

Polymer bulk homojunction light-emitting electrochemical cells

Corey Tracy and Jun Gao^{a)}

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

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We report polymer light-emitting electrochemical cells (LECs) based on the *in situ* formation of thousands of micrometer-sized light-emitting *p-n* junctions within the bulk of the device. These “bulk homojunction” LECs, achieved by mixing metallic particles into the LEC film, exhibit dramatically improved electroluminescence (EL) output and response time. This is confirmed by EL intensity and absolute luminance measurements, which reveals an increase in quantum efficiency of more than tenfold, relative to a conventional single junction LEC of similar dimensions. The high performance of a bulk homojunction is attributed to its large specific emitting area. Further, we demonstrate red-, green-, and blue-emitting bulk homojunction LECs by using various combinations of luminescent polymers and metallic particles. © 2006 American Institute of Physics.
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I. INTRODUCTION

Early research on conjugated polymers focused on doped materials that exhibit extremely high extrinsic electrical conductivity.¹ The discovery of polymer electroluminescence (EL) in the 1990's has drawn more attention to pristine, undoped polymers with a nondegenerate ground state due to their light-emitting properties that can be exploited for potential display and lighting applications.²⁻⁴ Since impurities and doping tend to quench the luminescence, polymer EL demands the use of high purity luminescent polymers. Without chemical or electrochemical doping of the active layer, most polymer light-emitting diodes (PLEDs) are metal/insulator/metal diodes,⁵ which are fundamentally different from traditional LEDs based on doped inorganic semiconductors. However, doping and polymer EL are not mutually exclusive, and intentional chemical doping has been exploited to improve the performance of PLEDs. For example, highly doped polyaniline,^{6,7} polyethylene dioxythiophene-polystyrene sulfonate (PEDOT-PSS),⁸ or polypyrrole⁹ are effective hole injectors and are now widely used in PLEDs as transparent electrodes. In addition, dopants such as I₂,¹⁰ FeCl₃,¹¹ or LiClO₄ (12) have been directly introduced into the luminescent polymer to lower the charge carrier injection barrier.

A truly revolutionary polymer device concept utilizing both the intrinsic and doped properties of a luminescent conjugated polymer is the polymer light-emitting electrochemical cell (LEC).¹³⁻²³ A LEC is based on a mixed ionic/electronic conductor consisting of a solid-state polymer electrolyte and a luminescent polymer. The polymer electrolyte contributes and transports free ions, rendering the LEC operation fundamentally different from a conventional PLED. When a large enough voltage is applied, electrons and holes are injected and subsequently compensated by the insertion of free cations and anions between the polymer chains. As a result, the luminescent polymer is electrochemically doped to *p* type on the anode side and *n* type on the

cathode side. With time the *p*- and *n*-doped regions expand toward the center of the device until they make contact to form a *p-n* junction. The initial formation of a *p-n* junction triggers a sharp increase in both doping level (area) and current flow. This is accompanied by the onset of EL in the vicinity of the junction, caused by the radiative recombination of the injected electrons and holes.

The LEC operating process described above has been visualized by the time-lapse fluorescence imaging of planar LECs with millimeter interelectrode spacings.²⁴⁻²⁸ Such extremely large planar devices are possible because of the dramatically reduced resistance of doped conjugated polymers. Imaging also reveals the following properties of the light-emitting junction formed: (1) A *single* light-emitting *p-n* junction, albeit sometimes highly irregular in shape, is formed between uniformly *p*- and *n*-doped regions. (2) Both *p*- and *n*-doped regions suffer from heavy photoluminescence (PL) quenching. EL originates from partially PL quenched *n* side of the junction. (3) The width of the EL emission zone is small compared to the thickness of the single layer device (or interelectrode spacing, denoted as *D*). (4) The specific EL emitting area (EL emission zone width/interelectrode spacing ratio, denoted as R_E) increases with decreasing interelectrode spacing. For example, R_E is less than 1% for planar LECs with $D=6$ or 11 mm,^{25,27} and approximately 5% for $D=1.5$ mm.²⁴ For much smaller micrometer-sized planar LECs ($D=15-40$ μm),^{13,29-32} R_E is considerably larger (6% to 20%). R_E is the largest in thin sandwich LECs, ranging from 10% to 80% (voltage dependent), as determined by the impedance measurement.^{33,34}

The LEC characteristics (2) and (3) severely limit the EL efficiency of conventional LECs. The problem of heavy PL quenching associated with a *p-n* junction has been recently overcome by intentionally relaxing a fully formed *p-n* junction into a *p-i-n* junction.²⁸ This is achieved by simply subjecting a frozen-junction LEC to a warming-cooling cycle to alter the doping profile. A dramatic improvement in EL effi-

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

ciency has been realized due to the formation of an “intrinsic” emission zone when doping relaxes preferentially in the junction region.

The increasing R_E with decreasing D (4) suggests that the solution to a small R_E is to form multiple light-emitting p - n junctions of smaller dimensions, as opposed to a single junction for any predefined D . This has previously been achieved by depositing multiple electrically floating metallic strips between the cathode and anode of a large planar LEC.³⁵ As many as 53 light-emitting junctions have been simultaneously formed in series when a voltage bias is applied, resulting in near uniform EL emission to the naked eye. A more elegant approach for forming multiple junctions in a LEC is demonstrated by blending metallic indium tin oxide (ITO) particles directly into the polymer film, leading to the formation of thousands of tiny light-emitting p - n junctions within the bulk of the device. These “bulk homojunction” LECs exhibit much larger EL emitting area as well as a giant open-circuit voltage when operated in photovoltaic mode.

Here we present quantitative measurements of EL intensity in bulk homojunction LECs, confirming the dramatic increase in EL efficiency due to a vastly improved R_E . We also demonstrate bulk homojunction devices emitting in red, blue, and green by using various luminescent polymers and conductive particles.

II. EXPERIMENT

The luminescent polymers used in this study were poly[5-(2'-ethylhexyl-oxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV), poly[(9,9-dioctyl-2,7-divinylene-fluorenylene)-alt-co-{2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene}] hereafter referred to as the “green emitter,” and poly[(9,9-dioctylfluorenyl-2,7-diyl)-alt-co-(9-hexyl-3,6-carbazole)] hereafter referred to as the “blue emitter.” All luminescent polymers were obtained from American Dye Source and were used as received. The solid-state polymer electrolyte consists of poly(ethylene oxide) (PEO) and lithium trifluoromethanesulfonate (Li triflate) in a weight ratio of 5 (PEO) to 1 (Li triflate). The molecular weight of the PEO used was $M_n=1 \times 10^5$ for the MEH-PPV devices and $M_n=2 \times 10^6$ for the blue and green emitting devices. For MEH-PPV LECs, cyclohexanone solutions of the luminescent polymer and the polymer electrolyte were mixed to create a 1.3% (w/v) LEC solution containing luminescent polymer, PEO, and Li triflate in a weight ratio of 5:5:1 (e.g., 130 mg of MEH-PPV, 130 mg of PEO, and 26 mg of Li triflate dissolved in 10 ml of cyclohexanone). All green- and blue-emitting LEC solutions have the same polymer/electrolyte ratio of 5:5:1, but are slightly more concentrated at 1.4% (w/v). Solutions for bulk homojunction LECs were made by directly adding LEC solutions to vials containing solid metal particles (Au, Ag, Zn, or ITO).

All devices were fabricated in an MBraun double glovebox/evaporator system filled with dry nitrogen. The oxygen and water vapor contents were kept below 1 ppm. Polished synthetic sapphire substrates, $15 \times 15 \times 1$ mm³, were used as substrates for their good thermal conductivity.

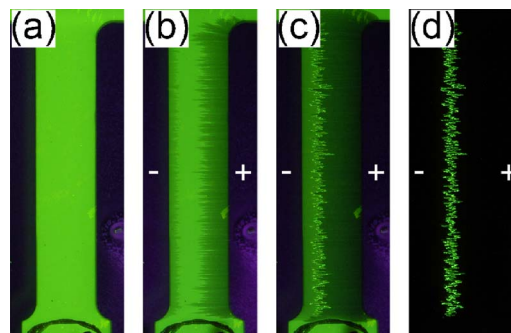


FIG. 1. (Color online) Time-lapse imaging of a green-emitting planar LEC with an interelectrode spacing of 2 mm. The device was operated by applying a 400 V bias at 330 K. Time elapsed since the voltage bias was applied: (a) 0 min, no bias was applied; (b) 1 min; (c) 10.5 min; (d) 12 min; (a)–(c) were imaged under UV illumination; (d) was imaged in the dark. Shutter speed: 10 s; aperture: $f/22$ except in (a), which is $f/25$.

Prior to use, each substrate was cleaned in acetone and isopropanol by ultrasonication and blown dry. LEC solutions were heated to 50 °C and stirred for at least 1 h prior to spin coating at 1400 rpm. Solutions containing metallic particles were sonicated in addition to stirring prior to spin coating in order to reduce particle aggregation. After spin coating, the film was annealed at 50 °C for at least 3 h prior to the deposition of electrodes. Aluminum electrodes were deposited on top of the polymer film by thermal evaporation through shadow masks. The electrodes were between 60 and 120 nm thick in all cases.

The completed LECs were loaded into a Cryo-Industries microscopy cryostat inside the glovebox. Thermal paste was used to ensure good heat transfer between the substrate and the copper cold finger of the cryostat. After loading, the cryostat was sealed and brought outside the glovebox for testing. A Leybold turbo pump with a diaphragm forepump was used to evacuate the cryostat to achieve a high vacuum of $\sim 10^{-5}$ torr or better. A Keithley 237 source measurement unit controlled via custom LABVIEW software was used to drive the LECs while simultaneously recording the device current. Imaging through the quartz cryostat window was carried out using a Nikon D100 or D200 digital camera with a Tamron 90 mm 1:1 macrolens at ISO 400 sensitivity. In devices that were not imaged during operation, a Hamamatsu amplified photodiode was used to measure relative EL intensity. The luminance of some devices was measured with a Minolta LS-110 luminance meter. The Specific emitting area R_E for the bulk homojunction was extracted using ERDAS IMAGINE 8.7 software.

III. RESULTS AND DISCUSSION

A. A 2 mm green-emitting single junction LEC

Figure 1 shows time-lapse fluorescence and electroluminescence images of a regular planar LEC with a 2 mm interelectrode spacing. Single junction planar LECs similar to this one are tested as control devices throughout this study for comparison with bulk homojunction devices. Without added metallic particles or strips, the simple planar device configuration is best suited for illustrating the fundamental LEC operating mechanism that is common to all LECs. Before

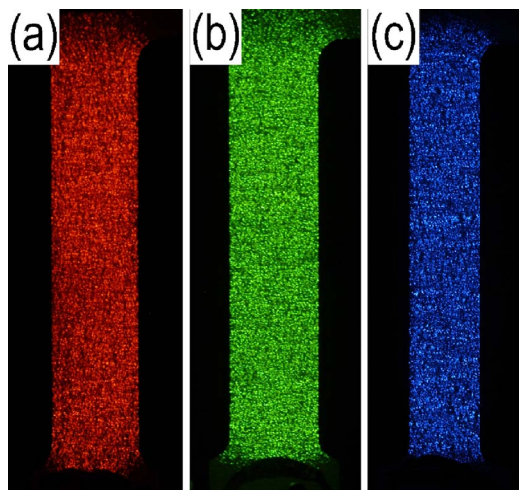


FIG. 2. (Color online) Red, green, and blue bulk homojunction LECs incorporating ITO particles into the film. (a) MEH-PPV device with a 2 mm interelectrode gap, operated at 315 K and 600 V. (b) Green-emitting device with a 2 mm gap, operated at 320 K and 500 V. (c) Blue-emitting film with a 1.5 mm gap, operated at 335 K and 700 V. Images were taken in a dark room at $f/16$ and 1 s exposure for (a) and (b), at $f/16$ and 4 s for (c).

any voltage bias is applied, the LEC film displays strong and uniform green photoluminescence when imaged under UV illumination [Fig. 1(a)]. 60 s after a 400 V bias was applied, significant PL quenching is visible in regions close to the electrode, caused by *in situ* electrochemical doping [Fig. 1(b)]. The doped regions expand with time until the entire LEC film is doped and a $p-n$ junction is formed. EL turns on when the $p-n$ junction is initially formed at about 2.5 min and becomes stronger with time. At $t=10.5$ min the EL is visible even under UV illumination [Fig. 1(c)]. The strong EL is confirmed when the device is imaged in the dark at $t=12$ min [Fig. 1(d)]. The edges of the planar electrodes are relatively rough at the microscale, caused by defects in the shadow masks. This leads to highly uneven doping initiation and propagation. The effect is amplified by the phase separation in the LEC film as well as the extremely large interelectrode spacing. As a result, the light-emitting $p-n$ junction formed is not straight. Nevertheless, the formation of a single light-emitting $p-n$ junction is confirmed, which only occupies a small portion of the entire device area.

B. Bulk homojunction LECs

A bulk homojunction LEC containing ITO particles was demonstrated with a green emitter in our previous report.³⁵ Here we apply the bulk homojunction device concept to other materials systems. Figure 2 shows red-, green-, and blue-emitting bulk homojunction planar LECs made with different luminescent polymers, but containing the same polymer electrolyte and ITO particles. All devices were turned on at slightly elevated temperatures as the doping propagation rate in a LEC increases superexponentially with temperature, but only linearly with driving voltage.³⁶ For these bulk homojunction devices, a voltage bias of few hundred volts is needed due to the simultaneous formation of many $p-n$ junctions in series. A voltage bias greater than the number of junctions formed in series times the intrinsic band

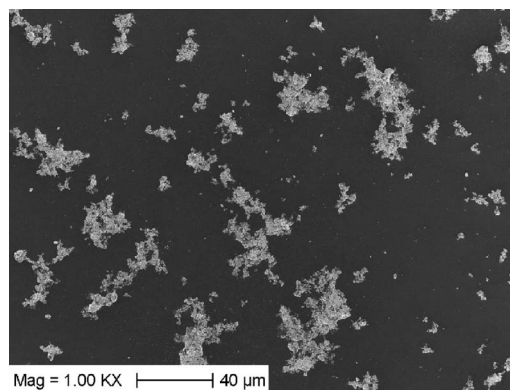


FIG. 3. Scanning electron microscopy (SEM) micrograph of an ITO particle green-emitting bulk homojunction LEC film.

gap of the luminescent polymer must be applied to turn on and sustain the EL. Despite having a smaller gap of 1.5 mm, the blue device demands the highest voltage bias and operating temperature because the band gap energy of the blue emitter is the largest among the three polymers.

While the nominal size of ITO particles used is less than $1 \mu\text{m}$, scanning electron microscopy of the LEC film reveals a large distribution in particle size, ranging from submicron to nearly $50 \mu\text{m}$ in diameter (Fig. 3). The larger particles are likely aggregates formed during device processing. The ITO particles are randomly embedded in the LEC film, which appears very smooth and approximately 200 nm in thickness as seen in tilted or cross-sectional view (not shown). When a voltage bias is applied, both p and n dopings are initiated from the same particle, but from opposite sides and propagating in opposite directions, until light-emitting $p-n$ junctions are formed between neighboring particles aligned with the electric field. This operating mechanism is illustrated in our initial study of bulk homojunction LECs.

Additionally, we have demonstrated bulk homojunction LECs using metallic particles other than that of ITO. Figure 4 shows MEH-PPV bulk homojunction LECs made with (a) gold particles with a nominal diameter of $0.5\text{--}0.8 \mu\text{m}$, (b)

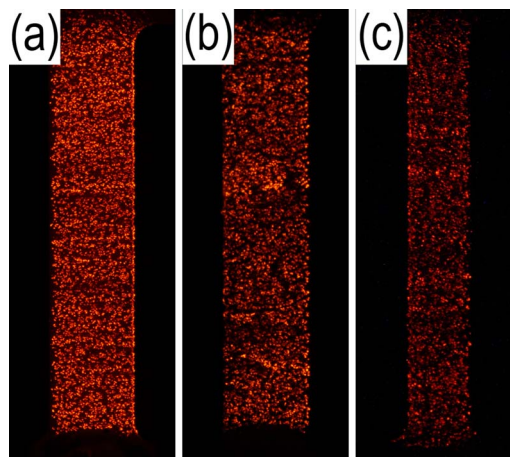


FIG. 4. (Color online) MEH-PPV bulk homojunction LECs using (a) Au particles, (b) Ag particles, and (c) Zn particles. (a) 2 mm interelectrode gap, operated at 320 K and 500 V. (b) 2 mm gap, operated at 320 K and 500 V. (c) 1.5 mm gap, operated at 320 K and 700 V. All images were taken in a dark room at $f/16$ with exposures of 3, 6, and 10 s, respectively.

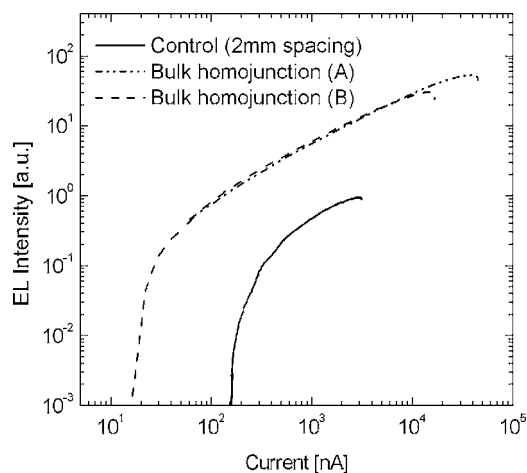


FIG. 5. EL intensity vs device current for two green-emitting ITO particle bulk homojunction LECs and a single junction control device. All devices have a 2 mm gap. The bulk homojunction devices were tested at 325 K and (a) 750 V and (b) 700 V. The control device was tested at 330 K and 700 V.

silver particles with a nominal diameter of 0.5–1 μm , and (c) zinc dust $<10 \mu\text{m}$ in diameter. All devices show similar EL profiles as ITO-particle-based bulk homojunction LECs. It is clear that bulk homojunction LECs can be realized with various combinations of luminescent polymer and metallic particles.

C. Electroluminescence measurements

The main benefit of a bulk homojunction is enhanced EL emission due to increased specific emitting area. Indeed, the preliminary devices we demonstrated appear to be much brighter than regular single junction LECs of similar dimensions.³⁵ This is confirmed in the current study by EL intensity and luminance measurements. Figure 5 displays EL intensity measured with an amplified photodiode from two identical green bulk homojunction LECs containing ITO particles and a control single junction LEC.

Since the EL intensity is plotted against the device current (L vs I), the plots also give a comparison of the external quantum efficiency. The L - I curves of the two bulk homojunction LECs nearly overlap, but are significantly higher than that of the control device across the entire current range, indicative of a much higher EL efficiency in bulk homojunction devices. More specifically, EL is detectable in the bulk homojunction LEC at a current level that is an order of magnitude lower than in the control device. An efficiency difference approaching 1000-fold exists between the devices at a very low current level (150–200 nA). At a high current level ($>1 \mu\text{A}$), the bulk homojunction LECs remained approximately ten times more efficient than the control device. Furthermore, both peak current and peak EL intensity attainable are more than ten times higher in bulk homojunction devices. A similarly large efficiency increase has also been observed in MEH-PPV based bulk homojunction LECs containing ITO particles.

Figure 6 compares the EL of a bulk homojunction LEC with multiple p - n junctions formed in series in the bulk of a planar LEC and that of a single junction LEC of the same interelectrode spacing (5.1 mm). The L - I curves display very

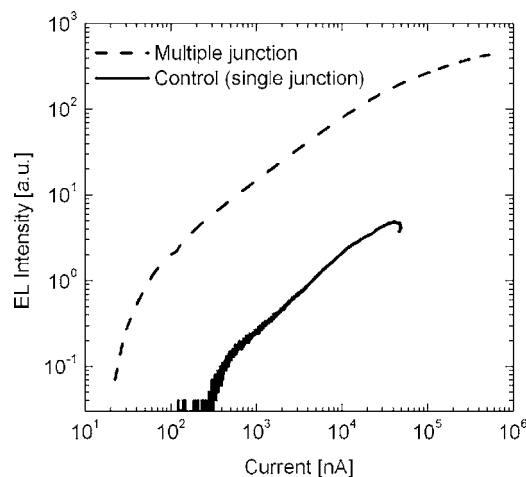


FIG. 6. EL intensity vs device current of a “53-junction” LEC device vs a control device of the same interelectrode spacing (5.1 mm). Devices were made on identical MEH-PPV LEC films. The multiple junction device was tested at 310 K and 400 V, and the control device was tested at 325 K and 500 V.

similar trends as those seen in Fig. 5, except that the efficiency increase is even more pronounced. For example, the bulk homojunction LEC remains ~ 40 times more efficient than the control device even at a very high current level of 40 μA . The larger efficiency increase in this “53-junction” LEC can be attributed to its device configuration. The device is fabricated by depositing 52 evenly spaced 60 μm wide aluminum strips between the two outer electrodes.³⁵ Each individual p - n junction formed runs parallel to the electrode edges and across the entire device width, so that there is no leakage current bypassing neighboring junctions during operation.

The high EL output of bulk homojunction LECs is further confirmed by absolute luminance measurements. The maximum luminances of red-, green-, and blue-emitting bulk homojunction LECs were measured to be 52.4, 60.2, and 27.0 cd/m^2 respectively, while the maximum luminance was only 4–5 cd/m^2 for both green-emitting and MEH-PPV single junction LECs. Note that both measurements are conservative estimates of true junction luminance since the sampling circle of the luminance meter (1 mm in diameter) cannot be entirely filled by a single light-emitting p - n junction.

The dramatically increased EL in a bulk homojunction LEC can be largely attributed to its larger specific emitting area. Analyzing the previously reported green-emitting bulk homojunction LEC image³⁵ [similar to Fig. 2(b) but with better focus] yields a R_E of 45.8%, which is quite remarkable considering that a large portion of the device area is taken up by ITO particles, which do not emit light. In addition to higher EL efficiency, bulk homojunction LECs exhibit much faster current and EL turnon. This is illustrated in Fig. 7, which compares the time evolution of the device current and EL intensity between a bulk homojunction LEC and a control device after a 700 V bias is applied. Since the EL and significant current flow can only occur after a p - n junction is formed, the turnon time for the single junction LEC is relatively slow (>1 min), as the p and n dopings must travel the entire 2 mm interelectrode spacing to make initial contact. In

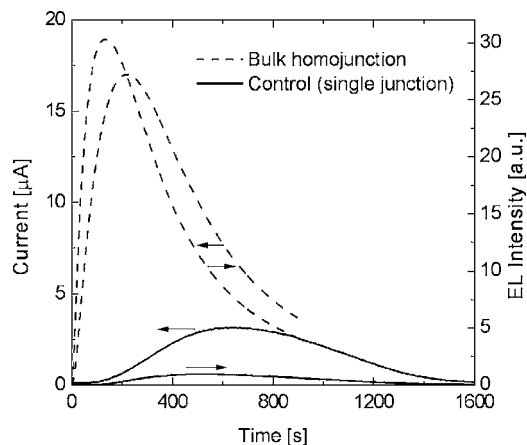


FIG. 7. Time evolution of EL intensity and current under constant voltage stress of green-emitting ITO particle bulk homojunction and control devices. The bulk homojunction device was tested at 325 K and 700 V, and the control device tested at 330 K and 700 V. The devices have identical 2 mm gaps.

contrast, the bulk homojunction LEC exhibits near instantaneous (beyond the temporal resolution of our testing instruments) EL and current turnon, due to the fact that doping only needs to travel the average distance between neighboring particles (on the order of tens of micrometers) to form a light-emitting p - n junction.

IV. SUMMARY

In summary, we have demonstrated bulk homojunction LECs with red-, green-, and blue-emitting luminescent polymers and several commonly available metallic particles. A bulk homojunction provides an approach to achieving efficient electroluminescence from luminescent conjugated polymers. The improved EL efficiency and response time of a bulk homojunction LEC over a conventional single junction LEC has been confirmed by EL intensity and luminance measurements. Additional work is in progress to further improve the device performance by optimizing particle type, size, and concentration.

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