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Light-Emitting Electrochemical Cells with Millimeter-Sized Interelectrode Gap: Low-Voltage Operation at Room Temperature

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π-Conjugated polymers (CPs) frequently offer the opportunity of electrochemical doping to attain a high (and controllable) electronic conductivity.[1] The polymer light-emitting electrochemical cell (LEC) is a device that exploits this property in an interesting and attractive manner, since it contains a CP that is simultaneously p-type doped at the anode and n-type doped at the cathode during the initial electrochemical operation. After a turn-on time, during which the p-type and n-type doped regions grow toward each other, a highly efficient light-emitting p−n junction is formed in the active material of the LEC.[2]

Gao and co-workers[3] recently demonstrated that it is possible to operate a new type of macroscopic LEC, with a millimeter-sized interelectrode gap separating two identical electrodes in a planar configuration, and attain efficient light emission. However, their LECs, which contained a CP-solid electrolyte blend as the active material, exhibited the drawback that they required a very high turn-on voltage, $V_{\text{turn-on}} \approx 100$ V.[3] We, thereafter, demonstrated that the high $V_{\text{turn-on}}$ originated in that solid electrolyte [a solid solution of $LiCF_3SO_3$ in poly(ethylene oxide) (PEO)] is in a semicrystalline state with a very limited ionic conductivity (σ) at room temperature (RT).[4] By increasing the operational temperature to 360 K, at which the solid electrolyte melts and attains a high σ, we were able to demonstrate a low $V_{\text{turn-on}}$ of 5 V for such LECs.[4] In this Communication, we report a further development of the macroscopic LEC concept by demonstrating that it is possible to turn-on and attain light emission from pristine LECs with 1-mm-sized interelectrode gaps operating at 3 V *and* RT.

A mixture of the CP poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV, Organic Vision) and the ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate (EMI-ES, Solvent Innovation) was employed as the active material (for chemical structures, see Figure 1). EMI-ES was selected since it is reported to be in a molten state at RT and consequently exhibits a significant σ of 3.76 mS/cm at RT.[5] MEH-PPV and EMI-ES were separately dissolved in chloroform in a 10 mg/mL concentration, and then mixed together into blend solutions with different stoichiometries. Planar Au/MEH-PPV+EMI-ES/Au devices were prepared by spin-casting a blend solution onto Au electrodes with an interelectrode distance of 1 mm deposited on glass substrates. All measurements were done at RT with the sample mounted in an optical-access vacuum cryostat ($p < 10^{-5}$ mBar). (For a more detailed description of device preparation and device testing, see ref 6.)

Figure 2 presents current and light intensity as a function of voltage for a Au/MEH-PPV+EMI-ES/Au device operating at RT. The voltage was ramped in a very slow manner at $dV/dt = 2$ mV/s to compensate for the extremely large interelectrode gap of 1 mm, since the time required for an LEC to turn on (i.e., for the p−n junction to form) is dependent on the size of the interelectrode gap. It is notable that the device turns on already at a modest voltage of ~3.0 V, as evidenced by the onset of detectable light emission. This value is very close to the thermodynamic limit for MEH-PPV, which has an optical and electrochemical band gap in the range between 2.1 and 2.2 eV.[7] The current exhibited three distinct regimes: a low value below ~1.4 V, a rapid exponential increase between ~1.4 and ~3.0 V, and a slower exponential increase above ~3.0 V. At voltages below the band gap potential, the current is consumed by a non-Faradaic formation of electric double layers at the interfaces and possibly by a limited amount of unipolar doping.[2f] At larger voltages, it is initially ideally consumed by a balanced p-type and n-type doping, and thereafter, when the p−n junction formation is complete, it is used for the formation of excitons.

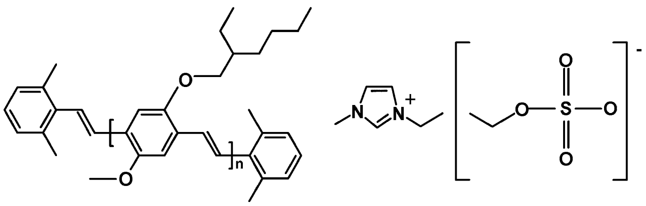

Figure 1. Chemical structures of MEH-PPV and EMI-ES.

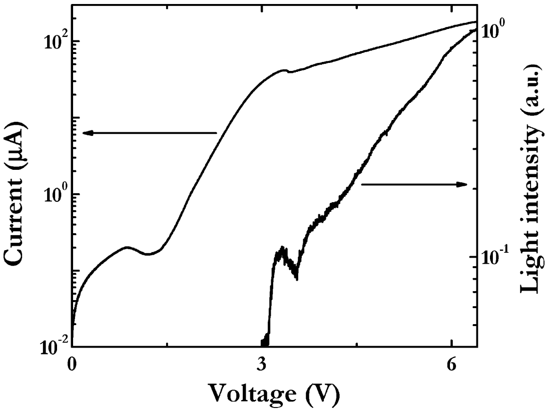

Figure 2. Current and light intensity as a function of voltage for a planar Au/MEH-PPV+EMI-ES/Au device with an interelectrode gap of 1 mm operating at RT. The scan rate was 2 mV/s.

The mass ratio between the two active material components for the device in Figure 2 (and in Figure 3) is MEH-PPV/EMI-ES = 1:0.16, which corresponds to a salt concentration of ~0.6 M. We have also investigated devices with different mass ratios, and we consistently find that devices with a lower salt content exhibit a lower current and a weaker light intensity. For instance, for a device with a MEH-PPV/EMI-ES mass ratio of 1:0.08 (~0.3 M), the onset of detectable light emission was shifted to ~6.9 V, and the transition in current between the rapid exponential increase and the slower exponential increase was shifted to ~2.4 V.

Figure 3 presents current as a function of time (top part) and photographs showing the formation of doped regions and the subsequent light emission (bottom part) for a Au/MEH-PPV+EMI-ES/Au device during the initial operation at 3 V and RT. The

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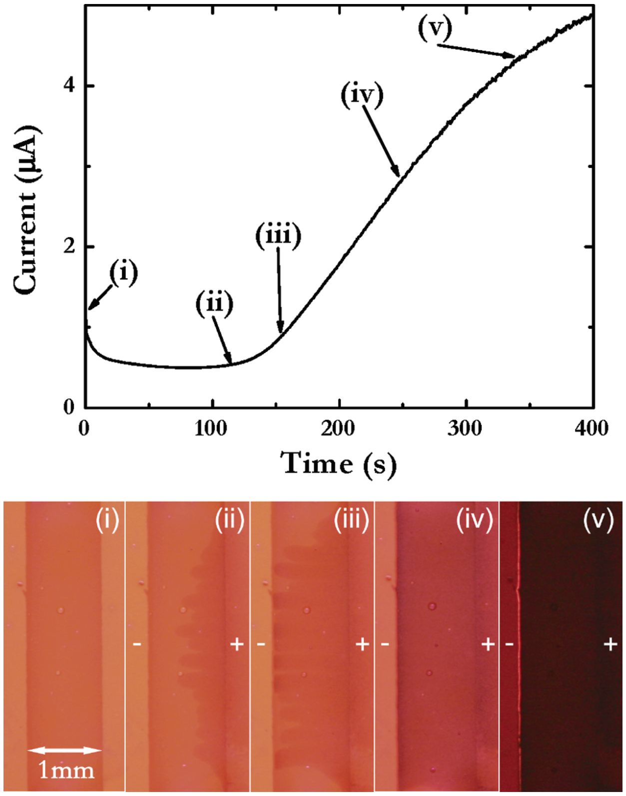

Figure 3. Current as a function of time (top part) and photographs showing progression of dark doped regions and subsequent light emission (bottom part) for a planar Au/MEH-PPV+EMI-ES/Au device during operation at 3 V and RT. The Roman numerals in the photographs correspond to those in the upper graph, thus indicating the time of each photograph. The exposure time and aperture value were 1 s and 2.8 in photographs (i)−(iv) and 20 s and 3.5 in photograph (v).

UV-excited (orange-colored) photoluminescence of MEH-PPV is effectively quenched by electrochemical doping, and the photographs were therefore taken under UV illumination in a dark room so that the formation of doped regions would be visible as dark regions. Roman numerals are included in Figure 3 to allow for a correlation between the current measurement and the doping progression, as detected by the photographs.

The current exhibits an initial decay with time during which electrical double layers are formed at the interfaces. Thereafter, the electrochemical doping process begins, as evidenced by the appearance and progression of a (relatively uneven and finger-shaped) p-type doping front [see photograph (ii)]. After a complete device turn-on, during which the doped regions first make contact and then become more heavily doped [see photographs (iii) and (iv)], a light-emitting p−n junction is formed in close proximity to the negative electrode [see photograph (v)].

At a higher applied voltage, identical devices turned on faster (e.g., ~1 min at 5 V compared to ~6 min at 3 V) and emitted more intense light. The light-emitting p−n junction was, however, still positioned close to the negative electrode. We have also prepared devices with PEO as a third component in the active material. In contrast to the devices presented herein, such MEH-PPV+PEO+EMI-ES devices exhibited a significant phase separation and also required $V_{\text{turn-on}} \approx 10$ V.

To summarize, by carefully selecting appropriate active material components, we have for the first time been able to demonstrate that it is possible to turn-on macroscopic planar LECs with mm-sized interelectrode gaps operating at a low voltage of 3 V and at room temperature. This observation could potentially open up for a simple and straightforward (reel-to-reel) production of new types of efficient surface-emitting solid-state devices.

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