

## Electric Field Distribution in Polymer Light-Emitting Electrochemical Cells

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We use electroabsorption spectroscopy and modeling studies to probe the electric field in light-emitting electrochemical cells. At room temperature and constant applied bias, the steady-state internal field is zero for a range of biases. However, when the ions are *frozen* in place by cooling under steady bias, and the bias is subsequently changed, the profile of the electric potential resembles a typical *p-n* junction.

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Luminescent polymers are of interest owing to their potential use in thin-film emissive devices [1]. High power efficiency is important in these devices, and an interesting technique for achieving this has been reported by Pei *et al.* [2], in which mobile ions are incorporated into the polymer layer. Devices formed by sandwiching the ion/polymer layer between two electrodes show low threshold voltages for light emission, which are broadly independent of the work functions of the electrodes. The operation of these *light-emitting electrochemical cells* (LECs) is of considerable interest, owing to their properties as *mixed* electron-ion conductors [3].

It is generally agreed that the low threshold for charge injection results from movement of the mobile ions towards the electrodes. However, there is some disagreement in the literature about the role of the ions [4–7]. We have previously used Debye-Hückel theory (DHT) to show how the accumulation of uncompensated ions near the electrode-polymer interfaces screens the bulk polymer from the external field and reduces the interfacial barrier widths for charge injection [7]. According to DHT, significant improvements in charge injection are expected only for densities of free ions greater than  $10^{20} \text{ cm}^{-3}$ , and experimental measurements comparing devices with differing ion densities support this prediction. The agreement of theory and experiment indicates near-complete ion dissociation in our devices. Smith has previously considered a different regime in which strong ion association is present (he assumes a binding energy of 0.6 eV), lowering the density of free ions significantly [6].

At voltages above the semiconductor gap  $U_G$ , substantial electronic charge is also present within the polymer but, for relatively low current densities, this is screened by equal and opposite ionic space charge, maintaining a field-free bulk. Within the field-free regime, electronic charge carriers move under the influence of diffusion only, and the concentrations of electrons and holes decrease approximately linearly from the parent electrode to zero at the recombination zone. At sufficiently high current densities, local charge (and field) neutrality breaks down [7].

Pei *et al.* have suggested an alternative mechanism in which electrochemical doping creates oxidized and reduced chains of polymer which are electrically compen-

sated by nearby counterions [2]. Because highly doped conjugated materials exhibit high conductivities, they considered that the electrode-polymer interfaces should form Ohmic contacts. It was proposed that the doped layers meet in the polymer bulk to form an *in situ p-n* junction where the electrons and holes recombine radiatively. Doping was not considered to occur in the recombination zone itself (owing to the depletion of electronic carriers by recombination), and the entire electric potential was therefore developed across the low-conductivity junction region.

In this paper, we provide a unified description of device operation, in which the field-free picture is appropriate for a range of biases under normal operating conditions, and the *p-n* junction picture is appropriate when the devices are cooled under steady pre-bias (to freeze in nonequilibrium ion distributions) and subsequently operated away from that pre-bias.

For our electroabsorption (EA) measurements, an alternating external field was applied across the LEC device, perturbing the energy levels of the polymer and modulating the absorption spectrum. The fractional change in transmission is proportional to the imaginary component of the third order susceptibility  $\text{Im}\chi^{(3)}$  and to the square of the average electric field  $E$ . Consequently, the differential transmission is modulated at both the 1st- and 2nd-harmonic frequencies in accordance with Eqs. (1a) and (1b).

$$I_{\omega} = -\frac{\Delta T}{T} \Big|_{\omega} \propto 2 \text{Im}\chi^{(3)}(\lambda) E_{\text{dc}} E_{\text{ac}} \sin \omega t$$

(1st harmonic), (1a)

$$I_{2\omega} = -\frac{\Delta T}{T} \Big|_{2\omega} \propto \frac{1}{2} \text{Im}\chi^{(3)}(\lambda) E_{\text{ac}}^2 \cos 2\omega t$$

(2nd harmonic), (1b)

Under conditions of low carrier injection,  $E_{\text{dc}}$  is related to the dc component of the applied voltage  $V_{\text{dc}}$  by Eq. (2):

$$E_{\text{dc}} = \frac{V_{\text{dc}} - V_{\text{oc}}}{d}, \quad (2)$$

where  $V_{\text{oc}}$  is the open circuit voltage, and  $d$  is the width of the device.  $I_{\omega}$  therefore varies linearly with  $V_{\text{dc}}$ , and  $I_{2\omega}$  is independent of  $V_{\text{dc}}$ .

The LECs used here were fabricated from a 20:5:1 weight blend of precursor Br-PPV (a copolymer of phenylene-vinylene and phenylene-methoxy-ethanediyl with  $U_G \approx 2.5$  eV, see Ref. [8]) with poly(ethylene-oxide) and lithium triflate [9] dissolved in a 6:1 volume mixture of acetonitrile and water, corresponding to an ion density of about  $10^{20}$  cm $^{-3}$ . The films (of final thickness 200 nm) were spin coated from a precursor solution onto indium tin oxide substrates and annealed in vacuum at 180 °C for ten hours. Aluminum top contacts were thermally evaporated at  $10^{-5}$  mbar. EA measurements were made at 5 kHz using lock-in detection, following the technique of Campbell *et al.* [10].

Our measurements were obtained using *static* LECs which had been cooled below the glass transition temperature of the polymer electrolyte to *freeze-in* the ion distributions. Different ion distributions may be established by varying the voltage or *pre-bias* applied to the device during cooling. In each case, the pre-bias was applied 30 min before cooling to allow steady state to obtain, and was maintained until reaching 200 K. The phrase *relaxed dynamic* LEC is used to describe devices operating in steady state at room temperature.

Figure 1(a) shows how the magnitude of the 1st-harmonic response  $I_\omega$  of the static LEC varies with dc offset for pre-biases between 0 and 2.5 V (all data obtained at 496 nm using the same device). As expected, for each scan  $I_\omega$  varies linearly with dc offset, passing through zero when the offset equals the pre-bias. Although the most general inference from a null 1st-harmonic response is a spatially varying electric field with a mean value of zero

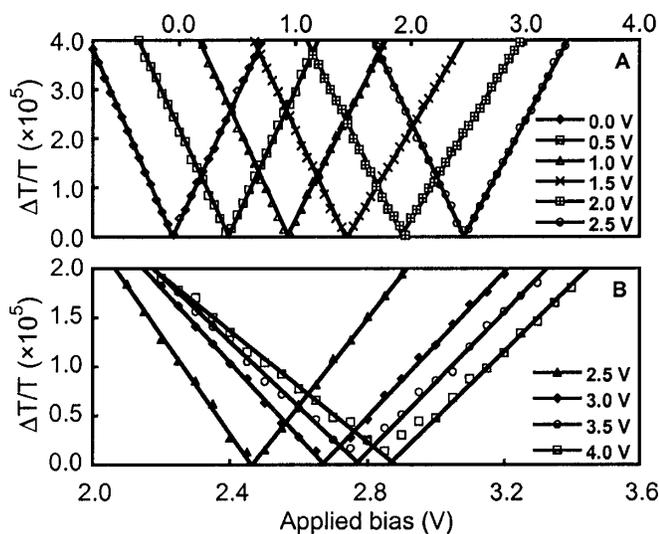


FIG. 1. Variation of 1st-harmonic EA response (496 nm) with dc offset for static LECs formed using pre-biases: (A) Less than  $U_G/e$ , for which the null point matches the pre-bias indicating a zero-field bulk at the pre-bias; and (B) above  $U_G/e$ , for which the null point deviates from the pre-bias owing to significant charge injection.

(when averaged across the bulk), it is almost always appropriate to assume the field is zero everywhere. If this were not the case, the electric field would necessarily change direction in the bulk, requiring a distribution of charge carriers which could not arise directly from the simple application of an external field. We therefore infer from Fig. 1(a) that the field is zero everywhere when the device is driven at the pre-bias under static conditions; in other words, the polymer is neutral everywhere except in the thin regions close to the interfaces. This local neutrality must also have existed when the device was operating dynamically at 300 K, at which stage the charge distributions were originally established. Hence, this result provides important experimental confirmation of the underlying assumption of the model for dynamic LECs described in Refs. [7] and [11].

We note that the width of the interfacial regions is strongly dependent on the ion concentration. We have previously shown that it falls from several tens of nm at  $10^{19}$  cm $^{-3}$  to less than 1 nm at  $10^{20}$  ions cm $^{-3}$ . In order to account for the measured EA responses [Fig. 1(a)], the interfacial regions must be very much thinner than the polymer layer to keep the bulk field-free, which provides additional evidence that the concentration of free ions exceeds  $10^{19}$  cm $^{-3}$ , and by necessity that the binding between ions is weak in our devices.

In Fig. 2(a), the ratio of the 1st- and 2nd-harmonic responses  $I_\omega/I_{2\omega}$  is plotted against  $4V_{dc}/V_{ac}$  for each value of the pre-bias. From Eqs. (1a) and (1b), the slope of the

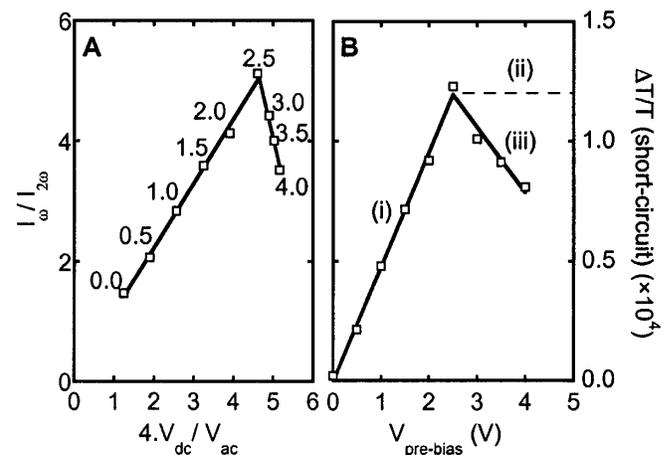


FIG. 2. (A) Variation of the ratio of the 1st- and 2nd-harmonic EA responses ( $I_\omega/I_{2\omega}$ ) with  $4V_{dc}/V_{ac}$ . The slope deviates from unity for  $V_{pre-bias} > U_G/e$  (2.5 V) indicating significant charge injection in this regime. (B) Pre-bias dependence of the short-circuit 1st-harmonic EA response. (i) For pre-biases below the band gap, the 1st-harmonic response (and so the built-in electric field) increases linearly with pre-bias, as expected. (ii) In the absence of electronic carrier injection in the relaxed dynamic LEC, the built-in field would saturate at  $U_G/e$  for pre-biases above  $U_G/e$ . (iii) Experimentally, a reduction in 1st-harmonic response is observed above  $U_G/e$ .

line should equal unity, and indeed does for biases in the range  $0 < V < 2.5$  V. Above 2.5 V, however, the slope deviates sharply from 1 (in other words, the average field is no longer increasing linearly with applied bias), indicating that significant charge injection is occurring. We have discussed the reasons for this abrupt discontinuity at the semiconductor band gap in a previous paper [7].

The consequences of charge injection are evident in Fig. 1(b) which shows that, for pre-biases greater than  $U_G/e$ , the null point deviates from the pre-bias. Relaxed dynamic devices formed using such high pre-biases will contain high densities of compensating electronic and ionic charge in the bulk. During cooling, the ion mobilities fall rapidly and the ionic space charge (present at the interfaces and at lower density throughout the polymer bulk) is effectively frozen in place. The electronic carriers, by contrast, remain mobile (albeit with their mobilities decreasing) and are therefore able to respond to any changes in the applied field. Furthermore, owing to their temperature dependent mobilities, the net charge distribution will also vary with temperature. If local charge neutrality exists at room temperature, it may not be maintained on cooling. Equally, if a finite field is measured at 200 K, the same field may not have been present at 300 K.

Figure 2(b) shows how the short-circuit 1st-harmonic response—which from Eq. (1a) is proportional to the built-in field—varies with pre-bias. The maximum sustainable built-in field is  $\pm U_G/ed$ , so one might expect it to increase linearly with pre-bias ( $E_{\text{built-in}} = -V_{\text{pre-bias}}/d$ ) until satu-

rating abruptly above  $V_{\text{pre-bias}} = U_G/e$ . However, the data in Fig. 2(b) would seem to imply that the built-in field actually decreases for pre-biases above the band gap. This behavior is, in fact, a manifestation of the injected electronic carriers which were present in the dynamic device, but are absent in the short-circuit static device operating at 200 K.

In a relaxed dynamic LEC, charge neutrality in the bulk requires the net ionic charge distribution to mirror the net electronic charge distribution. The ions are frozen in place during cooling, and, hence, their distribution in the static device may be determined from the original distribution of electrons and holes in the relaxed dynamic device, which, in turn, is determined by three factors [7]: the absolute and relative densities of electrons and holes at the cathode and anode, respectively ( $a = n_e^d/n_h^0$ ); the relative mobilities of the electrons and holes ( $b = \mu_e/\mu_h$ ); and the rate of electron-hole recombination. To a good approximation in an *electron-hole symmetric* device (i.e.,  $a = b = 1$ ), the electron and hole concentrations fall linearly with distance from the parent electrode to zero at the device center (the recombination zone). The ions mirror this behavior in the bulk, while in the high-field regions close to each interface there exists the usual sheet of uncompensated charge [see Fig. 3(a)]. The calculations outlined below are relatively insensitive to the actual shapes of the interfacial layers, so we assume here for convenience that the electric potential may be approximated by exponentials of the form shown in Eq. (3c). Therefore, we can write the following:

$$\rho_{\text{ion}}^{\text{bulk}} + \rho_e^{\text{bulk}} + \rho_h^{\text{bulk}} = 0 \quad (\text{charge neutrality in bulk}), \quad (3a)$$

$$\rho_e^{\text{bulk}} + \rho_h^{\text{bulk}} = +en(1 - 2x/d) \quad (\text{electron and hole densities fall linearly with distance from parent electrode to zero at device center}), \quad (3b)$$

$$\phi = \phi_0 \exp\left(\frac{-x}{D}\right) - \phi_d \exp\left(\frac{x-d}{D}\right) \quad (\text{potential is taken to be zero in the bulk of the device}), \quad (3c)$$

$$\varepsilon_0 \nabla^2 \phi = \rho_{\text{ion}}^{\text{interface}} + \rho_{\text{ion}}^{\text{bulk}} + \rho_e^{\text{bulk}} + \rho_h^{\text{bulk}} \quad (\text{Poisson's equation}), \quad (3d)$$

$$\Rightarrow \rho_{\text{ion}} = \varepsilon_0 \nabla^2 \phi - en(1 - 2x/d), \quad (4)$$

where  $\rho$  is the density of the appropriate charge carrier,  $\phi$  is the electric potential,  $D$  represents the characteristic width of the high-field regions (typically 5–10 Å) and  $n = n_e^d = n_h^0$  (under relaxed dynamic conditions).

When the device is cooled and the pre-bias is subsequently removed, the electronic charges redistribute to minimize the free energy of the system, subject to the constraints imposed by Fermi-Dirac statistics (and the presence of the fixed distribution of ions). Consequently, the hole distribution  $\rho_h$  is governed by

$$\rho_h = \int_{E_v}^{-\infty} \frac{eg_h(E_v - E) dE}{1 + e^{(E_F - E)/kT}}, \quad (5a)$$

$$E_v(x) = \phi(x) - \Delta h, \quad (5b)$$

$$\varepsilon_0 \nabla^2 \phi = \rho_{\text{ion}} + \rho_h + \rho_e, \quad (5c)$$

where  $E_v(x)$  is the energy of the valence band,  $E_F$  is the Fermi level,  $g_h(E_v - E)$  is the density of states for holes,  $\Delta h$  is the height of the barrier to hole injection at the anode, and all other symbols have their usual meanings. A similar set of equations applies for the electrons. In the self-consistent Thomas-Fermi approximation, the electronic charge distributions may then be calculated by selecting arbitrary distributions of electrons and holes, and iterating until self-consistency obtains.

Figure 3(a) shows how the electronic charge distribution is affected by the removal of the pre-bias: In effect, electrons (holes) are redistributed from the device center towards the cathode (anode) in order to compensate some of the interfacial ions, and thereby reduce the widths of the high-field layers at the interfaces. The electric potential is instead dropped across the middle of the device by the now-uncompensated ions there. For clarity, we have shown charge distributions only for the specific case of  $n = 10^{18} \text{ cm}^{-3}$ . For lower values of  $n$ , the profile of the short-circuit electronic charge distribution tends more closely to that of the relaxed dynamic device, with better charge compensation in the device center.

Figure 3(b) shows the electric potential for a range of values of  $n$ . For the simplest case of  $n = 0$  (no electrons and holes present in the relaxed dynamic device), the built-in field is  $U_G/ed$  as expected. However, for values of  $n$  greater than about  $10^{17} \text{ cm}^{-3}$  (which as we have seen is the case for pre-biases in excess of  $U_G/e$ ), the electric field in the static device is pushed away from the interfaces towards the original location of the recombination zone, creating a region of high field at the site of the recombination zone and regions of constant potential on either side. This redistribution of the electric field has important

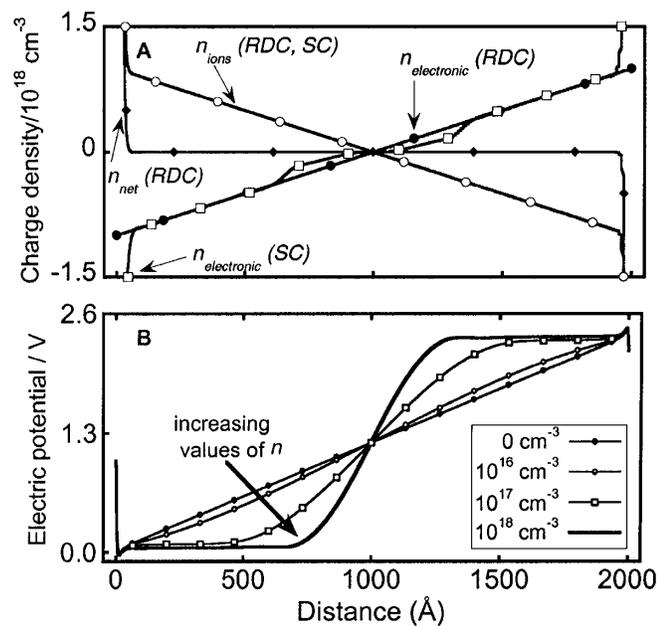


FIG. 3. (A) Charge profiles for an LEC operating under relaxed dynamic conditions (RDC) and in short circuit under static conditions (SC), assuming RDC electron and hole densities of  $n = 10^{18} \text{ cm}^{-3}$  at the cathode and anode, respectively [ $n_{\text{ions}} = (\rho_{\text{cation}} - \rho_{\text{anion}})/e$ ;  $n_{\text{electronic}} = (\rho_h - \rho_e)/e$ ; and  $n_{\text{net}} = n_{\text{ions}} + n_{\text{electronic}}$ ]. (B) Graph showing how the short-circuit profile of the electric potential in a static LEC is affected by the density electronic carriers under RDC. All profiles assume equal electron and hole mobilities, and equal RDC electron and hole densities  $n$  at the cathode and anode, respectively.

consequences for the magnitude of the 1st-harmonic EA signal. For example, if  $n_e^d = n_h^0 = 10^{18} \text{ cm}^{-3}$  in the relaxed dynamic device, 80% of the light will be absorbed in the low-field region (given an absorption coefficient of  $0.002 \text{ \AA}^{-1}$  at 496 nm) leading to a reduction in signal, as seen experimentally in Fig. 2(b).

We note that these modeled results are consistent with the potential distribution inferred from photovoltage measurements on planar LECs reported by Dick *et al.* [12]. Their measurements—which in agreement with the modeling presented here identified a high-field region in the center of the device surrounded on either side by regions of constant potential—were obtained under similar conditions (low-temperature, pre-bias = 5 V, and short circuit). We stress that this field distribution is a consequence of the particular arrangement of charged species presented in the shorted static device, and that the field distribution in an operational relaxed dynamic LEC will be different.

Gao *et al.* [13] have recently reported EA measurements on LECs operating at room temperature, which—unlike our measurements—suggest that the field-free assumption breaks down at biases below  $U_G/e$ . We note, however, that applying an alternating field to a dynamic LEC does not permit steady state to obtain with proper ion-electron compensation. Hence, the observation of a finite 1st harmonic response under alternating conditions need not imply the existence of a nonzero electric field for the pertinent condition of relaxed steady state. In order to understand the nature of the electric field in a relaxed dynamic device, all our measurements were performed on devices which had previously been allowed to approach true steady state for 30 min and had subsequently been cooled to freeze-in the distribution of ions established at room temperature.

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