

Improving the efficiency of polymer light-emitting electrochemical cells by controlled doping relaxation

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(Received 13 December 2005; accepted 2 March 2006; published online 19 April 2006)

We show that a frozen *p-n* junction in a polymer light-emitting electrochemical cell can relax into a *p-i-n* junction when heated briefly to above the glass transition temperature of the polymer electrolyte used. This results in a less doped “quasi-intrinsic” emission zone with reduced photoluminescence quenching due to electrochemical doping. A 408%–2678% increase in electroluminescence efficiency has been demonstrated by controlled doping relaxation. The formation of a *p-i-n* junction has been confirmed by spatially resolved imaging of the doping profile in a planar device structure. © 2006 American Institute of Physics. [DOI: 10.1063/1.2195967]

Light-emitting electrochemical cells (LECs) are solid-state polymer devices operating through the formation of a light-emitting *p-n* junction by *in situ* electrochemical doping.^{1,2} Doping leads to superior contact characteristics and reduced bulk resistance, which are responsible for the amazingly low operating voltage of nearly all LECs. Even extremely large planar LECs with an interelectrode spacing of 1.5 mm can exhibit electroluminescence (EL) at below 5 V,³ and planar LECs with an interelectrode spacing of 11 mm have been demonstrated.^{4,5} On the other hand, doping and associated ionic processes are also the source of major LEC drawbacks such as slow response and poor stability, but these can be easily overcome by employing a frozen-junction operating scheme or fine tuning the phase morphology of the polymer blend.^{6–8} A frozen-junction LEC is achieved by cooling a fully turned on device to below the glass transition temperature (T_g) of the polymer electrolyte used, thus freezing out all the ionic activities and achieving a static doping profile.⁹ Surprisingly, the much improved contact characteristics in LECs have not led to higher device efficiencies than conventional polymer light-emitting diodes (PLEDs), which are based on pristine luminescent polymers.¹⁰ A likely cause is photoluminescence (PL) quenching of the luminescent polymer when it is electrochemically doped.¹¹

PL quenching by electrochemical doping in a LEC was first observed by scanning PL measurement in micrometer-scale planar LECs.^{12,13} Recently demonstrated extremely large planar LECs allow the visualization of heavy PL quenching by direct imaging.^{3–5,14} For a fully turned on device exhibiting maximum EL, the PL quenching is 100% in the *p*-doped polymer and approaches 80% in the *n*-doped polymer. EL originates only from a narrow region along the *p-n* junction. Since no “intrinsic” or undoped region exists between the doped regions, the EL is severely limited despite the extremely high current density (>10 A/cm²) achieved due to excellent contact characteristics. However, imaging also reveals that when left to relax without bias at elevated temperature, a fully formed *p-n* junction can relax into a *p-i-n* junction with a progressively widening intrinsic region with significantly less PL quenching. This is caused by the highly uneven dedoping process, which occurs initially at the

p-n junction, and then propagates toward the electrodes without immediately affecting the contact characteristics. This suggests that we can overcome the adverse PL quenching by partially relaxing a *p-n* junction to create a more efficient EL emission zone while maintaining Ohmic contacts. In this letter we report dramatic improvement in the EL efficiency of frozen-junction LECs by realizing a frozen *p-i-n* junction through controlled doping relaxation.

All devices in this study are planar LECs with an interelectrode spacing of 0.6 mm. This modest interelectrode spacing allows spatially resolved imaging of the EL and doping profile as well as easily measurable current flow and luminance at cryogenic temperatures.¹⁵ The luminescent polymer used is poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV). The polymer electrolyte consists of poly(ethylene oxide) (PEO) and lithium trifluoromethanesulfonate (Li triflate). The cyclohexanone solution of MEH-PPV, PEO, and Li triflate (15:20:4 by weight) was spin cast onto a 15×15 mm² sapphire substrate to form a polymer film of approximately 600 nm in thickness. After drying at 50 °C for 3 h, 100 nm thick aluminum strips were deposited on top of the polymer layer to serve as contact electrodes. All device fabrication procedures were carried out in a glovebox/evaporator system filled with dry nitrogen. The devices were then transferred into an optical cryostat for testing under a vacuum of 18 mTorr. For imaging the device was loaded in a microscopy cryostat and imaged under a Nikon fluorescence microscope through the cryostat window. The use of a thin sapphire substrate (1 mm) in combination with a thermally conductive paste ensures good thermal contact between the device and the copper cold finger.

A constant 150 V bias was used to turn on the devices, which were initially held at 315 K. During the turn on process both device current and light intensity would increase by nearly four orders of magnitude before starting to decline due to degradation. When the light intensity was near its maximum, the device was cooled from 315 to 150 K in less than 5 min while maintaining the constant voltage bias. This led to a frozen-junction LEC with a quasistatic doping profile.

In order to study the effect of doping relaxation on EL efficiency and driving voltage, the frozen-junction LECs were slowly warmed to above room temperature while being held under a constant driving current. Figure 1 shows the

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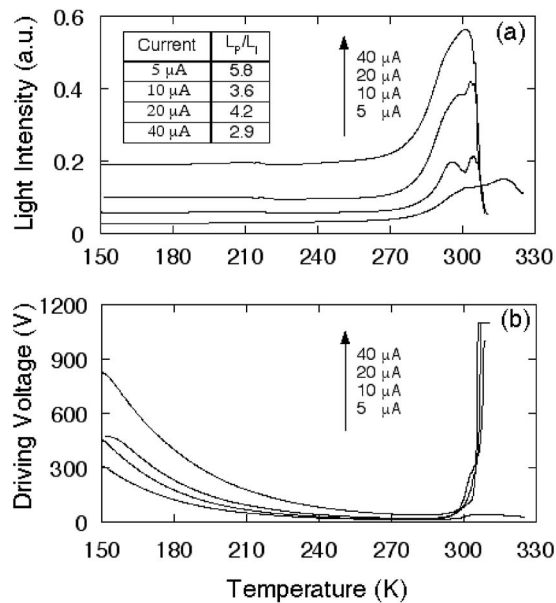


FIG. 1. EL light intensity and driving voltage as a function of increasing temperature. The devices are identical frozen-junction planar LECs driven with various constant currents. The temperature is increased from 150 to 350 K at a rate of approximately 2.7 K/min. (a) Light intensity vs temperature characteristics; the inset shows the ratios of peak EL intensity (L_p) vs initial EL intensity (L_i) for various currents applied during the warming process. (b) Driving voltage vs temperature characteristics.

evolution of light intensity and driving voltage during the warming process for four identical frozen-junction LECs with various constant currents applied. All devices exhibit nearly constant EL intensity between 150 and 270 K. The driving voltage, on the other hand, drops to approximately 3%–5% of the initial value going through the same temperature range, indicative of a dramatically reduced device resistance. This can be attributed to the change in charge carrier mobility, which has been shown to be strongly temperature dependent in MEH-PPV.¹⁶ Around 270 K the EL intensity begins to increase sharply until peak intensities are reached at around 302 K (for the 5 μA device, the EL peaked at around 317 K). The peak EL/initial EL ratios have been tabulated and are shown in the inset of Fig. 1(a). Since the device currents were kept constant, any increase in EL intensity corresponds to a proportional increase in the EL quantum efficiency (η_{EL}). In PLEDs, η_{EL} has been shown to be either temperature independent¹⁷ or decreasing with temperature.¹⁸ An increase in η_{EL} of this magnitude over such a narrow temperature range has never been observed in any polymer light-emitting devices and can only be caused by an increased PL efficiency due to doping relaxation. This explanation is also supported by the observed driving voltage increase over the same temperature range [Fig. 1(b)], as expected when the device becomes more resistive during dedoping. The increase in driving voltage lags behind the EL increase, possibly due to the competing mobility decrease with temperature. The EL intensity finally undergoes a sharp decline to well below the initial EL intensity. This is accompanied by a sharp increase in driving voltage until it is limited by instrument compliance (1000 or 1100 V). Devices at this stage are permanently damaged. The 5 μA device, however, is far more stable than devices with higher driving current.

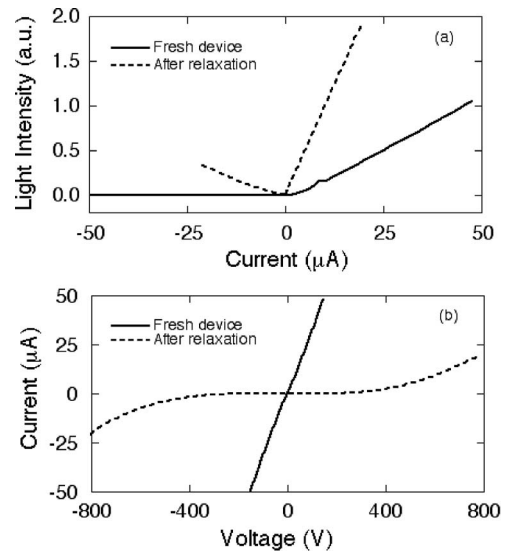


FIG. 2. (a) Light intensity vs current and (b) current vs voltage characteristics of a frozen-junction planar LEC, measured before and after a doping relaxation cycle. The frozen-junction LEC was warmed from 200 to 285 K and held at 285 K for 6 min without bias and then cooled back to 200 K. All measurements were made at 200 K.

To provide further proof of a dedoping-induced η_{EL} increase, a frozen-junction LEC was rapidly warmed from 200 to 285 K and let to relax for 5 min and then frozen again by fast cooling back to 200 K. No bias was applied during the warming-relaxation-cooling cycle. Comparison of η_{EL} and driving voltage at the same temperature (200 K) before and after relaxation can rule out the effects due to temperature-dependent PL efficiency and charge carrier mobility. Figure 2 shows the light intensity versus current (L - I) and current versus voltage (I - V) characteristics of the same frozen-junction LEC before and after relaxation. The EL intensity is significantly higher after the simple doping relaxation procedure, with a percentage increase ranging from 408% at 19.9 μA to 2678% at 2.4 μA . Note that even at 2.4 μA , the current density is quite high ($\sim 50 \text{ mA}/\text{cm}^2$) due to the extremely small cross-sectional area of the planar device configuration. In addition, the relaxed device exhibits EL under both forward and reverse biases. Unlike a “bipolar” dynamic-junction LEC operated at room temperature, the reverse bias EL observed in a frozen-junction LEC originates from the same emission zone as forward bias EL. The puzzling reverse bias EL in a frozen-junction LEC has also been observed when the device is subjected to a reverse bias stress for an extended period at 200 K.⁴ Since both reverse bias stress and high temperature promote dedoping, it is reasonable to believe that doping relaxation is the cause of the reverse bias EL observed in both frozen-junction LECs. This also suggests that a LEC is only quasifrozen at 200 K. The device resistance increases significantly as a result of doping relaxation, as shown in Fig. 2(b). The I - V curve of the fresh frozen junction is linear and symmetric between positive and negative biases, indicative of predominately Ohmic conduction. The lack of rectification despite the existence of a unipolar p - n junction is not surprising in these large planar structures due to the large bulk resistance. After relaxation, the I - V curve remains symmetric but shows a larger curvature, suggesting the onset of space-charge limited conduction.

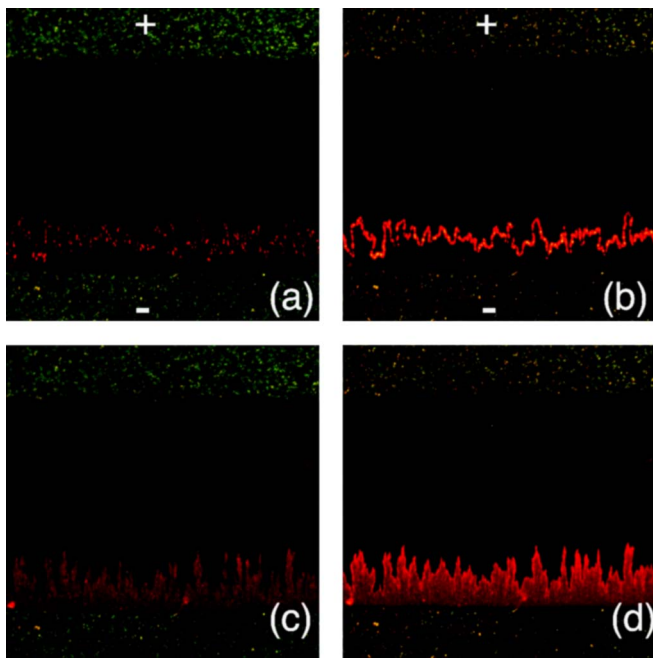


FIG. 3. (Color online) EL and doping profiles of a 0.6 mm frozen-junction LEC imaged before and after doping relaxation. The device was identical to the one shown in Fig. 2 and subject to the same doping relaxation procedure. (a) EL before relaxation, (b) EL after relaxation, (c) doping profile before relaxation, and (d) doping profile after relaxation. A driving current of $30 \mu\text{A}$ was applied for EL imaging. UV illumination filtered from a 100 W mercury lamp was applied when imaging the doping profiles without bias. All imaging was carried out with the device at 200 K and with a shutter speed of 4 s. Some room light was filled in to reveal the electrodes. The overall contrast of the composite image has been enhanced by adjusting the input level in PHOTOSHOP.

A dedoping-induced p - i - n junction is visualized by direct imaging of EL and doping profile, which is made possible by the planar configuration of the device. Figures 3(a) and 3(b) display the EL before and after doping relaxation, imaged under identical conditions at 200 K. In both cases a constant current of $30 \mu\text{A}$ was supplied to the device. The EL of the fresh frozen junction appears very weak and scattered; this is partially caused by the low throughput of microscope imaging and a relatively fast shutter speed. Similar devices imaged without a microscope display brighter and continuous EL at lower resolution.⁴ The EL after relaxation is much stronger, consistent with the large EL increase measured with a photodiode (Fig. 2). Figures 3(c) and 3(d) compare the doping profiles measured before and after relaxation, illustrating the stark difference between a p - n and a p - i - n junction. The 285 K warming cycle has led to dedoping predominated at the p - n junction, creating an intrinsic region with much less PL quenching between heavily p - and n -doped regions. The high PL of the intrinsic region is responsible for the greatly improved EL. Closer examination

of the doping profile reveals that dedoping mainly occurs on the p -doped side of the junction. The dark p -doping boundary becomes visibly smoother with the disappearance of many sharp features. This differs from the previous observation in extra large 11 mm planar LECs where dedoping appears to only occur on the n -doped side of the junction.⁵

In summary, we have demonstrated a simple approach that can significantly improve the quantum efficiency of frozen-junction LECs. By relaxing the frozen p - n junction into a p - i - n junction at elevated temperatures, the PL quenching in the emission zone due to electrochemical doping is effectively alleviated. This results in a 408%–2678% increase in electroluminescence efficiency in the same device. This doping relaxation technique can also be applied to sandwich LECs. Our preliminary results have shown a 100% increase in quantum efficiency with only a 10% increase in driving voltage. Improvement upon the already high quantum efficiency of sandwich LECs may lead to highly efficient polymer light-emitting structures suitable for achieving an electrically pumped polymer laser.

The authors thank the American Dye Source, Inc. for providing the luminescent materials used in this work. The research is supported by the Natural Sciences and Engineering Research Council of Canada (NSERC).

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