



# Long-term testing of polymer light-emitting electrochemical cells: Reversible doping and black spots



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## ABSTRACT

Polymer light-emitting electrochemical cells (PLECs) have been tested either continuously or intermittently for a long duration. *In situ* electrochemical doping of the polymer film causes fluorescence quenching and apparent luminance decay when the effect of quenching outweighs the effect on charge injection. The quenching-induced luminance loss, however, is partly recoverable when the cell is allowed to relax without an applied bias. The long test duration causes the appearance of large black spots in both photoluminescence and electroluminescence. Two very startling observations shed light on the nature of the black spots. First, black spot growth was completely suppressed when a cell was tested with a freshly deposited top aluminum electrode, even though the polymer film had been stored for up to nine months. Second, the black spots in photoluminescence gradually faded when the applied bias voltage was removed. The black spots in these PLECs were therefore sites of heavy doping that were promoted by changes that occurred at the cathode/polymer interface.

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## 1. Introduction

Polymer light-emitting electrochemical cells (PLECs) are solid-state devices whose active layer is doped *in situ* during operation [1]. Doping in PLECs bears similarity to the doping of conventional semiconductors, which requires the presence of counter-ions (i.e., ionized donors and acceptors in conventional semiconductors) to stabilize the additional charge carriers [2]. As a result of doping, both the electrical and optical properties of the luminescent polymer are significantly altered [3,4]. Injection electroluminescence occurs in the vicinity of the junction formed between p- and n-doped regions [5]. The interest in PLECs is motivated by both a desire to understand their complex device processes and the PLECs' application potential [6–16].

Like polymer light-emitting diodes (LEDs), PLECs possess the same processing and mechanical advantages of polymer devices [11,17–20]. A major obstacle preventing the practical application of PLECs is their poor operational stability. Early reports of PLEC lifetime are scant and the lifetime is typically on the order of tens of hours [21,22]. By reducing the electrolyte loading and using electrolytes with a wide electrochemical stability window, sandwich PLECs with an operating lifetime on the order of 1000 h at display brightness have been recently demonstrated [23–25]. These figures are expected to improve when better materials become available or when the PLEC junction is chemically stabilized [7,26–29].

The operating lifetime of a PLEC is typically studied in the same way as a polymer or organic LED [30,31]. A constant current is applied to the cell and a half-life is determined when the luminance has reached 50% of the peak value [23]. The apparent luminance decay in a PLEC, however, is not only caused by irreversible changes to

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the luminescent polymer and/or electrical contacts, but is also the result of fluorescence quenching when the polymer is doped.

In our study of large planar cells, the electrochemical doping manifested as fluorescence quenching is observed to be largely reversible when the applied voltage bias is removed or reversed [32]. The reversibility of doping explains why sandwich PLECs, when operated intermittently, display dramatic recovery of loss luminance when the polymer film is allowed to relax (de-dope) when idled [33,34]. Similar luminance recovery has also been observed in small molecule-based LECs [35]. On the other hand, there is evidence that the doping is not entirely relaxed even after an extended idling period and the cells develop large black spots in their electroluminescence (EL) images [34]. In this study, we elucidated the complex decay mechanisms of PLECs by subjecting identical sandwich cells to long-term intermittent and continuous testing. We identify dominant decay mechanisms during different stages of operation. We also present results that provide important clue as to the nature of the black spots in these PLECs.

## 2. Materials and methods

The sandwich PLECs used in this study were nominally identical and similar to the cells used in our previous studies [33,34]. All cells contained a luminescent polymer, poly[5-(2'-ethylhexyloxy)-2-methoxy-1,4-phenylene vinylene] (MEH-PPV), an ion-solvating polymer, poly(ethylene oxide) (PEO,  $M_n = 4 \times 10^5$  g/mol), and the salt lithium trifluoromethanesulfonate (Li triflate or LiTf). The cyclohexane solutions of MEH-PPV and PEO:Li triflate were blended to have a solute composition of MEH-PPV:PEO:Li triflate = 24:5:1 by weight. Polymer films were spin cast from this solution and subsequently dried at 50 °C for 5 h to remove any excess solvent. The polymer films were then thermally annealed at 130 °C for 30 min and quickly cooled to room temperature by placing them on a large copper heat sink. Using atomic force microscopy, the active layer thickness was measured using atomic force microscopy to be  $142 \pm 3$  nm. Aluminum (ca. 100 nm) was thermally evaporated on top of the LEC films through a shadow mask to serve as a cathode and define an active emitting area of 0.12 cm<sup>2</sup>. The devices were tested in a black box fitted with a calibrated photodiode. All devices were processed and tested inside a glove-box/evaporator system that was filled with dry nitrogen at room temperature. A computer-controlled Keithley source measurement unit (238) was used to bias the cells while simultaneously measuring the operating voltage and luminance. All cells were operated by applying a constant current of 20 mA with the ITO electrode biased positively relative to the aluminum electrode. The EL and PL images were captured using a Nikon D300s camera through the glove box window. For PL imaging, a handheld UV lamp was positioned below the PLEC with the biasing current removed.

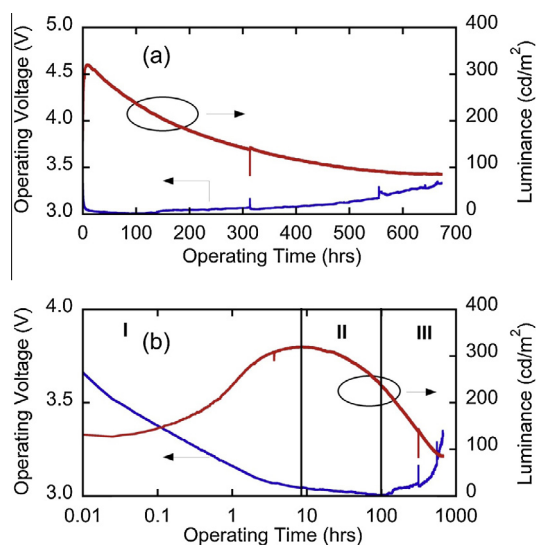
Intermittent testing was carried out on the same cell (Cell 2). For each run, the cell was stressed for 23 h. Subsequently, the cell was stored for 7 days in the glove box at 25 °C. This ON/OFF cycle was repeated 15 times. The first

run (virgin run) commenced after the deposition of the top aluminum electrode without delay.

## 3. Results and discussion

Fig. 1(a) shows the continuous operation of a cell (Cell 1) under a 20 mA constant current (or 167 mA/cm<sup>2</sup> in current density). The luminance and operating voltage were monitored as a function of time during the test. There was a brief interruption of the test at around  $t = 313$  h when the applied current was removed for less than 30 s. But this did not affect the overall test, as both luminance and operating voltage quickly recovered when the test current was re-applied. The brief recovery period (about 60 s) is included in the data for completeness but not discussed in the following. The total test period was 673 h or 4 weeks, among the longest for a PLEC. The total charge that passed through the cell during the test amounts to  $4.04 \times 10^5$  C/cm<sup>2</sup>, which is the highest to date for a sandwich PLEC. The long test duration brought out features that were not present in shorter tests. The cell luminance degraded sufficiently so that a luminance half-life of approximately 230 h can be inferred. The cell luminance displayed a monotonic decay after peaking at about  $t = 10$  h. The operating voltage, however, decreased for nearly 100 h before rising slowly. Much information can be deduced by considering the different behaviors of cell luminance and operating voltage in concert.

Fig. 1(b) shows the same data in semi-log form. The entire test duration can be divided into three regions based on the dominant decay mechanisms. In stage I, the cell displays “normal” PLEC behaviors when the cell luminance increased while the operating voltage decreased rapidly



**Fig. 1.** (a) Time evolution of luminance and operating voltage of a ITO/MEH-PPV:PEO:LiTf/Al sandwich LEC (Cell 1) operated at a constant current density of 167 mA/cm<sup>2</sup>. The cell was operated for the first time after the deposition of the top aluminum electrode. The test commenced after the deposition of the top aluminum electrode without delay. (b) The same data presented in (a) but plotted in a semi-log form with various regions of operation marked.

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