



Doping dynamics in light-emitting electrochemical cells

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ABSTRACT

A major drawback of light-emitting electrochemical cells (LECs) is the long time scale associated with switching, during which ions redistribute in the active layer. We present a numerical modeling study that gives fundamental insight in the dynamics during turn-on. The characteristic response of LECs to an applied bias is the electrochemical doping of the active layer by doping fronts moving across the active layer. Formation and motion of such doping fronts are shown to be intimately related to both the electronic and ionic mobility and therefore provide useful information regarding these two quantities in LECs. In particular, it is shown that the switch-on time in LECs is directly related to the time an ion needs to cross approximately half the device, enabling the extraction of the ion mobility from the switch-on time.

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1. Introduction

Light-emitting electrochemical cells (LECs) [1] are a promising alternative to the organic light emitting diode (OLED) [2]. Unlike OLEDs, LECs have an active layer that consists of a blend of an organic semiconductor and a solid electrolyte containing mobile ions. These ions solve a couple of challenges encountered in OLEDs: (1) injection of carriers in the active layer is strongly enhanced, even past large injection barriers, which (2) allows the use of high workfunction, air stable electrodes; (3) electrochemical doping of the normally insulating active layer greatly enhances the conductivity and allows the use of relatively thick active layers. These properties facilitate the use of a simple device design consisting of organic single active layer as opposed to multilayer-stacks typically encountered in OLEDs. The possibility to use thicker devices furthermore enables the use of characterization techniques like scanning Kelvin probe microscopy on planar devices to gain insight in transport through the active layer [3–5]. Concomitant with these benefits the ions complicate the study and understanding of transport in LECs as four

instead of two types of charge carriers must be taken into account: anions, cations, electrons and holes [6,7]. Furthermore, the addition of a solid electrolyte also results in a relatively slow and complex switch-on behavior and an inadequate lifetime [8–10]. Recent progress in the understanding of the device physics as well as adaptations to the device design [11–13] and the manner of operation [14,15] have led to significant improvements in both these limiting factors. However, processes determining the turn-on time in LECs are far from completely understood, highlighted by the inability of present models to accurately describe the doping dynamics in LECs.

This study focuses on the transient operation of LECs, starting with the application of an above-bandgap bias voltage until steady state operation. Summarizing present understanding, qualitatively the following happens [4]. Initially, only ions are present in the cell. Due to the applied external field anions and cations move in opposite directions. Since ions are blocked by the electrodes, thin sheets of uncompensated charge form, which result in increased electric fields at the electrodes. If the applied potential is larger than the bandgap of the semiconductor, the corresponding potential drops at the electrodes continue to increase until they equal the energy level offset between the electrode workfunction and the electron (at the

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cathode) and hole (at the anode) transport level in the organic semiconductor. From then on, electrons and holes are injected in the active layer. The ions react by (electrostatically) compensating the injected charge, in other words the anions and cations respectively stabilize the oxidation and reduction of the polymer. This process is called electrochemical doping [4].

In wide-gap planar LECs, this electrochemical doping can be visualized by monitoring the PL of the active layer under UV illumination; [16] in the presence of doping, PL is quenched in the active layer [17]. Particularly interesting is the way in which this doping occurs. Starting from the electrodes, doped regions expand towards each other. During this expansion, doping fronts are visible as sharp transitions between the undoped region and the n- and p-doped regions. These fronts have been observed to accelerate. Fig. 1a (blue symbols) shows a typical measurement [18] of the front position versus time.

Several experimental studies [19–21] have been performed on these fronts as well as analytical [22,23] and numerical modeling [24]. Robinson and co-workers developed an analytical model that predicts the position of the doping fronts and the resultant switch-on time. They assumed that both the potential over the shrinking undoped region and the conductivity through this region remain equal. The first assumption is however not necessarily true in LECs. Recent measurements of the electrostatic potential have shown that the potential does not strongly evolve during doping front progression [25]. Results presented in the present work confirm these findings.

Here we demonstrate by numerical modeling [4] that a doping dependent mobility [26] is required to generate the accelerating doping fronts observed experimentally (Fig. 1b, blue symbols). In addition the ion mobility with respect to the electron/hole mobility is critical for front formation as well as for other transient properties like the formation of electric double layers (EDLs) [27] and a light-emitting p–n junction. For formation of accelerating doping fronts, the ion mobility needs to be approximately equal to the electron/hole mobility in the undoped polymer. In simulations that obey these criteria, the doping

front propagation shows an excellent agreement with experimentally observed doping fronts as shown in Fig. 1a (black solid line) [18]. As opposed to the t^2 dependency of the front position obtained by Robinson et al. [22] (Fig. 1a, red solid line) our model shows a less strong time dependence of the front position. Next to this fundamental understanding of the formation of doping fronts, also the transient behavior and the switch-on time in LECs are rationalized by means of numerical modeling. The simulations indicate that the switch on time is mostly related to the time an ion needs to cross approximately half the device.

2. Material and methods

2.1. Computational details

A 1-dimensional model was used in which an active layer with a length of $2\ \mu\text{m}$ was divided in discrete, equidistant grid points [4,25]. The numerical model solves the drift–diffusion equations for electrons, holes, anions and cations and Poisson's equation on this grid by forward integration in time. Devices with a bandgap $E_g = 2\ \text{eV}$ were simulated during operation at a bias voltage $V_{\text{bias}} = 5\ \text{V}$. A detailed description of the numerical model can be found in the Supplementary Information sections A and B. Simulations were ran for devices with an initial homogeneous ion concentration $c_0 = 1 \times 10^{-1}\ \text{nm}^{-3}$. No binding energy was assumed between anions and cations. The electrodes were ionically-blocking and electrons and holes were injected from the contacts according to a dedicated injection model that gives rise to field dependent injection [4]. The injection model is described in detail in the Supplementary Information and has the advantage that injection is not affected by grid-point spacing. At the start of the simulations, no electrons and holes are present in the device. The hole and electron injection barriers were set at 0.5 and 1.5 eV respectively to simulate an asymmetric device. Such an asymmetry is realistic for actual planar LECs, in which both the anode and the cathode are made from a single material, e.g. Au. Bimolecular electron–hole

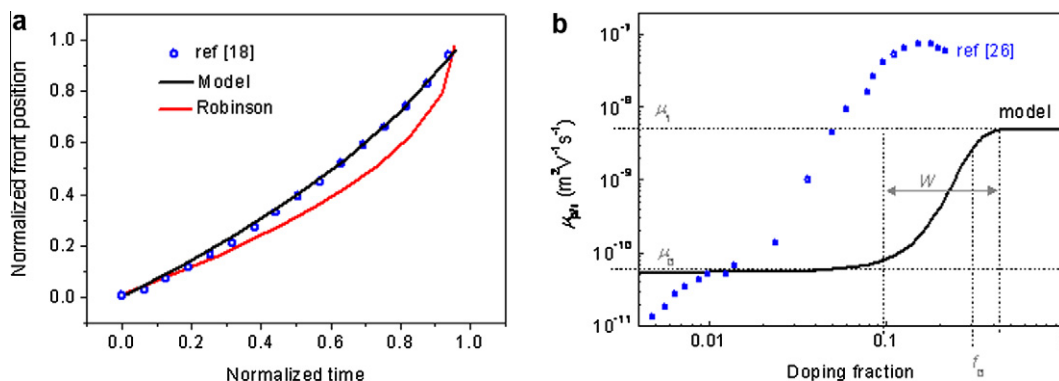


Fig. 1. (a) Front position during switch-on in an LEC as obtained experimentally (blue markers) [18], analytically (red line) [22] and by numerical modeling (black line). The model curve follows from modeling of a planar LEC with a doping dependent $\mu_{p/n}$ according to Eq. (1) for $\mu_0 = 5 \times 10^{-11}\ \text{m}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_1 = 5 \times 10^{-8}\ \text{m}^2\text{V}^{-1}\text{s}^{-1}$, $f_0 = 0.13$ and $W = 0.015$. (b) The electron/hole mobility as a function of the doping fraction. The blue graph was experimentally determined by Shimotani et al. [26] in regioregular P3HT (here the mobility values are divided by 10^2) and the black graph follows from Eq. (1) for $\mu_0 = 5 \cdot 10^{-11}\ \text{m}^2\text{V}^{-1}\text{s}^{-1}$, $\mu_1 = 5 \times 10^{-9}\ \text{m}^2\text{V}^{-1}\text{s}^{-1}$, $f_0 = 0.3$ and $W = 0.04$. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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