Charging and discharging of a planar polymer light-emitting electrochemical cell

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ABSTRACT

Planar polymer light-emitting electrochemical cells (LECs) with an interelectrode gap size of 670 μm and 495 μm have been activated by applying a fixed voltage bias of 20 V at a temperature of 340 K to enable them to reach different terminal currents before being discharged under short-circuit conditions. These discharging, or dedoping currents have been monitored for an extended period during which they have decreased by five orders of magnitude. The total dedoping charge has been determined by integrating the time-dependent dedoping current, which allows for the calculation of the cell's doping level. The data suggest that some additional doping has occurred after the formation of the LEC junction. The overall level of doping, however, is not strongly affected by the large amount charges injected after junction formation. In fact, the total dedoping charge can be approximated as the amount of injected charge, up to the moment of junction formation. The total dedoping charge, however, is sensitive to the interelectrode gap size of the planar cells. The results demonstrate the feasibility of detecting the minute discharging current of a large planar LEC down to pA level. The ability to determine the dedoping charge and its dependence on various operational and device-related parameters provides additional tools to facilitate understanding of the complex doping and dedoping processes in a polymer LEC.

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1. Introduction

Light-emitting electrochemical cells (LECs) are solid-state electroluminescent devices that employ a mixed ionic/electronic organic conductor as their active layer [1,2]. Polymer LECs are based on a mixture of a conjugated light-emitting polymer and a polymer electrolyte [3–8]. LECs can also be made with ionic transition metal complexes and other organic small molecules [9–14]. The operation of LECs involves both ionic and electronic charges. When electronic charges are injected from the electrodes, the luminescent polymer is simultaneously reduced (on the cathode side) and oxidized (on the anode side). Subsequently, the mobile ions migrate to the sites of the reduced and oxidized polymer chains, causing *in situ* electrochemical doping of the luminescent polymer. The LEC becomes fully functional when the p- and n-doped regions meet to form a light-emitting p-n or p-i-n junction.

Compared to organic or polymer LEDs, LECs are insensitive to the active layer thickness and the electrode work function. These unique device characteristics make them attractive candidates for

potential display and lighting applications. The versatility of LEC has been evidenced by the recent demonstration of light-emitting fibres and light-emitting papers, among other interesting applications [15–19].

The polymer LEC's insensitivity to active layer thickness allows for the demonstration of strongly-emitting planar LECs with an interelectrode gap ranging from a few μm to more than 10 mm [1,20–22]. Extremely large planar cells are particularly interesting due to their ease of fabrication and slow activation. The latter characteristic facilitates time-resolved studies of the dynamic LEC processes. It was from the time-lapse fluorescence imaging of extremely large planar cells that dynamic doping and junction formation processes were first visualized [20,23]. Much has been learned by examining how the doping profile and the doping propagation speed are affected by the salt used [24,25], the electrode work function [26,27], the thermal treatment and so on [28]. Moreover, the open structure of a planar LEC cell is ideally suited for various scanning probe studies of the junction electronic structure [22,29–33].

Planar LECs are typically turned on, or activated by applying a fixed voltage bias. It has been observed that the p and n-doping of the luminescent polymer originates from the electrode interfaces. And the doping fronts propagate, leaving behind a doped region

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until they meet to form a p-n junction. The cell current changes accordingly [23]. Initially it increases slowly as the doping fronts propagate. Since the doped regions are still seperate, the cell current is limited by the ionic conduction of the undoped region. After junction formation, the cell current begins to increase rapidly as the LEC becomes a forward-biased pn junction and an electronic current begins to flow. In the last stage the cell current reaches a plateau before decreasing as a result of degradation [23,34]. While these activation characteristics have been widely documented [27,34–36], the discharging of the planar cell, when the voltage bias is removed, has rarely been reported. The most significant observation so far has been that the dedoping of an activated cell is approximately equal to the time reversal of the doping process [21]. The doping fronts recede towards the electrode interfaces, leaving behind a widening quasi-intrinsic region between the still doped regions. This phenomenon has been exploited to realize a frozen p-i-n junction that displays a very high open-circuit voltage [37].

The dedoping current of a planar LEC, however, has never been measured. It is particularly difficult to measure the dedoping current of an extremely large planar LEC, which discharges slowly and at a very minute current. This requires a highly sensitive ampere-meter to monitor the dedoping current over a long period of time. The dedoping current will, howerver, allow for straightforward determination of the amount of doping charge injected and the doping level of the cell. Currently the doping level of a large planar cell is estimated by integrating the turn on/charging current up to the moment of junction formation [26,38,39]. This approach, however, relies on the assumption that additional doping does not occur after junction formation. Since the LEC current can increase by several orders of magnitude after the initial formation of junction, this approach must be justified for its validity.

In this study, several large planar cells were discharged after they were turned on to reach different terminal currents. In each run the dedoping current was recorded for an extended period and down to pA level. We discovered that the amount of dedoping charge was approximately equal to the amount of injected charge up to the moment when a p-n junction is fully formed. However, there was also evidence that some additional doping had occurred after junction formation. At low to medium injection levels, the total dedoping charge increased logrithmatically with the amount of total injected charges. At high injection levels, the total dedoping charge is independent of the amount of injected charge. Overall, the total dedoping charge varied by less than three fold when the terminal current and the amount of total injected charge increased by two orders of magnitude.

2. Experimental

All planar LECs in this study were fabricated via solution processing. The luminescent polymer, poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV), was obtained from OLEDKing Optoelectronic Materials Ltd, China with a molecular weight of $M_w = 3.3 \times 10^5$ and a polydispersity index of 1.4. The electrolyte polymer, polyethylene oxide (PEO, $M_w = 0.4 M$), and a salt, potassium triflate (KTf, 98%), were purchased from Sigma Aldrich and used as received. A cyclohexanone solution of MEH-PPV, PEO, KTf was prepared to have a weight ratio of 5:5:1.2 by mixing the solutions of MEH-PPV and PEO:KTf. The LEC solution was spin cast onto a $15\,mm \times 15\,mm \times 1\,mm$ sapphire substrate and subsequently dried for five hours at $50\,°C$ on a hot plate. On top of the LEC film, 75 nm of gold was thermally evaporated through a shadow mask with a BOC Edwards AUTO306 evaporator built into one of the gloveboxes. The finished cells had an active area of 7 mm by $670\,\mu m$ (Cells 1 and 2). Two other cells with a size of 7 mm by $495\,\mu m$ were also fabricated. The size of the cells was defined by the evaporated gold electrodes. The thickness of the gold electrodes was measured *in situ* with a quartz microbalance. All
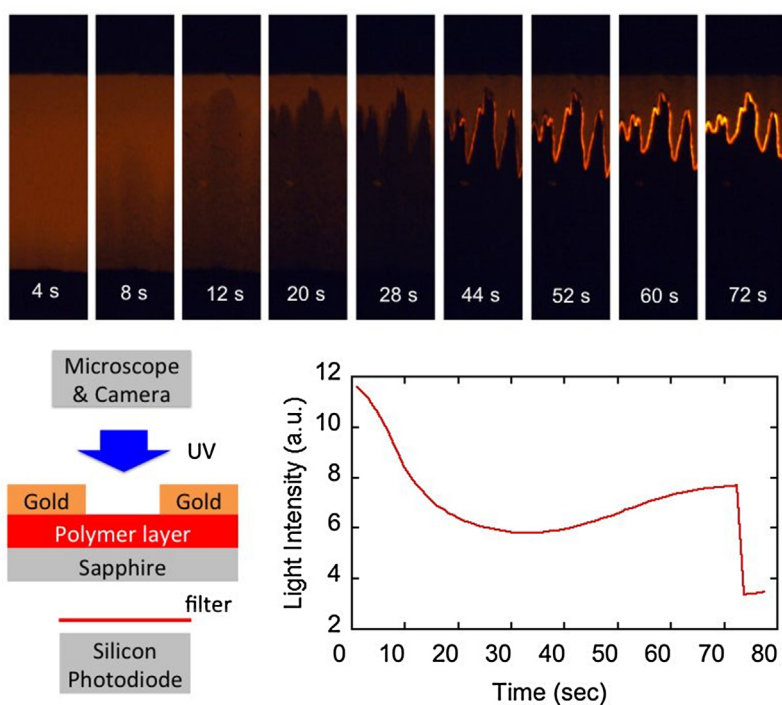
Fig. 1. Top: time-lapse fluorescence images of Cell 1 under activation at 340 K. The cell was biased at 20 V. The images were cropped to show the same region of the cell. Bottom left: schematic of the experimental set-up. Note that the cell was mounted inside a cryostat with two transparent quartz windows. Bottom right: light intensity as a function of time since the application of the voltage bias.