Operating mechanism of light-emitting electrochemical cells

To the Editor — In the December 2007 issue of *Nature Materials*, Slinker *et al.*[1] reported the measurement of the electric field distribution in a light-emitting device consisting of a $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ thin-film placed between a pair of gold electrodes separated by 8 μm. They found that the electric field in the organic film was greater near the electrodes, particularly near the cathode, compared with the middle of the film. This observation is consistent with the redistribution of the mobile ions in the $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ when viewed as an electrolyte. deMello argued that the high electric field in a double layer would facilitate the injection of electrons and holes in such electronic–ionic mixed conductor materials[2].

The potential profile in an operating light-emitting electrochemical cell (LEC) in a similar surface cell configuration was first published more than ten years ago. Dick *et al.* described data from optical-beam-induced current that demonstrate zero electric field except in a narrow region within the cell[3]. They showed furthermore that it is precisely from this same narrow region (width approximately 2 μm) that light is emitted. These data, along with the prior observation of doping, are fundamental to the assertion that the LEC functions via the formation of an electrochemically induced p–i–n junction[4,5]. Figure 1 shows the narrow light-emitting junction formed in a Au/polymer admixture/Au junction[5]. The different colours of the regions on either side of the light-emission zone demonstrate that these regions are in fact 'doped'. The junction was observed by Hu *et al.*[6] to drift over time, possibly due to degradation in the n-doped regime.

The formation of a p–i–n light-emitting junction was proposed for semiconducting polymers admixed with an ionic conductor. This p–i–n junction model is based on the well-understood electrochemical doping of conjugated polymers. The fundamental assumptions of the LEC model are that the semiconductor can be electrochemically doped n-type (reduced) or p-type (oxidized), and that the doped (n-type or p-type) semiconductor is highly conducting. Many conjugated polymers can both be p-doped and n-doped. Light-emitting junctions have been observed in LECs fabricated from a number of different semiconductor polymers (for a recent review, see ref. 7). However, any electrochemical system has a finite window of stability. Doped polymers may be susceptible to degradation by moisture and oxygen, and even by the dopant or other components such as polyethylene oxide (PEO) and the electrode materials used in the LECs.
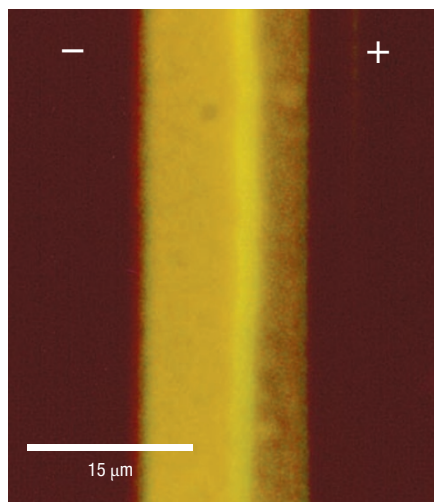

Figure 1 Optical microphotograph of the Au/polymer admixture/Au LEC (surface cell configuration) during operation at 4-V bias. The polymer layer is composed of poly(1,4-phenylene vinylene), polyethylene oxide, and lithium triflate. Green light is emitted from the narrow p–i–n junction near the centre of the spacing between the gold electrodes (dark rectangular areas)[5].

The LEC is an electrochemical device with two operating regimes corresponding to $eV < E_g$ and $eV > E_g$, respectively, where E_g is the energy gap between the π- and π*-bands of the conjugated polymer and V is the voltage applied across the polymer. When the voltage is too small to redox-dope the semiconductor ($eV < E_g$), double layers form near the electrodes. When the applied voltage is increased to $eV > E_g$, the formation of a p–i–n junction will occur. The formation process can be slow due to the generally low ionic conductivity in the solid-state devices. Until an electrochemical equilibrium is established, the mobile ions will redistribute but ion motion becomes insignificant in the steady state when high-efficiency electroluminescence is observed in the junction. The onset of electrochemical doping can also be delayed through the existence of an overpotential. Such an overpotential could exist, for example, in semiconducting polymer/PEO blends wherein ions that are initially in the PEO are not able to move into the semiconducting polymer. The so-called electrodynamic model would require that this overpotential be sufficiently large to prevent electrochemical doping. If doping does not occur and the double layers persist for $eV > E_g$, the issue to be addressed is the origin of the overpotential.

For the $[Ru(bpy)_3]^{2+}(PFF_6^-)_2$ system[8], the $[Ru(bpy)_3]^{2+}$ can be oxidized to $[Ru(bpy)_3]^{3+}$ or reduced to $[Ru(bpy)_3]^{1+}$ with associated redistribution of the PF_6^- counterions. It is not known whether the 'doped' forms of $[Ru(bpy)_3]^{2+}(PF_6^-)_2$ have greater conductivity for holes and electrons, respectively, than that of the 'undoped' $[Ru(bpy)_3]^{2+}(PF_6^-)_2$. Moreover, the observation that the device functions even under application of 120 V is evidence that the system is operating far from electrochemical equilibrium. Thus, the $Au/[Ru(bpy)_3]^{2+}(PF_6^-)_2/Au$ surface cells do not satisfy the requirements of the electrochemical model used to describe the operation of LECs.

The 'electrodynamic' model predicts the highest field at the electrode interface (see simulated results shown in Fig. 5 of ref. 1). In contrast, all the data show low field at the electrode interfaces; the maximum field is up to 1 μm away from the cathode. The high field 1 μm away from the cathode could result from unsustainable n-doping of the Ru complex. A closer examination of Fig. 6a,b of ref. 1 reveals a relatively large field in the bulk of the organic film under 120-V bias where the electroluminescence is intense.

In summary, the data presented by Slinker *et al.*[1] are far more complex than can be explained by a basic electrochemical model even with a significant overpotential. The light-emitting p–i–n junction model accounts for the intense and efficient electroluminescence in polymer LECs. This model has been proven in many material systems. The junction can be unstable and unsymmetric. LECs with air-stable electrodes and thick polymer films can be fabricated via screen printing of the polymer layer in the production of low-cost light-emitting devices[9].

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Authors' response — The comments by Pei and Heeger on our paper published in *Nature Materials*[1] call for a clarification of the mechanism of the operation of light-emitting electrochemical cells (LEECs).

The simplest configuration of an organic light-emitting diode (OLED) consists of an organic semiconductor layer sandwiched between two electrodes, the anode and the cathode. The anode is selected to have a high work function in order to minimize the barrier for hole injection to the highest occupied molecular orbital of the organic layer (the equivalent of the valence band). Equivalently, a low-work-function cathode is required for efficient electron injection to the lowest unoccupied molecular orbital of the organic layer (the equivalent of the conduction band). Charge injection creates oxidized and reduced forms of the organic semiconductor molecules near the anode and cathode, respectively, and the different optical properties of these species have been used to measure charge densities in devices. Some of the injected charges recombine to produce light emission, and the efficiency of OLEDs is critically dependent on the ability of the electrodes to inject electrons and holes in a balanced manner[2]. Low-work-function metals such as calcium make great cathodes to most organic semiconductors, but are not air-stable. When a high-work-function metal such as gold is used as the cathode, the large energy barrier prohibits electron injection[3], and such devices are called 'hole only'. By definition, an operating OLED is not at electrochemical equilibrium.

A way to work around energy barriers and improve charge injection involves the introduction of mobile ions to the organic semiconductor film. These devices are called light-emitting electrochemical cells, after the first report of a device using a semiconducting polymer layer with ions introduced in it[4]. On the application of a bias, mobile ions inside an organic film respond by accumulating near the electrodes (double-layer formation). This ion redistribution screens the electric field in the bulk and leads to interfacial electric fields that enhance charge injection. The ions may redistribute further to accommodate changes in the local electric field caused by the injected electrons and holes, but electric fields remain present at the contacts to maintain charge injection. The bulk remains essentially field-free until the applied bias becomes too high

for ions to be able to completely screen it. This essential physics, which is the basis of the electrodynamic model[5,6], is missing from the electrochemical model, which postulates that no electric field is present at the contacts[4]. Potential drops at contacts can in principle be accounted for by introducing an 'overpotential' into the electrochemical model, but such generalizations do not help understand the operation mechanism of LEECs.

The question is how significant are these interfacial electric fields in LEECs? The answer depends on the size of the energy barriers, the applied bias, and the details of the ions' distribution near the electrodes. The latter is hard to predict, as it depends on the availability of 'free volume' near the electrodes. Our paper[1] reported the first direct measurement of electric-field distribution in an LEEC and found that, at steady state, interfacial fields are indeed significant. The measurements were carried out in LEECs with two high-work-function electrodes, so a larger electric field was observed near the cathode and a smaller one near the anode, as predicted by the electrodynamic model. At 5 V applied across the 7.5-μm device, the electric field near the cathode was 50 kV cm^{-1}, whereas the bulk remained essentially field-free. Only when the bias reached 120 V (and the field near the cathode reached 800 kV cm^{-1}) were the ions unable to completely screen the applied field, and a field began to appear in the bulk.

The spatial resolution of our electrostatic potential measurement is 200 nm. As we determine the lateral electric field by numerically differentiating the measured electrostatic potential[7], this finite resolution necessarily results in an electric field that peaks at least 200 nm away from the metal electrode. Given an additional ±250 nm uncertainty in the location of the electrode — determined from measured capacitance — we can locate the peak of the electric field to within only approximately ±450 nm. Figure 4 in the paper[1] shows the field maxima to be 450 nm and 220 nm away from the cathode and the anode, respectively. The measured locations of the electric field maxima are thus entirely consistent with the hypothesis that the electric field peaks right at the contacts.

The material of choice for our work[1] was the ionic transition metal complex [Ru(bpy)$_3$]$^{2+}$ with PF$_6^-$ counter ions. The

exact mobilities of electrons and holes in this material are not known, as the presence of ionic conduction makes the usual techniques, such as time-of-flight, challenging to apply (the same holds for any semiconductor with mobile ions). However, the mobilities must be substantial to support electroluminescence, which has been extensively studied in LEECs made from [Ru(bpy)$_3$]$^{2+}$(PF$_6^-$)$_2$ and its derivatives over the past decade[8]. We would thus expect that the observed interfacial fields are not a peculiarity of the [Ru(bpy)$_3$]$^{2+}$(PF$_6^-$)$_2$ material. Indeed, in a recent publication[9], the Ginger group at the University of Washington reported scanning Kelvin probe measurements of potential profiles in LEECs made using a poly(*p*-phenylene vinylene) with mobile ions. Most of the potential in their study was also found to drop near the cathode.

In conclusion, direct measurements of electric-field distribution in LEECs made with ionic transition metal complexes[1] and, more recently, conjugated polymers[9] show high electric fields near the electrodes. The electrochemical model fails to account for these interfacial electric fields as it ignores important aspects of the physics of metal–semiconductor contacts.

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