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Doping front propagation in light-emitting electrochemical cells

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Observations of the expansion of the *p*- and *n*-doped regions in planar (lateral) polymer light-emitting electrochemical cells with large (mm-sized) interelectrode gaps driven with 5 to 50 V have inspired a model describing the doping front propagation. We find that the propagation is limited by the movement of ions in the electronically insulating region between the *p*- and *n*-doped regions. Two consequences of an ion-limited front propagation are that the doping fronts accelerate as they approach each other, and that fingerlike protrusions are formed, particularly at larger drive voltages.

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I. INTRODUCTION

Polymer light-emitting electrochemical cells (LECs) are highly efficient light-emitting devices, with a number of appealing properties, such as insensitivity to electrode material and interelectrode distance, that distinguish them from more common polymer light-emitting diodes (PLEDs).^{1–7} The drawbacks of LECs are that the turn-on time typically is slow and the operational lifetime is inadequate. In order to overcome these drawbacks it is fundamentally important to understand the physics behind their operation—a topic that has been intensely debated in the scientific literature,^{8–23} particularly regarding where the electric field in the device is largest and consequently most important.

Gao *et al.* recently introduced planar LEC structures, with large-scale interelectrode gaps in the mm range, that allow device operation (doping front propagation and emission) to be probed directly in unprecedented detail.^{24–27} Shin *et al.* further developed this concept when they demonstrated that it is possible to turn on wide-gap devices at low voltages.²⁸ In this article, we employ this type of planar device to demonstrate that doping front propagation (or turn-on time) in LECs is limited by ion motion in the undoped region, and consequently that a significant electric field is located in this undoped region between the two doping fronts during the turn-on process. The resulting model not only predicts the turn-on time, but also explains the high aspect ratio fingers often observed in photographs of wide-gap devices under operation, which under some conditions are suspected of short-circuiting the anode and cathode resulting in device failure.²² Thus, this work addresses two of the critical hurdles that must be overcome before commercial production of LECs becomes common.

II. EXPERIMENT

Planar LEC devices were fabricated by spin coating a blend of poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene] (MEH-PPV), poly(ethylene oxide) (PEO), and LiCF₃SO₃ (with a 1:1.35:0.25 mass ratio) onto prepatterned Au electrodes with interelectrode gaps of 1–3 mm on a glass substrate. All device fabrication took place in an Ar-filled dry box (O₂, H₂O < 1 ppm). The LECs

were then transferred to a vacuum cryostat, where extensive *in situ* drying took place, before optoelectronic characterization at 360 K and 10^{−3} Pa was carried out. UV-excited photoluminescence in MEH-PPV is quenched by electrochemical doping, allowing the doping propagation to be imaged in photographs taken under UV illumination in a dark room through the optical window of the cryostat using a digital camera equipped with a macro lens. Further experimental details can be found in Refs. 28 and 22.

III. THEORY

To date, there are two significant and conflicting models describing the behavior of LECs. The consensus is that ions from the active material bulk migrate to the metal electrodes and build a double layer at each electrode when a potential is applied between them. Thereafter, the descriptions diverge. One model suggests that the double layer remains at the metal electrode edge, decreasing the injection barrier from the metal electrodes, so that the device effectively behaves like a PLED. Alternatively, in the electrochemical model, the conjugated polymer is *p*- and *n*-doped at the anode and cathode, respectively, transforming the semiconducting film into a conducting film, effectively moving the electrode interface toward the opposite electrode (see Fig. 1, inset). The findings of this article strongly favor the latter description, so we consider only this model in the remainder of this text.

If the electrochemical doping process renders the doped polymer regions relatively conductive compared to the ionic conductivity of the undoped polymer region and the injection process is not limiting, then the overpotential $V_i = \Delta V - E_g/e$ (where ΔV is the applied voltage, E_g is the band gap of the conjugated polymer and e is the elementary charge) will fall primarily across the undoped region. Assuming a constant ionic conductivity, the electric field in the insulating region E_i can be approximated as $E_i = V_i/x_i$, where x_i is the width of the insulating region. When the electrodes inject charges, the *p*- and *n*-doped regions grow while the insulating layer diminishes. As a result, the electric field E_i increases as the *p*- and *n*-doping fronts approach each other.

In order for the above picture to hold, ion transport in the insulating region must be the process that limits electrochemistry at, and thus the speed of, the *p*- and *n*-doped

FIG. 1. Doping front positions ($x=0$ at anode, $x=1$ at cathode) shown as a function time (scaled by the predicted collision time) as predicted by the one-dimensional model for γ_n/γ_p as indicated by symbols in the legend. Solid lines indicate the p -doping front position. Dotted lines represent the n -doping front position. Inset: sketch of lateral LEC component. A potential ΔV is applied between two gold electrodes coated with a blend of an electrolyte and a conducting polymer. The resulting doped regions grow with time, causing x_p and x_n to increase while x_i decreases.

fronts. If true, we would expect a direct relationship between the applied potential ΔV (and consequently E_i) and the speed of the fronts, since the motion of ions in the insulating region must be driven by electromigration or ion transport would not be the limiting process. Furthermore, we would expect the fronts to accelerate as they approach each other, since the field E_i is inversely proportional to x_i . This would seem to contradict the findings of Gao *et al.*²⁵ who report a constant front velocity from experimental measurements.

The velocity of a front in a one-dimensional system can be estimated by solving a nonlinear differential equation that we will derive here. Consider two fronts (the p -doping and n -doping fronts) moving in one dimension towards each other from fixed electrodes. We choose to scale the problem such that the distance between the electrodes is unity. Then, $x_p + x_i + x_n = 1$ where x_p and x_n are the widths of the p - and n -doped regions, respectively. If we assume that the conjugated polymer is doped uniformly, but with a different doping fraction in the p - and n -doped sides, then charge balance requires that the rate of each front's propagation is proportional to the total current density passing through the device, J ,

$$\gamma_p \frac{dx_p}{dt} = \gamma_n \frac{dx_n}{dt} = J, \quad (1)$$

where γ_p and γ_n represent the charge density required to p and n dope the polymer, respectively. If the current is limited by the ionic conductivity σ_i within the electronically insulating span x_i , then $J = V_i \sigma_i / x_i$. Differentiating $x_p + x_i + x_n = 1$ with respect to time and eliminating dx_p/dt and dx_n/dt in favor of J yields

$$\frac{dx_i}{dt} = -J \left(\frac{1}{\gamma_n} + \frac{1}{\gamma_p} \right). \quad (2)$$

Substituting for J in (2) yields

$$\frac{dx_i}{dt} = -\frac{V_i \sigma_i}{x_i} \left(\frac{1}{\gamma_n} + \frac{1}{\gamma_p} \right). \quad (3)$$

Assuming that V_i is constant, separating the variables based on position and time dependence and integrating results in

$$\frac{1}{2} x_i^2 = -V_i \sigma_i \left(\frac{1}{\gamma_n} + \frac{1}{\gamma_p} \right) t + C_1, \quad (4)$$

where C_1 is the integration constant. C_1 is clearly $1/2$ if $x_i = 1$ at $t=0$. Solving for x_i yields

$$x_i = \pm \left[1 - 2V_i \sigma_i \left(\frac{1}{\gamma_n} + \frac{1}{\gamma_p} \right) t \right]^{1/2}. \quad (5)$$

Since $x_i \geq 0$ for the solution to make physical sense, we disregard the solution with $x_i < 0$. The relationship

$$\gamma_p x_p = \gamma_n x_n \quad (6)$$

can be obtained by integrating (1) and noticing that $x_p = x_n = 0$ at $t=0$. Rewriting (5) explicitly for x_p results in

$$x_p = \frac{1 - \left[1 - 2V_i \sigma_i \left(\frac{1}{\gamma_n} + \frac{1}{\gamma_p} \right) t \right]^{1/2}}{1 + \frac{\gamma_p}{\gamma_n}}, \quad (7)$$

with an obvious analog for x_n . The time τ when the fronts meet can be determined by solving (5) for $x_i = 0$. The result is

$$\tau = \left[2V_i \sigma_i \left(\frac{1}{\gamma_n} + \frac{1}{\gamma_p} \right) \right]^{-1}. \quad (8)$$

IV. RESULTS AND DISCUSSION

Plots of the dimensionless front position with time (scaled by τ) predicted by the model are shown in Fig. 1. Notice that, when they reach each other, the size of the p -type region with respect to the n -type region is proportional to the ratio γ_n/γ_p and for dimensionless time $t/\tau < 0.5$ the curves are approximately linear. The latter prediction may explain the previously published experimental results indicating a linear front velocity.²⁵ However, our model predicts that the fronts are actually each accelerating towards one another until they collide.

Actual experimental measurements of the average p -front position in devices where Au electrodes drive doping in a MEH-PPV/PEO/LiCF₃SO₃ blend at 5, 10, 20, and 50 V are shown by the symbols in Fig. 2. The position was calculated by analyzing snapshots of UV light-excited photoluminescence, which is quenched where the polymer is doped. The result is a clear picture of the p -doping front, which advances quickly across the gap between the electrodes, and a less visible n -doping front. As predicted, the velocity increases continually.

FIG. 2. Average measured p -doping front position x_p scaled by the gap width as a function of time and applied potential, plotted until the first fingers of n - and p -type doping meet. Error bars (shown above each point) indicate the standard deviation of the front position.

A consequence of the acceleration of the doping fronts is that the front shape (initially a straight line parallel to the electrode) is unstable. Any perturbation in the front shape that allows one small region to advance faster than the rest, caused for example by inhomogeneity in the active material, will result in a local increase in the field across the insulating region and thus a further local increase in the front velocity. Thus, small perturbations should grow into features with a large aspect ratio.

This result is evident in the standard deviation of the p -front position calculated from each image shown by the error bars in Fig. 2. The measured variation increases both with time and applied potential. Figure 3 illustrates the same effect with four images at different ΔV and at a time where the p front has traversed approximately 50% of the distance between the electrodes. Given the instability argument above, one would expect the aspect ratio of disturbances in the doping fronts to increase with applied potential (diffusion has the time to “smooth out” the front during low-voltage experiments while electromigration becomes overwhelmingly large as the potential is increased). This is clearly evident in Fig. 3. Digital movies showing front propagation for several ΔV can be found in the supplementary material associated with this article.²⁹

The growth of the fingers with time under high electric field ($E_{\text{applied}} = 20$ V/mm corresponding to $E_i \approx 18$ V/mm) is shown in a sequence of images in Fig. 4. The initially flat interface between the p -doped region (appears dark) and the insulating region (gray) goes immediately unstable and develops high aspect ratio protrusions. A similar effect can be seen between the n -doped region and the insulating region, although the quenching in the n -doped region is not as apparent as in the p -doped region. The n -doped region is also considerably smaller than the p -doped region. According to the model, this means that the doping fraction of the p - and n -doped regions differ significantly. We intend to address this in detail in a future publication.

Since the front observed in experiments is far from planar, we would not expect the one-dimensional model derived above to quantitatively predict its behavior, except possibly for the advancement of the foremost fingers. A two-dimensional analysis should predict both the front velocity

FIG. 3. Images showing the effect of applied potential on the shape of the p - and n -doping fronts in a LEC. The light region in the middle of each image is undoped polymer. The dark region to the left is the p -doped polymer. n -doped polymer appears on the right. The anode and cathode are visible on the left- and right-hand sides of each image, respectively. Images were chosen at times when the p -doping front was about halfway between the anode and cathode. The time since the potential was applied and the applied voltage are shown under each image. Only the red channel of the original red, green, blue (RGB) images is shown.

and growth of the instabilities. We intend to investigate these in another paper. There is, however, a simple comparison that can be made for $t \ll \tau$. The initial p -front velocity has been calculated using the first data points ($x_p < 0.3$) from several sets of experiments, and is summarized as a function of the electric field, E_i , in Fig. 5. As predicted, the velocity is approximately linearly related to E_i calculated as defined above [E_g is 2.2 eV for MEH-PPV (Ref. 30)]. By extrapolating the data to a front velocity of zero, we find an intercept of 1.3 V/mm, reasonably close to the origin, as expected for a device with a turn-on voltage equal to the band gap voltage, E_g/e .

FIG. 4. Images showing the growth of perturbations in the fronts' shape into high aspect ratio fingers at $E_i \approx 18$ V/mm. The time at which each image was taken (relative to when the potential was applied) is indicated.

FIG. 5. Calculated p -doping front velocity in 1 mm wide devices (open circles) and a 3 mm wide device (filled square) as a function of the electric field, E_i and a linear fit to the 1 mm wide device data.

Finally, we would like to point out the inconsistency between these experimental results and the front propagation we would expect if the process were injection limited or electron (or hole) transport limited. The front propagation speed should decrease with time in a hole- or electron-limited device as the distance that the charge carrier must migrate from the metal electrode to the front increases. An injection-limited system would exhibit a constant (not increasing) front velocity, and would show a superlinear (likely exponential) relationship between initial front velocity and applied potential, while we observe a linear behavior (as shown in Fig. 5). Consequently, in either case the front shape would be stable since perturbations in the doping interface would be smoothed out by the decreased electric field over the doped polymer (in the case of hole- or electron-limited transport) or by diffusion in the lateral direction.

There is further evidence that, under the experimental conditions presented here, supports our claim that ion mobility governs propagation of the fronts. By heating these devices to a temperature of about 360 K, where differential

scanning calorimetry shows that the PEO/salt phase transforms from predominately crystalline (with a low ionic conductivity) to amorphous (with a high ionic conductivity), the turn-on time decreases drastically (from several hours at 100 V when crystalline to six seconds at 50 V when amorphous).²⁸ Together with the results presented in this paper, this observation strongly suggests that it is the ion motion in the electronically insulating region that governs the propagation of the doping fronts during LEC turn-on.

V. CONCLUSION

In summary, under the conditions of these experiments, doping front propagation in wide-gap lateral LECs is limited by field-driven ionic motion in the insulating region between the two propagating fronts. The shape of each front is unstable—perturbations grow dramatically with time, particularly when a large field is used to drive the device. The highly nonlinear shape of the fronts when they meet causes the initial position of the emission to be uneven as well. Although increasing the applied potential decreases the turn-on time, it also enhances the instability of the doping fronts during turn-on, which should increase the risk of doping shorts connecting the anode and cathode. We believe that this insight into the mechanism for the formation of the p - n junction will assist in the development of commercially viable, long-lifetime LEC devices.

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