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Polymer Light-Emitting Electrochemical Cells

Qibing Pei, Gang Yu, Chi Zhang, Yang Yang, Alan J. Heeger

A device configuration for light emission from electroactive polymers is described. In these light-emitting electrochemical cells, a *p-n* junction diode is created in situ through simultaneous *p*-type and *n*-type electrochemical doping on opposite sides of a thin film of conjugated polymer that contains added electrolyte to provide the necessary counterions for doping. Light-emitting devices based on conjugated polymers have been fabricated that operate by the proposed electrochemical oxidation-reduction mechanism. Blue, green, and orange emission have been obtained with turn-on voltages close to the band gap of the emissive material.

Electrochemistry provides a convenient means of reversibly doping conjugated polymers to form *n*-type (electron carriers) or *p*-type (hole carriers) materials. When such charge carriers are introduced by electrochemical doping, they are compensated by counterions from the electrolyte. At high doping levels, the material becomes metallic, leading to low-resistance contacts and easy charge injection (both *n*-type and *p*-type) (*1–5*).

The active medium of a polymer light-emitting electrochemical cell (LEC) is a semiconducting and luminescent polymer with sufficient ionic species as an additive to provide the counterions necessary for *p*-type and *n*-type doping. In addition, because the ions must be mobile during the in situ electrochemical doping, an ionically conductive material is required. The ionically conducting material can be the semiconducting and luminescent polymer, possibly enhanced by blending with a known ion-transport polymer, for example, poly(ethylene oxide) (PEO). This blend is sandwiched between two metal electrodes (Fig. 1A) (*6*).

The operating mechanism of the polymer solid-state LEC is based on the following assumptions (*7*). (i) The electrodes M_1 and M_2 form good electrical contact to the medium between them and remain inert in the electrochemical reactions. (ii) The electrolyte (ions plus ionically conductive material) and luminescent conjugated polymer are initially distributed uniformly throughout the film so that the electroluminescent medium has ionic conductivity. (iii) The luminescent conjugated polymer must be capable of both *p*-type and *n*-type doping. (iv) The doping profile is changed in a controlled fashion through reversible electrochemical oxidation and reduction to form a *p*-type layer on one side, an *n*-type layer on the opposite side, and a *p-n* junction at the interface between the two. Light emission is from the compensated region within the *p-n* junction.

Because of the presence of the electrolyte in the active layer of the polymer LEC, thin double layers form at the interface of the active layer with both M_1 and M_2. When a sufficiently high voltage is applied between M_1 and M_2, electrochemical doping is initiated, and charge is injected from the electrodes into the active layer. If M_1 is wired as the anode and M_2 as the cathode, the luminescent polymer adjacent to the surface of M_1 is oxidized and *p*-type carriers are introduced, whereas the polymer adjacent to the surface of M_2 is reduced and *n*-type carriers are introduced. On both the *n*-type side and the *p*-type side, the electrochemical potential locally readjusts with an associated redistribution of the compensating ions (Fig. 1B).

Under the influence of the field created by the applied voltage, the *p*-type carriers (holes) move from the anode toward the cathode, and the *n*-type carriers (electrons) move from the cathode toward the anode. Between the regions of *n*- and *p*-type doping, the holes propagating toward the cathode and the electrons propagating toward the anode meet in a region that defines an electrochemically induced *p-n* junction. Within this region, the electrons and holes combine to form neutral pairs, which radiatively decay to the ground state (Fig. 1C).

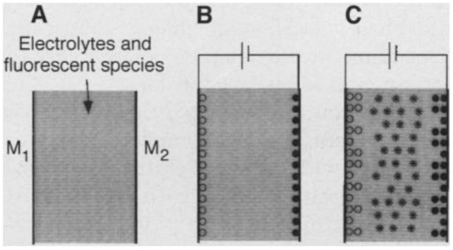

Fig. 1. Schematic diagram of the electrochemical processes in an LEC. The electrodes are labeled M_1 and M_2. (○) An oxidized species (*p*-type doped); (●) a reduced species (*n*-type doped); (*) a neutral electron-hole pair. (**A**) The cell before applying a voltage. (**B**) Doping opposite sides as *n*-type and *p*-type. (**C**) Charge migration and radiative decay.

There are many materials that are appropriate for use in the active layers of LECs, among which conjugated polymers such as poly(1,4-phenylene vinylene) (PPV) and its soluble derivatives are attractive. These semiconducting polymers exhibit the desirable properties of being luminescent in their neutral (undoped) state, readily oxidized and reduced electrochemically, and electrically conductive after electrochemical oxidation or reduction. The color of the light emitted by an LEC is determined by the energy gap of the semiconducting polymer in which the *p-n* junction is formed and can be changed in a straightforward way by substituting a different conjugated polymer in the active layer.

We fabricated LECs that emit orange light using the soluble derivative of PPV, poly[5-(2′-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV), as the fluorescent redox species. To prepare these prototype devices, a thin polymer layer (≈2500 Å) containing a 1:1 ratio (by weight) of MEH-PPV and PEO was spin-cast from solution in pyridine onto indium–tin oxide (ITO)-coated glass substrates; the PEO was added to improve the ionic mobility. The polymer layer also contained lithium trifluoromethanesulfonate, such that the molar ratio of the (CH_2CH_2O) moieties in the PEO to those in the salt was 20:1. Finally, a thin layer of aluminum (400 Å) was evaporated onto the polymer film. In separate experiments, devices were fabricated without PEO; in this case, the organic salt tetrabutylammonium doceylbenzenesulfonate was added to MEH-PPV to provide the necessary doping counterions.

The apparent threshold voltages for appreciable current injection and for detection of visible light emission (Fig. 2) are below 2.5 V for both forward-bias scans (sweeping from 0 to 4 V) and reverse-bias scans (sweeping from 0 to −4 V) with brightness increasing to greater than 100 cd/m^2 at ±4 V. In a darkened room, light emission can be ob-

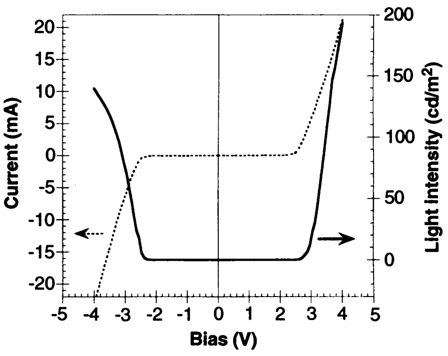

Fig. 2. Current and light output versus voltage for ITO/MEH-PPV + PEO/Al LECs with the ITO contact wired as the anode.

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served at >2.1 V. The forward- and reverse-bias current-voltage and light-voltage curves obtained from LECs are nearly symmetric about zero bias, in contrast to the diodelike behavior exhibited by "conventional" polymer light-emitting diodes (LEDs) (8, 9).

Figure 3 shows the spectrally resolved light output from one of the MEH-PPV devices (containing lithium trifluoromethanesulfonate) upon application of a voltage of either polarity. The spectrum of emitted light is the same in either case, indicating that the emission is independent of which electrode serves as the anode and which serves as the cathode: the LEC is bipolar. The photoluminescence spectrum, included for comparison, is slightly red-shifted.

Similar devices that emitted green light were fabricated with PPV as the semiconducting luminescent polymer. In this case, the PEO and salt were added to the precursor polymer, which was subsequently thermally converted to PPV (*10*) after the blend was spin cast into a thin film. The optical π-π^* band gap of PPV is approximately 2.5 eV, about 0.4 eV greater than that for MEH-PPV. Prototypes that emit blue light were made with a soluble derivative of poly(para-phenylene), poly[2-(3,6-dioxaheptyloxy-1,4-phenylene] (DOHO-PPP), as the fluorescent redox species. In all cases, turn-on occurred at a bias voltage approximately equal to the measured optical gap, as expected for a *p-n* light-emitting junction in which the doping is initiated by the setting of the electrochemical potential at the top of the π band (*p*-type doping) on one side and at the bottom of the π^* band (*n*-type doping) on the opposite side. For example, LECs made from MEH-PPV have a turn-on voltage $V_{on} \approx 2.1$ V, and LECs containing PPV turn on at $V_{on} \approx 2.5$ V; in both cases, the energy of the resulting photons is in agreement with the optical gap (as inferred from optical absorption). For the blue-emitting devices made with DOHO-PPV, the turn-on voltage was approximately 3 V, well below that needed for polymer LEDs made from the same material (15 to 20 V), where charge injection takes place by tunneling. The external quantum efficiencies obtained in these initial experiments were 0.1 to 0.2% photon per electron for LECs made with PPV and PEO, up to 1% photon per electron for LECs made with MEH-PPV (depending on whether or not PEO was included), and ≈2% photons per electron for LECs made with DOHO-PPP and PEO.

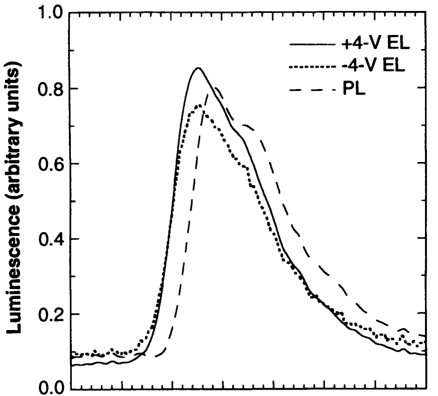

Fig. 3. Electroluminescence (EL) and photoluminescence (PL) spectra of a thin layer of a blend of MEH-PPV and PEO with lithium trifluoromethanesulfonate as the salt. The EL spectrum was generated by incorporation of the layer in an ITO/MEH-PPV + PEO/Al polymer LEC.

The dynamic response of the LEC is determined by the ionic mobility and is therefore dependent on whether or not the PEO ion-transport polymer was added to the blend. With PEO, light is observed within a second, whereas longer times (seconds to minutes, depending on the salt used) are required for devices without PEO.

The conventional static *p-n* junction so commonly used in inorganic light-emitting devices (*11*) is a diode with a large rectification ratio (ratio of forward to reverse current at a specific applied voltage), typically of order 10^3 to 10^8. In contrast, the current response of the bipolar LEC is more nearly symmetric (Fig. 2) with a rectification ratio near unity. The in situ formation of a *p-n* junction diode has been verified, however, by the fabrication of simpler devices consisting of luminescent polymer plus salt in the active layer, that is, without the PEO and consequently with low ionic mobility. Although much slower in response, in some cases taking minutes to turn on, the LEC bipolar operation could be observed under slow scan conditions. If the LEC was first biased in a given direction, however, rapid current-voltage scans yielded well-defined diode curves, thus demonstrating the in situ formation of the rectifying *p-n* junction. After creating the junction by *p*-type doping on one side and *n*-type doping on the opposite side, one has charged a "light-emitting polymer battery." Indeed, this charged electrochemical cell delivers external current in the direction opposite to the original charging current, decaying toward zero as the cell discharges over a period of a few minutes.

It is possible to make LECs in a sandwich configuration (Fig. 1) or in a surface configuration with interdigitated electrodes. Figure 4 is a photograph (taken through a microscope) of a polymer LEC in such a surface cell configuration with interdigitated gold electrodes (dark lines); the spacing between electrodes is 15 μm. The device was fabricated with PPV and PEO plus lithium trifluoromethanesulfonate as the salt. With 4 V applied across each pair of electrodes, the yellow-green emission from the dynamically formed *p-n* junction can be seen; the width of the emitting junction is about 1 to 3 μm.

Light-emitting electrochemical cells have a number of specific and important advantages over the "conventional" polymer LED (8, 9). (i) As *p-n* junctions created in situ by electrochemical doping, they turn on at an applied voltage approximately equal to the energy gap: $E_{on} \approx E_g$. For visible light emission, V_{on} is always less than 3 V. (ii) Because carrier injection occurs through ohmic contacts into the doped *n*-type and *p*-type regions, stable metals (such as Al and Au) can be used to form these contacts. In contrast, tunnel-diode polymer LEDs (8) need reactive metals with low work functions to achieve efficient electron injection. (iii) Even more important, there is no need to match the work functions of the anode and cathode to the π and π^* energies of the luminescent polymer, as must be done for the tunnel-diode device (8). Consequently, the same electrode materials can be used for either small-gap or wide-gap materials, thus promising significant manufacturing advantages for multicolor displays.

The LEC is fabricated with the semiconductor polymer in its neutral form with stable metals as the contacting electrodes, and the electrochemically induced *p-n* junction is generated in situ; thus, all components are environmentally stable in the quiescent off state. As a result, one anticipates intrinsically longer shelf life as compared with the conventional polymer

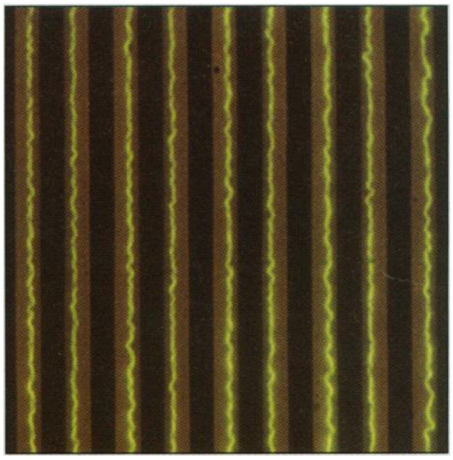

Fig. 4. Photograph of a polymer LEC in a surface cell configuration with interdigitated gold electrodes (dark lines); the spacing between electrodes is 15 μm. With 4 V applied across each pair of electrodes, the yellow-green emission from the dynamically formed *p-n* junction can be seen; the width of the junction is about 1 to 3 μm.

LED. Indeed, initial experiments have shown this to be the case. Devices have been stored for more than 1 year without the appearance of the black spots that typically limit the shelf life of polymer LEDs. After such relatively long-term storage, the polymer LECs operate without loss of efficiency. Although stress life measurements have just begun, the initial results obtained from nonoptimized devices appear promising with on lifetimes comparable to control devices made with the same luminescent polymer in the conventional polymer LED configuration.

The polymer LEC offers both opportunities and challenges. For example, because the *p-n* junction is created in situ, the thickness t of the luminescent polymer layer is less critical than in the conventional polymer LED, where the tunneling injection current I is exponentially sensitive to the electric field E: $I \propto \exp[-k/E] = \exp[-kt/V]$, where k is a constant (*8*). Moreover, the use of prepatterned interdigitated electrodes enables the polymer LEC to be fabricated simply, in a single step, with little sensitivity to film thickness. On the other hand, performance optimization will require the synthesis of multifunctional polymers that are luminescent semiconductors with high ionic mobility.

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Sprites, ELF Transients, and Positive Ground Strokes

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In two summertime mesoscale convective systems (MCSs), mesospheric optical sprite phenomena were often coincident with both large-amplitude positive cloud-to-ground lightning and transient Schumann resonance excitations of the entire Earth-ionosphere cavity. These observations, together with earlier studies of MCS electrification, suggest that sprites are triggered when the rapid removal of large quantities of positive charge from an areally extensive charge layer stresses the mesosphere to dielectric breakdown.

"Red sprites" are mesospheric, striated glows that typically recur at intervals of several minutes over mature and dissipating organized convection (*1–3*). They have recently been documented over the stratiform regions of mid-latitude MCSs (*4*). Sprites tend to occur in clusters, sometimes appearing to follow the horizontal progression of in-cloud lightning. Compared to the typical MCS lightning flash rates of 40 to 50 per minute (*5*), sprites are infrequent, although not rare, occurrences.

Electric field soundings through MCS stratiform anvils suggest a strongly layered charge structure, which includes concentrated positive charge near the 0°C isotherm (*6*); this structure differs considerably from the conventional dipole structure that is characteristic of active deep convection, in which positive charge overlies negative. In MCSs, cloud-to-ground (CG) lightning also occurs in a "horizontal bipole" pattern (*7, 8*), with negative strokes occurring in areas of active convection and positive strokes dominant in the stratiform regions. These positive CG strokes are infrequent but often exhibit extremely large peak return stroke currents (9) and may lower tens to hundreds of coulombs of charge to ground (*10, 11*). They are also often associated with horizontally extensive "spider lightning" discharges, long dendritic channels that may finger for many tens of kilometers along cloud base (*12–17*).

Positive CG strokes are also disproportionately associated with electromagnetic "Q-burst" events in the ELF Schumann resonance (SR) band (*18, 19*), the large-amplitude ringing of the entire Earth-ionosphere cavity (*20*). The SR "continuous" spectra are believed to be driven by the integrated effects of all global lightning, with Q-burst events identifiable as transient amplifications of the SR continuous signal of up to 20 dB. These Q bursts, separated in time by minutes to hours, are thought to be excited by the largest lightning events on the planet (*21, 22*).

Sprites, Q bursts, and positive CG strokes are all rather exceptional electromagnetic events. The MCS is an unusual meteorological phenomenon. We studied MCS systems on 2 days to search for possible physical connections among these various phenomena.

We obtained visual documentation of sprite events at ranges up to 1000 km with the low-light monochrome video systems located at the Yucca Ridge Field Station some 20 km northeast of Fort Collins, Colorado (*1, 23, 24*). Vertical electric (E_z) and horizontal magnetic (H_{NS} and H_{EW}) fields in the ELF SR band were measured at a culturally quiet field station in West Greenwich, Rhode Island, where long-term observations of the background SR have been under way (*23, 25, 26*). Large-amplitude transient events were frequently observed during the periods of study. Ground strokes were identified by the National Lightning Detection Network (NLDN) of magnetic direction finders, which has a detection efficiency of better than 70% and an accuracy of better than 10 km for negative CG strokes (*8, 27, 28*). The detection efficiency of positive CG strokes is as yet undocumented, although several studies have suggested that the NLDN robustly identifies positive flashes with negligible false detection (*29*).

The video system recorded at 17-ms time resolution during the period of study. The ELF data were sampled at 350 Hz with 12-bit resolution. We extracted ground flash data from the NLDN archives in 5-s windows around the reported sprite events and within a geographical region corresponding to satellite-observed cloud tops in the infrared.

On 12 July and 7 September 1994, we conducted intercomparisons between visual observations of sprites in Colorado and the SR signal in Rhode Island in real time using a phone link (Fig. 1). These communications suggested a connection

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