

Imaging the degradation of polymer light-emitting devices

Justin Dane and Jun Gao^{a)}

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

(Received 4 June 2004; accepted 7 September 2004)

Anode-to-cathode spatially resolved study of polymer light-emitting device degradation has been performed based on a massive planar device structure. The unique device configuration of the extremely large planar frozen-junction light-emitting electrochemical cell allows for the study of device degradation by direct imaging. Constant current stress for an extended period results in a very unusual net luminance increase as opposed to luminance decay. Imaging of the emission zone has shown changes that are consistent with polymer degradation by the loss of electron mobility. © 2004 American Institute of Physics. [DOI: 10.1063/1.1810213]

Polymer light-emitting devices have been studied extensively worldwide since the discovery of efficient electroluminescence (EL) from conjugated polymer thin film.^{1,2} Despite much improved device efficiency and available full-color emission, the eventual success of these devices in high-information content, flexible flat panel displays demands a better understanding of degradation mechanisms for engineering devices with longer lifetimes. Various degradation processes have been observed and mechanisms postulated.^{3–10} However, all the previous studies are based on extremely thin sandwich devices that cannot be imaged cross-sectionally and are susceptible to pinholes, high electric field, and adverse electrode effects. A planar metal–polymer–metal device structure with large interelectrode spacing offers an obvious advantage in elucidating the device degradation mechanisms, as any change to the electrode/polymer interface and the bulk of the emitting layer can be directly observed.

EL from conjugated polymers can be achieved through either a polymer light-emitting diode (LED) or a polymer light-emitting electrochemical cell (LEC).^{1,11} There are very few reports of polymer LED in a planar configuration.^{12–15} A planar polymer LED based on a non-ion-conducting light-emitting polymer exhibits an extremely high light emission turn-on voltage of 500 V for an electrode spacing of 30 μm . Light emission was only observed at low temperatures and no image of the device was taken.¹² The high operating voltage of a planar polymer LED is due to the high resistivity of the nondoped polymer film. On the other hand, a LEC operates on the principle of *in situ* electrochemical doping and the formation of a *p-n* or *p-i-n* junction. The bulk of the polymer film is doped upon applying a voltage bias and therefore becomes much less resistive. In fact, planar LECs with micrometer interelectrode spacing were demonstrated in the first LEC publications along with sandwich LECs. A distinctive, narrow emission zone has been observed which is consistent with the formation of a doping-induced light-emitting junction between *p*- and *n*-doped regions.^{11,16}

While the operation of a LEC at room temperature involves both ionic and electronic processes, a *frozen-junction* LEC operated at temperatures below the glass transition temperature (T_g) of the LEC polymer electrolyte involves only fast electronic processes similar to a common polymer LED.^{17,18} Hence the study of frozen-junction LECs should

provide useful insights into polymer light-emitting devices in general. Recently we demonstrated planar LECs with extremely large interelectrode spacings.^{19,20} With an interelectrode spacing up to 1 cm, these massive planar LECs offer unparalleled spatial and temporal resolution for imaging as well as ease of fabrication. In this letter, we present anode-to-cathode spatially resolved study of polymer light-emitting device degradation based on the imaging of frozen-junction planar LECs. Changes in the emission zone have been directly imaged, which can be attributed to polymer degradation by the loss of electron mobility.

We use poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV) as the light-emitting polymer, and poly(ethylene oxide) (PEO, $M_w=2$ million)/lithium trifluoromethanesulfonate complex as the polymer electrolyte. On top of a 1.5 cm by 1.5 cm glass substrate, the polymer film was formed by spin casting from a cyclohexanone solution containing the above-mentioned materials, followed by baking at 50°C for at least 5 h. The resulting polymer blend film has a thickness of $0.65 \pm 0.11 \mu\text{m}$, as determined by profilometry. In addition, all the devices were fabricated with an anode-to-cathode distance of 0.6 mm by thermally evaporating 100 nm of aluminum on top of the polymer film through a shadow mask. The device configuration is shown in the inset of Fig. 1. Current injection is through the opposite edges of the electrodes, which are 8 mm in length. All the planar LECs were fabricated in a dry nitrogen-filled glove box/evaporator system and then transferred to a cry-

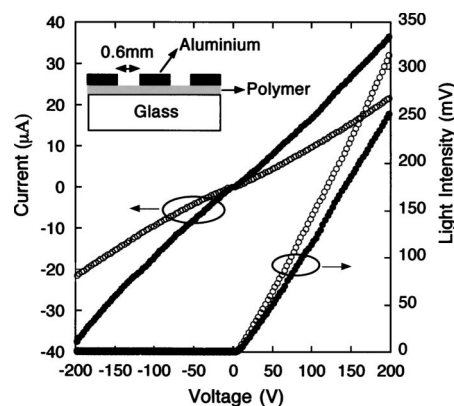


FIG. 1. Current–voltage–light intensity (I – V – L) characteristics of a 0.6 mm frozen-junction planar LEC (device 4), before (in closed circles) and after (in open circles) constant current stress at 605 mA/cm^2 that lasted 177 h.

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

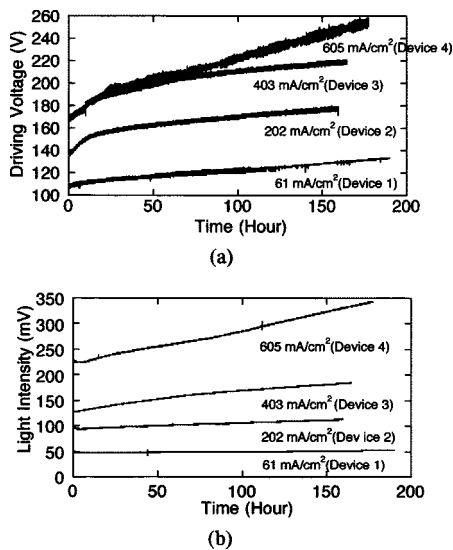


FIG. 2. The time dependence of device driving voltage (a) and light intensity (b) for four identical 0.6 mm frozen-junction planar LECs operated at 200 K at various driving current densities. Device numbers and driving current densities are labeled underneath the corresponding curves.

ostat for testing under a dynamic vacuum of 10 mTorr.

A set of four identical devices were turned on and frozen upon which stress measurements at various driving current densities were performed. Under a voltage bias of 150 V at 315 K, light emission is detected in less than 2 min when the light-emitting junction is initially formed, and continues to increase with increasing doping level and current density. The maximum light output is achieved after about 30 min, at which point the device is cooled in less than 3 min to 200 K while maintaining the 150 V “prebias.” This leads to a frozen-junction LEC whose characteristics can be studied without junction relaxation or continued doping. Current–voltage–light intensity (I – V – L) characteristics of a 0.6 mm frozen-junction planar LEC before and after stress measurement are shown in Fig. 1. The I – V curves are highly symmetric between -200 and 200 V. Light emission, however, is only detected under forward bias (the same polarity as the prebias) with a very low turn-on voltage of around 3 V. Despite the fact that our device is 20 times larger in interelectrode spacing than the planar polymer LED reported by Lemmer *et al.*,¹² the light emission turn on voltage is more than 100 times lower, indicative of a much smaller device resistance due to a strong doping effect. After stress, the device becomes more resistant and efficient, as indicated by a lower device current and higher light intensity.

Stress measurements are performed on four identical frozen-junction planar LECs at 200 K under constant driving currents of 3, 10, 20, and 30 μ A, respectively. The corresponding current densities are 61, 202, 403, and 605 mA/cm², respectively. During the stress measurement both the driving voltage and the light intensity are recorded every 15 s. Figure 2(a) shows the driving voltage as a function of time (V – t). In all devices the driving voltage increases with time under a constant current condition, indicative of an increasing device resistance. This voltage drift is very commonly observed in both organic and polymeric sandwich LEDs under constant current stress.^{3,7,10,21–23}

A very unusual observation is that all four devices showed an increase in light intensity after a small initial decay, as shown in Fig. 2(b). Furthermore, the rate of light

intensity increase, as determined from the linear region of the light intensity versus stress time (L – t) characteristics, increases exponentially with driving current density (not shown). On the other hand, nearly all the organic and polymer LEDs previously studied show monotonic decrease in light intensity with a device half lifetime inversely proportional to the driving current density. This *net* luminance increase over an extended period has only been observed previously by Parker *et al.* on a group of highly efficient sandwich polymer LEDs with long half lifetime.⁷ In fact, our devices show very similar trends to Parker’s, although we could not observe the ultimate decline of light intensity due to a relatively short testing period (~ 150 h), limited by the coolant volume of our cryogenic system.

The initial rapid increase in voltage and decrease in light intensity have been attributed to a morphological change related to polymer chain relaxation by Parker *et al.*⁷ However, there has been no explanation to the puzzling luminance increase. It can be seen from Figs. 2(a) and 2(b) that the L – t and V – t characteristics bear remarkable resemblance after the initial settling period, with corresponding inflections occurring at the same time. It suggests that the same dominating mechanism is responsible for both the increase in driving voltage and in luminance. The gradual increase in device resistance and therefore driving voltage has been commonly attributed to the formation of nonconductive “dark spots”²¹ and/or the decrease in charge carrier mobility.^{3,7} The formation of black spots, which leads to a loss of active area, will not cause an increase in device efficiency. The loss of charge carrier mobility, on the other hand, may result in a more balanced charge carrier injection and/or improved recombination, and therefore the observed luminance/efficiency increase under constant current.

There has been strong evidence from the study of single-carrier sandwich devices based on PPV derivatives indicating that it is the electron mobility that decreases during stress measurement. “Electron-only” devices show the largest voltage increase rate, while “hole-only” devices show almost no voltage increase, indicating that the hole mobility is not degraded with time.^{7,24} We expect the loss of electron mobility in a *dual-carrier* injection device will not only affect the driving voltage, but also the light emission characteristics. For example, with electron mobility reduced and hole mobility remaining the same, the emission maximum in space will shift toward the cathode. In addition, reduced carrier mobility should lead to an increase in charge carrier capture cross section, and therefore more efficient recombination and light emission at constant current. These behaviors have been predicted by organic LED and polymer LED models,^{25,26} but have never been observed experimentally. Based on direct imaging of large frozen-junction planar LECs, we have observed changes in light emission that are consistent with the loss of electron mobility. Figure 3 shows EL of the same device in dark and under UV illumination, before and after the stress measurement. The UV illumination also reveals doping-induced photoluminescence quenching and the electrodes. It can be seen very clearly that EL only occurs at the junction between p - and n -doped regions [Figs. 3(c) and 3(d)]. Initially the EL is more or less uniform within the emission zone [Fig. 3(a)]. After about 150 h of continuous operation under a constant current density of 61 mA/cm², the EL becomes nonuniform, with its maximum shifted 21 μ m toward the cathode, as determined by a custom image

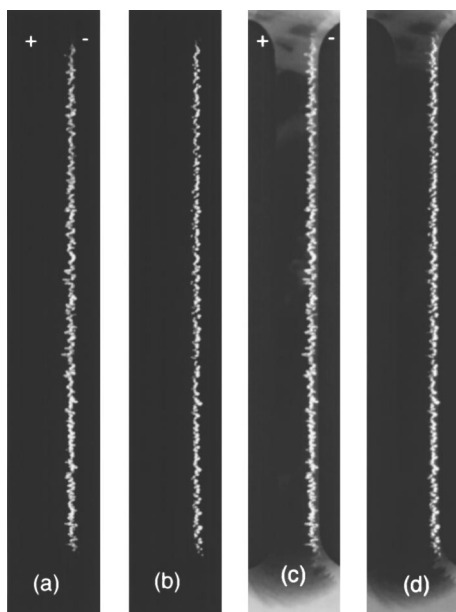


FIG. 3. Photographs of a 0.6 mm frozen-junction pLEC (device 1) before and after 190 h constant current stress at 200 K. The stress current density was 61 mA/cm². (a) EL in dark before stress; (b) EL in dark after stress; (c) EL under 365 nm UV illumination before stress; (d) EL under 365 nm UV illumination after stress.

processing software [Fig. 3(b)]. The shift of emission zone maximum toward the cathode is consistent with a reduced electron mobility relative to hole mobility after stress.

In addition, the full width at half maximum of the emission zone decreases from 84 to 77 μm . The emission zone in both sandwich and planar polymer LEDs have been shown to extend over the entire electrode spacing,^{12,27} indicative of a somewhat inefficient electron-hole capture process. The extremely wide emission zone observed in our large planar LECs lends further credit to this hypothesis. Despite the already low electron mobility in MEH-PPV,^{28,29} the decrease of electron mobility should increase the electron/hole capture radius and improve the recombination rate. This leads to the narrowing of the emission zone and an increase in light intensity as shown in Figs. 1 and 2(b).

The above-mentioned device behaviors have been observed in all our frozen-junction planar LECs (more than 10) that underwent stress measurement, regardless of driving current, film thickness, or interelectrode spacing. We emphasize here that the observations are not caused by doping propagation or any other ionic process associated with a dynamic-junction LEC. In a dynamic-junction LEC, light intensity will increase during turn on, but is always accompanied by a decreasing driving voltage due to an increasing doping level. While in our frozen-junction planar LECs, the light intensity and driving voltage increase simultaneously. Our separate study of doping propagation as a function of temperature shows that the junction is sufficiently frozen at 200 K,³⁰ which is below the glass transition temperature of the polymer electrolyte we used. In order to rule out any effect due to possible microscopic ionic motion under electrical field, stress was carried out under an ac driving scheme with zero net electrical field in order not to promote any net ionic motion. Exactly the same device behaviors were observed.

In conclusion, we have performed an anode-to-cathode spatially resolved study of polymer light-emitting device degradation. The device configuration of the extremely large frozen-junction planar light-emitting electrochemical cell allows for the study of device degradation by direct imaging. The observed net luminescence increase and changes in the emission zone are consistent with polymer degradation with reduced electron mobility.

The authors would like to thank Dr. My. T. Nguyen at the American Dye Source, Inc. for providing the luminescent polymers used in this work and Dr. Ted Sargent at the University of Toronto for generously providing profilometry measurements of our devices.

¹J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns, and A. B. Holmes, *Nature (London)* **347**, 539 (1990).

²R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, *Nature (London)* **397**, 121 (1999).

³J. C. Scott, J. H. Kaufman, P. J. Brock, R. DiPietro, J. Salem, and J. A. Goitia, *J. Appl. Phys.* **79**, 2745 (1996).

⁴B. H. Cumpston and K. F. Jensen, *Trends Polym. Sci.* **4**, 151 (1996).

⁵D. G. J. Sutherland, J. A. Carlisle, P. Elliker, G. Fox, T. W. Hagler, I. Jimenez, H. W. Lee, K. Pakbaz, L. J. Terminello, S. C. Williams, F. J. Himpel, D. K. Shuh, W. M. Tong, J. J. Jia, T. A. Callcott, and D. L. Ederer, *Appl. Phys. Lett.* **68**, 2046 (1996).

⁶B. H. Cumpston, I. D. Parker, and K. F. Jensen, *J. Appl. Phys.* **81**, 3716 (1997).

⁷I. D. Parker, Y. Cao, and C. Y. Yang, *J. Appl. Phys.* **85**, 2441 (1999).

⁸V. N. Bliznyuk, S. A. Carter, J. C. Scott, G. Klarnar, R. D. Miller, and D. C. Miller, *Macromolecules* **32**, 361 (1999).

⁹C. Giebeler, S. A. Whitelegg, D. G. Lidzey, P. A. Lane, and D. D. C. Bradley, *Appl. Phys. Lett.* **75**, 2144 (1999).

¹⁰G. C. M. Silvestre, M. T. Johnson, A. Giraldo, and J. M. Shannon, *Appl. Phys. Lett.* **78**, 1619 (2001).

¹¹Q. B. Pei, G. Yu, C. Zhang, Y. Yang, and A. J. Heeger, *Science* **269**, 1086 (1995).

¹²U. Lemmer, D. Vacar, D. Moses, A. J. Heeger, T. Ohnishi, and T. Noguichi, *Appl. Phys. Lett.* **68**, 3007 (1996).

¹³M. D. McGehee, D. Vacar, U. Lemmer, D. Moses, and A. J. Heeger, *Synth. Met.* **85**, 1233 (1997).

¹⁴E. Smela, Y. Kaminorz, O. Inganas, and L. Brehmer, *Semicond. Sci. Technol.* **13**, 433 (1998).

¹⁵Y. Kaminorz, E. Smela, T. Johansson, L. Brehmer, M. R. Andersson, and O. Inganas, *Synth. Met.* **113**, 103 (2000).

¹⁶Q. B. Pei, Y. Yang, G. Yu, C. Zhang, and A. J. Heeger, *J. Am. Chem. Soc.* **118**, 3922 (1996).

¹⁷J. Gao, G. Yu, and A. J. Heeger, *Appl. Phys. Lett.* **71**, 1293 (1997).

¹⁸J. Gao, Y. F. Li, G. Yu, and A. J. Heeger, *J. Appl. Phys.* **86**, 4594 (1999).

¹⁹J. Gao and J. Dane, *Appl. Phys. Lett.* **83**, 3027 (2003).

²⁰J. Gao and J. Dane, *Appl. Phys. Lett.* **84**, 2778 (2004).

²¹J. McElvain, H. Antoniadis, M. Hueschen, J. N. Miller, D. M. Roitman, J. R. Sheats, and R. L. Moon, *J. Appl. Phys.* **80**, 6002 (1996).

²²P. E. Burrows, V. Bulovic, S. Forrest, L. S. Sapochak, B. McCarthy, and M. E. Thompson, *Appl. Phys. Lett.* **65**, 2922 (1994).

²³H. Aziz, Z. Popovic, N. Hu, A. Hor, and G. Xu, *Science* **283**, 1900 (1999).

²⁴F. Cacialli, R. H. Friend, S. C. Moratti, and A. B. Holmes, *Synth. Met.* **67**, 157 (1994).

²⁵D. V. Khramtchenkov, H. Bassler, and V. I. Arkhipov, *J. Appl. Phys.* **79**, 9283 (1996).

²⁶G. G. Malliaras and J. C. Scott, *J. Appl. Phys.* **83**, 5399 (1998).

²⁷A. R. Brown, N. C. Greenham, J. H. Burroughes, D. D. C. Bradley, R. H. Friend, P. L. Burn, A. Kraft, and A. B. Holmes, *Chem. Phys. Lett.* **200**, 46 (1992).

²⁸L. Bozano, S. A. Carter, J. C. Scott, G. G. Malliaras, and P. J. Brock, *Appl. Phys. Lett.* **74**, 1132 (1999).

²⁹I. H. Campbell, D. L. Smith, C. J. Neef, and J. P. Ferraris, *Appl. Phys. Lett.* **74**, 2809 (1999).

³⁰J. Dane and J. Gao (unpublished).