

High-resolution imaging of electrochemical doping and dedoping processes in luminescent conjugated polymers

Yufeng Hu, Corey Tracy, and Jun Gao^{a)}

Department of Physics, Queen's University, Kingston, Ontario, K7L 3N6, Canada

(Received 19 November 2005; accepted 3 February 2006; published online 21 March 2006)

We report fluorescence imaging of extremely large planar polymer light-emitting electrochemical cells (LECs) with high spatial and temporal resolution. The type of cation used has been shown to strongly affect *n*-doping propagation. When left to relax, *p* doping undergoes significantly faster relaxation than *n* doping. Imaging also confirms that a *p-n* junction, rather than a *p-i-n* junction, is formed in fully turned on LECs, which suffer from heavy photoluminescence quenching throughout the polymer film. However, a *p-i-n* junction with a much less quenched "intrinsic" region can be formed by relaxing a *p-n* junction without bias, suggesting a simple approach for achieving more efficient LECs. © 2006 American Institute of Physics. [DOI: 10.1063/1.2187408]

Light-emitting electrochemical cells (LECs) are solid-state polymer devices operating on the principle of *in situ* electrochemical doping. A working LEC is essentially a polymer *p-n* junction diode possessing some very attractive device characteristics for potential display applications.²⁻¹² Due to vastly reduced bulk and contact resistance by *in situ* doping, LECs can operate in an open planar configuration that enables between-the-electrodes imaging of the complex electrochemical and optical processes involved. However, the application of the planar LEC imaging technique had been limited by the small micrometer interelectrode spacing of early devices.^{13,14} With the recent demonstration of extremely large millimeter planar LECs, the technique of planar LEC imaging has proven to be a simple and powerful tool for studying luminescent polymers.¹⁵⁻¹⁸ Here, we report time-lapse fluorescence imaging of planar LECs with an interelectrode spacing of 11 mm, the largest demonstrated to date. The unparalleled spatial and temporal resolution afforded by these massive planar cells allows the capture of many dynamic doping and dedoping phenomena in the luminescent polymer. The implication of the observations to device application has been discussed.

The active material of an LEC is a mixed ionic-electronic conductor consisting of a luminescent conjugated polymer and a solid-state polymer electrolyte. The luminescent polymer used is poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV), one of the most studied luminescent polymers and of great importance to potential device applications. The polymer electrolyte consists of an ion-solvating polymer, poly(ethylene oxide) (PEO) and either lithium trifluoromethanesulfonate (Li triflate) or europium (III) trifluoromethanesulfonate (Eu triflate). All LECs in this study were prepared by spin casting the composite polymer film on synthetic sapphire substrates, followed by thermal evaporation of planar aluminum electrodes on top of the polymer film. Detailed planar LEC fabrication procedures can be found in our previous publications.¹⁸

The operation of a LEC involves *in situ* electrochemical doping and the formation of a light-emitting *p-n* junction. A voltage bias of 800 V and moderate heating ($\sim 70^\circ\text{C}$) are

key to fully turn on these enormous 11 mm planar electrochemical cells due to their large initial resistance ($\sim G\Omega$). The cells were tested in an optical cryostat under 10^{-5} Torr vacuum. A Nikon D100 digital camera with a Tamron 1:1 macrolens was used to image the devices through the cryostat window. For fluorescence imaging, a 4 W ultraviolet lamp (365 nm) was placed approximately 10 cm away from the device for illumination.

Figure 1(a) displays the photograph of an 11 mm planar LEC containing Eu salt before any voltage bias was applied. The polymer film exhibits the characteristic orange photoluminescence (PL) of MEH-PPV under ultraviolet (UV) illumination. An 800 V bias was then applied to the cell and photographs were taken at every 30 s. Heavy PL quenching can be seen to propagate inward from both electrode/

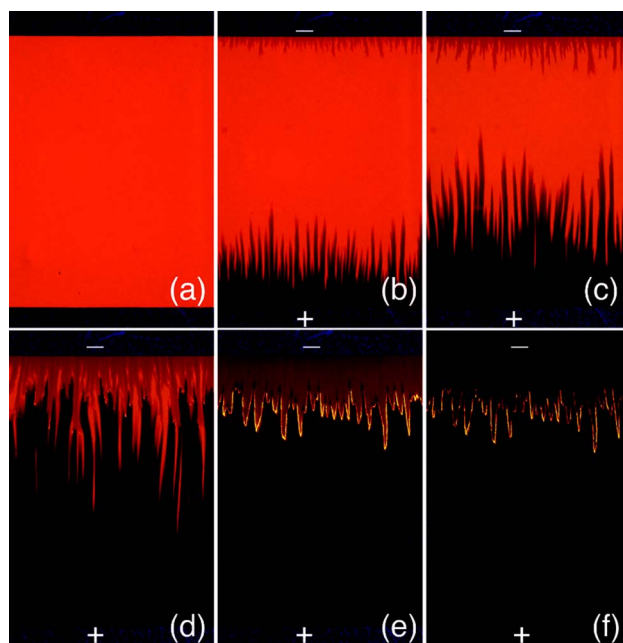


FIG. 1. (Color online) Photographs of a MEH-PPV: PEO: $\text{Eu}(\text{CF}_3\text{SO}_3)_3$ (5:5:1.26 by weight) planar LEC with a cathode-to-anode spacing of 11 mm. The cell was kept at 340 K under 365 nm UV illumination. (a) Image taken before any voltage bias was applied. Time since an 800 V bias was applied: (b) 1.5 min, (c) 2.5 min, (d) 4.0 min, (e) 7.5 min, and (f) 6.5 min with UV illumination turned off.

^{a)}Electronic mail: jungao@physics.queensu.ca

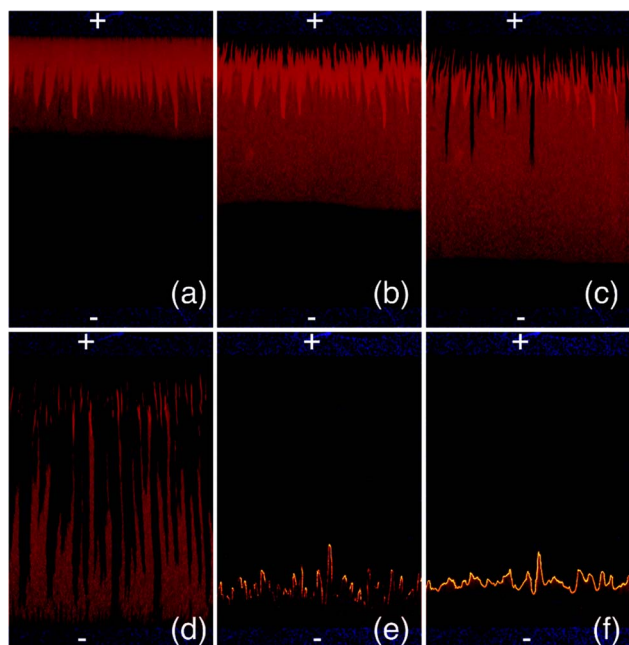


FIG. 2. (Color online) Photographs of the same cell as in Fig. 1 after reversing the polarity of the 800 V bias. The cell was kept at 340 K under 365 nm UV illumination. Time since the voltage bias is reversed (a) 0.5 min, (b) 1.5 min, (c) 3.0 min, (d) 6.0 min, (e) 10.0 min, and (f) 13.5 min.

polymer interfaces [Figs. 1(b) and 1(c)]. The PL quenching is a manifestation of *in situ* electrochemical doping, which creates additional energy states within the band gap of the polymer.¹⁹ Most notable in Fig. 1 is the highly visible PL quenching by *n* doping, which is nearly indistinguishable in smaller planar MEH-PPV cells. *p* doping propagates at a faster speed and quenches the PL more heavily than *n* doping, a phenomenon consistently observed in our MEH-PPV-based planar cells.¹⁶ The continuous propagation of *p*- and *n*-doping eventually leads to the formation of a light-emitting *p-n* junction near the cathode, where the *p*- and *n*-doped regions meet [Figs. 1(d) and 1(e)]. The existence of electroluminescence (EL) is verified by switching off the UV illumination [Fig. 1(f)].

With a light-emitting *p-n* junction fully formed [Fig. 1(e)], the polarity of the voltage bias was reversed. This procedure allows us to study the fast dedoping process under bias. The high temporal resolution of the 11 mm cell enabled the capture of both the propagation of fresh *p* doping from the anode (marked “+”) as well as the rapid relaxation of the dark *p*-doped region established under forward bias, as shown in Figs. 2(a)–2(c). Strikingly, the dedoping does not occur simultaneously across the entire *p*-doped region, but rather in a propagating fashion showing a sharp dedoping front rapidly retreating toward the cathode (marked “–”). The orange PL from MEH-PPV partially recovers behind the dedoping front, until it is quenched again by the propagating fresh *p* doping. Only when the dedoping front reaches the cathode can the fresh *n* doping be observed to propagate toward the anode [Fig. 2(d)]. Approximately 10 min after the bias is reversed, a fresh light-emitting *p-n* junction is formed with an uneven EL intensity distribution mirroring that of the forward bias junction [Fig. 2(e)]. However, the EL becomes more uniform along the junction as the level of doping increases [Fig. 2(f)].

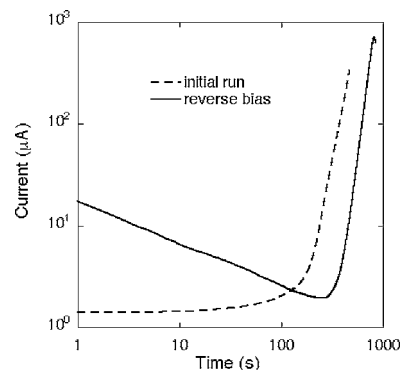


FIG. 3. Cell current vs time for the cell shown in Figs. 1 and 2.

The time-lapse fluorescence images also offer visual interpretation of the cell current flow during the doping and dedoping processes, as shown in Fig. 3. Under initial bias, the small microampere current during the first 200 s must be of an ionic nature, as the *p*- and *n*-doping fronts have not yet made any contact and the vast undoped polymer film has negligible electronic conductance. The ionic conductivity of the LEC film at 340 K is estimated to be approximately 3.1×10^{-5} S/cm from the initial forward bias current. The current turn on at around 200 s coincides with the onset of EL when the highly diffuse *p*- and *n*-doped fronts first make contact to form isolated emitting junctions [see Fig. 1(d)]. Thereafter, the total doping area (or volume) has little change as the entire polymer film becomes either *p* or *n* doped. However, during the same period, the cell current has increased by more than two orders of magnitude, and reached 0.34 mA before the bias is removed. Since the voltage bias is fixed at 800 V, this large current increase indicates a dramatic reduction in cell resistance, which is in turn caused by the increase in doping level. The increase in doping level is easily verified by noticing the darkening of the *n*-doped region as seen in Fig. 1(e). There is a simultaneous increase in *p*-doping level as required by charge neutrality, although the *p* doping is too dark to notice any change in shade. When the bias polarity is reversed, the initial current is 11 times higher than the initial forward bias current, since the polymer film is already highly doped. However, the current would first decrease as a result of rapid doping relaxation under reverse bias. At around 220 s, the current again turns on sharply when a light-emitting *p-n* junction starts to form and a peak current of 0.7 mA is reached.

Planar LEC imaging is also a sensitive probe that can be used to study the effect of salt on electrochemical doping. Figure 4 shows an 11 mm cell containing lithium triflate rather than Eu triflate as the salt. In this cell, the *n*-doping propagation is much more uniform than that in the Eu salt-based cell as shown in Fig. 1. Although doping and LEC performance are known to be affected by the phase morphology of the composite polymer film,²⁰ this is unlikely the case here as no significant difference in film morphology has been observed by scanning electron microscopy imaging of polymer films containing Li and Eu electrolytes. In fact, Eu-based LEC films even appear smoother than Li-based LEC films in some cases when inspected visually. Since electrochemical *n* doping is achieved by the insertion of cations between the reduced conjugated polymer chains, a likely cause for the drastic difference in *n*-doping shape is the difference in ionic radius. No data are available regarding the

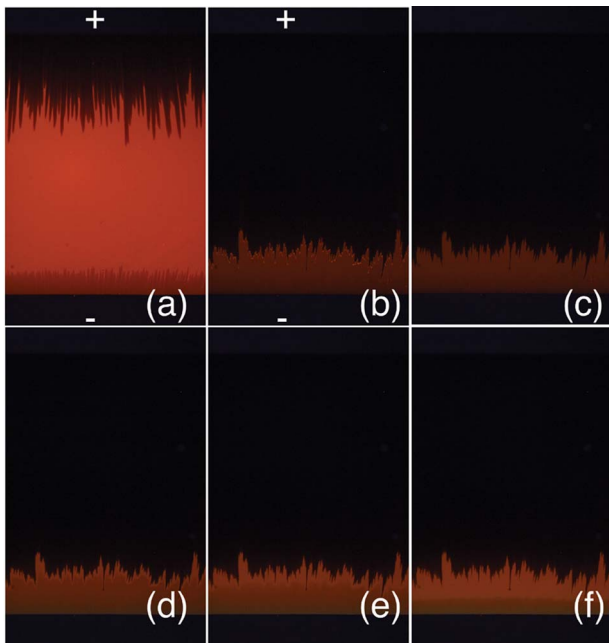


FIG. 4. (Color online) Photographs of an 11 mm planar LEC at 340 K. The LEC film has the composition of MEH-PPV: PEO: LiCF_3SO_3 (5:5:1 by weight); time since an 800 V bias was applied: (a) 40 s and (b) 116 s. Time since the 800 V bias is removed: (c) <4 s, (d) 16 s, (e) 22 s, and (f) 32 s.

ionic radii of Li^+ and Eu^{3+} for the specific PEO: Cation ratios we used. However, Eu^{3+} is considerably larger than Li^+ for the same coordination number (e.g., 95 pm versus 76 pm for $\text{CN}=6$).²¹ The smaller Li^+ makes the insertion more uniform and compact, which in turn results in more uniform n doping. The two cells demonstrated here contain the same anion (and anion concentration), CF_3SO_3^- , which explains the similar p -doping pattern observed in Figs. 1 and 4. The more diffuse p -doping propagation is also consistent with the larger anion size.

When a light-emitting p - n junction is fully formed, as shown in Fig. 4(b), the 800 V bias was removed and the cell was let to relax. Figure 4(c) shows the doping profile immediately (~ 5 s delay) after the voltage bias was turned off. A very significant observation is that the junction between p - and n -doped regions is sharp, with no less-quenched “intrinsic region” being resolved by our camera. This is contrary to the idea that the homojunction formed in an LEC is a p - i - n junction due to the depletion of ions near the junction region as has been previously postulated.²² Scanning PL or absorption measurements can determine whether the junction is a graded p - n junction.

A p - i - n junction, however, can indeed form when a fully established p - n junction relaxes. Figures 4(d)–4(f) show the continuous relaxation of the doping profile after the voltage bias was removed. No change is observed in the p -doping region, but the n -doping front can be seen to recede rapidly away from the junction, leaving a widening “intrinsic” region with significantly less PL quenching between p - and n -doped regions.

The intriguing doping and dedoping phenomena shown above clearly demonstrate the complex electrochemical behaviors of luminescent polymers, as well as the power of planar LEC imaging in elucidating the underlying mechanisms. The observation of highly visible PL quenching by n doping (Fig. 4) proves that Li ion can in fact effectively n -dope MEH-PPV, which is not the case in a traditional liquid electrochemical cell.¹⁹ In addition, imaging implies that a p - n junction, rather than a p - i - n junction, is formed in an LEC by contact of heavily PL quenched p - and n -doped regions. In such a case, the EL efficiency of an LEC is severely limited by the adverse doping-induced PL quenching despite enjoying other beneficial effects of doping. However, the above observation of dedoping suggests a fully formed p - n junction can be relaxed in a controlled manner to achieve a p - i - n junction with low PL quenching in intrinsic emission zone while maintaining ohmic contact at the electrode interfaces. Our preliminary results have shown a 400% increase in EL efficiency by the controlled relaxation of 0.6 mm planar “frozen-junction” LECs.

The authors would like to thank American Dye Source, Inc. for providing the luminescent polymers used in this study.

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