A biased at 3.5 V. As expected, the device turned on slowly and emitted red light. The slowly increasing current and emission intensity was probably due to the formation of *p*-type and *n*-type doped regions near the

<sup>a)</sup>Electronic mail: yangy@ucla.edu

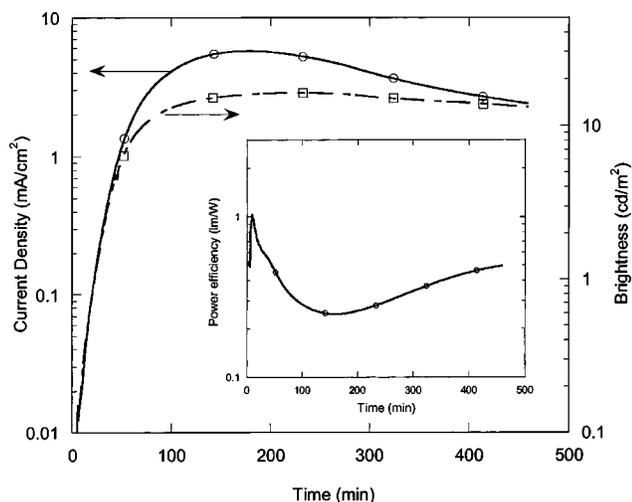


FIG. 1. The time-dependent  $I$ - $L$ - $V$  curves of device A; device structure was ITO/BDOH-PF:LiCF<sub>3</sub>SO<sub>3</sub>:BtpIr/Al. Inset: The time-dependent power efficiency of device A.

electrodes.<sup>10</sup> Device turn-on speed increased with higher bias voltage. The highest quantum efficiency was 1.2 cd/A. The inset of Fig. 1 illustrates the power efficiency as a function of operating time. The power efficiency increased first and reached the maximum, 1.0 lm/W, at the brightness of 0.2 cd/m<sup>2</sup>. At the highest brightness, 16 cd/m<sup>2</sup>, the power efficiency was about 0.30 lm/W.

It has been proved that there are two components of electrical currents in LECs: the electronic and ionic contributions.<sup>2</sup> When the device was initially biased, ions began to flow, and subsequently doped the polymer. Therefore, the initial current contributes mainly to the ionic component. Since the electrical resistance of doped polymer becomes lower, at a certain bias, the electronic current increased rapidly, and subsequently, the device efficiency decreased. Once the system approaches the thermodynamic equilibrium (steady-state) of the ion distribution in the polymer film, the ionic current contributed from the doping process began to decrease, and the power efficiency, in turn, increased.

The EL of a regular LEC originates from the recombination of electrons and holes at the undoped region between the  $p$ -

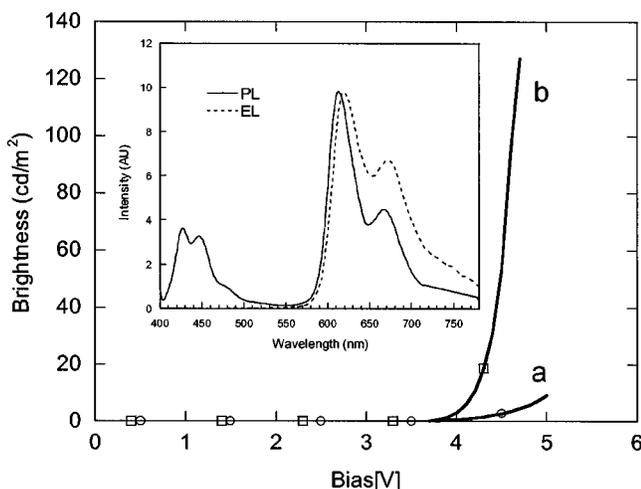


FIG. 2. The PL (solid line) and EL (dashed line) spectra of device A.

and  $n$ -doped regions.<sup>10</sup> For the LECs containing luminescent dye molecules, the process is slightly more complicated than for the pure polymer system, since two extra processes are involved: the exciton energy transfer from polymer to dye molecules, and the charge trapping at dye dopant sites. For the energy transfer process, the injected electrons and holes form excitons in the polymer that transfer to the dye dopants, and are subsequently radiatively recombined. For the carrier trapping process, the injected electrons and holes are trapped at the dye molecules and forming excitons directly at the dye molecules. To verify these two processes, the PL and EL spectra of device A were obtained (inset of Fig. 2). The EL exhibited solely red emission with a maximum wavelength of 616 nm. The spectrum was consistent with the PL of BtpIr in a dilution solution,<sup>18</sup> which suggests the emission indeed came from the triplet excitation state of the dopants. On the other hand, the PL of device A came from the host (BDOH-PF) and the dopant (BtpIr) as well, implying incomplete energy transfer. The difference between PL and EL suggests that the carrier trapping occurred while the device was operating.<sup>19</sup> This indicates that the carrier trapping is one of the main mechanisms of our dye-doped LECs in addition to energy transfer.

The major technical challenge of LEC devices comes from their slow turn-on speed. To overcome this problem, the device was prebiased first to induce the doping process, which enabled the establishing of the dynamic  $p$ - $n$  junction.<sup>14</sup> The curve (a) in Fig. 2 shows the  $L$ - $V$  curves of device A after pre-biasing at 4.0 V for a few minutes. The scan rate was 10 mV/s. The light turn-on voltage, defined as the brightness of 0.01 cd/m<sup>2</sup>, was 3.1 V. The highest quantum efficiency is 0.42 cd/A. The power efficiency was 0.38 lm/W at 0.1 cd/m<sup>2</sup> (3.6 V) and decreased slightly to 0.34 lm/W at 9.0 cd/m<sup>2</sup> (5.0 V).

In addition, it has been shown that the low mobility of ions delays the formation of  $p$ - $n$  junction.<sup>10</sup> The slow response results from the short length of the PEO-like side chain of BDOH-PF in device A, and hence low ionic mobility in the polymer.<sup>14</sup> To increase the turn-on speed, a small amount of PEO was added into the emissive polymer layer to increase the ionic conductivity. Figure 2, curve (b) shows the  $L$ - $V$  curves of device B without prebias. The light turn-on voltage, further decreased to 2.8 V, which is consistent with the optical band gap of BDOH-PF.<sup>13</sup> However, once PEO was added, the power efficiency of the device decreased 0.20 lm/W. This observation is similar with the LEC device made with BDOH-PF without blending dopants, as reported earlier.<sup>14</sup> The phase separation resulted from adding PEO into the active polymer films probably cause the lower quantum efficiency.<sup>14</sup>

For comparison, we also fabricated conventional PLEDs based on the same materials without the addition of salts and PEO. Curve (a) of Fig. 3, shows the device performance of the PLEDs based on BtpIr-doped BDOH-PF as single layer PLED with Al as the cathode and ITO as the anode. The light turn-on voltage was 12.1 V. The highest quantum efficiency was 1.0 cd/A. The highest power efficiency was 0.16 lm/W at 40 cd/m<sup>2</sup> (inset of Fig. 3). Compared with the power efficiencies of device A with this LED, approximately a six-fold enhancement has been achieved in the LEC device by adding

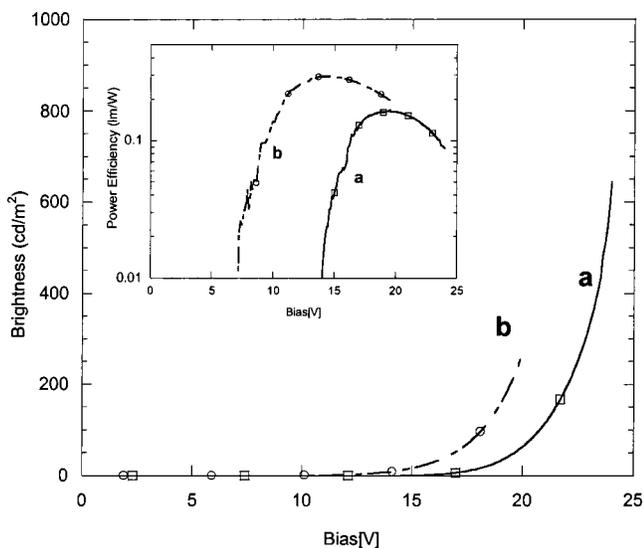


FIG. 3. The  $I-L-V$  curves of doped PLEDs based on BDOH-PF with device structures (a) ITO/BDOH-PF:BtpIr(5wt%)/Al and (b) ITO/PEDOT/BDOH-PF:BtpIr(5wt%)/Ca/Al. The inset shows the power efficiencies as a function of voltage.

salts. In order to enhance the device performance by enhance the charge injection, we adopted ITO/PEDOT (3,4-polyethylenedioxythiophene-polystyrenesulfonate) bilayer anode and Ca/Al bilayer cathode.<sup>20,21</sup> Figure 3(b) illustrates the  $L-V$  curves of 5% BtpIr-doped BDOH-PF LEDs. The quantum efficiency increased to 1.4 cd/A. The highest power efficiency was 0.27 lm/W at 21 cd/m<sup>2</sup>. The onset voltage of EL emission decreased to 7.4 V; however, it is still much higher than that of the doped LECs (device A).

The effect of inserting the PEDOT layer into LEC device is illustrated in Fig. 4. The highest power efficiency of the device with the PEDOT layer was 0.18 lm/W, which is not

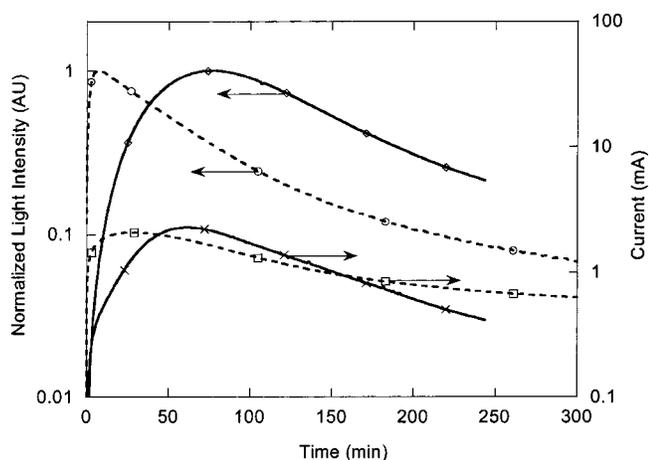


FIG. 4. Normalized time-dependent light intensity of device. (a) ITO/BDOH-PF:PEO:LiCF<sub>3</sub>SO<sub>3</sub>:BtpIr/Al (solid line). (b) ITO/PEDOT/BDOH-PF:PEO:LiCF<sub>3</sub>SO<sub>3</sub>:BtpIr/Al (dashed-line). The weight ratio of the polymer blend was BDOH-PF:PEO:LiCF<sub>3</sub>SO<sub>3</sub>:BtpIr=1:0.1:0.1:0.05. Both devices were biased at 3.5 V.

significantly different from that of device B. By comparing these two curves, it is clearly observed that the device with the PEDOT layer has fast turn-on speed. Although the characteristics of LECs, in principle, are not sensitive to the work function of the electrodes,<sup>22</sup> they do require the initial injection of charges to initiate the electrochemical process near the interface. Hence, we infer that the PEDOT serves as a buffer layer, which can modify the surface of ITO and/or lower the barrier height to assist hole injection into polymer films.

In summary, the power efficiency of a phosphorescent emission PLED has been enhanced about six times by creating a LEC format. The turn-on voltage of the device is as low as the optical band gap of the host polymer material; this is by far the lowest turn-on voltage that has been demonstrated in polymeric light-emitting devices using phosphorescent dopants as emitters.

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