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Shaping electroluminescence with a large, printed bipolar electrode array: solid polymer electrochemical cells with over a thousand light-emitting p-n junctions

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Abstract: The electroluminescence from a solid polymer light-emitting electrochemical cell typically originates from a single, narrow p-n or p-i-n junction. The bulk of the active material is non-emitting, and must be doped before an emitting junction is formed. Here we show that the doping and emission profiles of a planar cell can be drastically altered with the introduction of a large, printed array of inkjet printed bipolar electrodes. Redox doping reactions induced at the wireless bipolar electrodes led to the simultaneous formation of over a thousand highly emissive p-n junctions uniformly distributed throughout the active layer of the large planar cell. The multi-junction cell achieved an 8-fold increase in light-emitting area, a 14-fold increase in peak current and 10 times faster response speed compared to a single-junction cell. Moreover, a giant open-circuit voltage of ~35 V was observed when the doped cell was allowed to discharge. Here, bipolar electrochemistry offers a simple and yet elegant solution to engineer a better light-emitting electrochemical cell.

Electroluminescence (EL) from an electrochemically induced p-n junction is a fascinating phenomenon that blurs the boundary between electrochemistry and semiconductor device physics. In a solid light-emitting electrochemical cell (LEC), the redox doping reactions involving a luminescent organic semiconductor and mobile electrolyte ions give rise to a dynamic light-emitting p-n junction.^[1, 2] Unlike the well-known organic light-emitting diodes (OLEDs), LECs perform well in a single-layer device structure made with air-stable contacts. LECs are attractive candidates for low-cost lighting applications due to their excellent compatibility with solution processing techniques.^[3-8]

The very junction formation process in an LEC is also responsible for a much slower turn on response than OLEDs as well as a narrow emitting junction that does not fully utilize the active layer material. In large planar LECs, it can take minutes for a narrow emitting junction to form.^[9] Electrochemistry offers an elegant and effective solution to these tradeoffs. Since only the p-n junction is EL-active, it is advantageous to form many equally spaced light-emitting junctions between the driving electrodes. To accomplish this without introducing additional electrical connections to the LEC, the bipolar electrodes (BPEs) are introduced. A BPE is an electrically floating conductor that can drive redox reactions wirelessly.^[10, 11] BPEs are traditionally used in liquid electrochemical cells for a wide range of applications.^[12-18] This includes the use of a large array of 1,000 micro-fabricated BPEs to generate electrochemiluminescence (ECL) for potential sensing applications.^[19] Using immobilized carbon micro-beads as BPEs, Sentic et al. demonstrated 3D ECL in a capillary filled with ECL reagents. The 3D ECL cell exhibits fast reaction kinetics and vastly enhanced light output.^[20] Recently, polymer-based LECs (PLECs) offer a solid-state platform for bipolar electrochemistry research with the demonstration of several unconventional BPE types.^[21-24]

Here, we show how large, closed BPE arrays can be exploited to shape and greatly enhance the EL output in a planar PLEC. 27×21 or 46×36 inkjet-printed silver nanoparticle (Ag-NP) discs were embedded in planar PLECs with an interelectrode gap size of 11 mm. The regular arrangement of the BPEs led to highly uniform initial doping and the subsequent formation of 567 or 1620 bright light-emitting p-n junctions. This resulted an 8-fold enhancement in the active emitting area, a 14-fold increase in peak current, and a 10-time faster turn on response compared to a single-junction control device. The intricate doping patterns also revealed how the various doping fronts interact to form some unexpected light-emitting junctions. Moreover, a large open-circuit voltage far exceeding the fundamental limit set by a single p-n junction was detected when the multi-junction cells were allowed to relax/de-dope under open-circuit conditions.

Figure 1. (a) A schematic of a planar PLEC with a 27 x 21 printed Ag-NP disc BPE array embedded in the polymer layer. (b) Height profile of the printed Ag-NP BPEs. (c) top view of the printed Ag-NP BPEs.

The PLECs in this study had a pair of 14.5 mm long driving electrodes (DE) separated by 11 mm at their inner edges. This allowed for the placement of a large number of printed BPEs between the DEs. Figure 1(a) shows the schematic of such a planar cell with a printed BPE array. The active material consists of poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene], or MEH-PPV, polyethylene oxide, or PEO, and potassium triflate, KCF₃SO₃. The 2D array was characterized before the polymer layer was cast on top, showing an average height of 340 ± 10 nm (Figure 1(b)) and an average diameter of 150 ± 2 μm (Figure 1(c)). The printed Ag-NP discs are not perfectly circular in shape, but are fairly uniform in size. The center-to-center spacing of nearest BPEs was 300 μm.

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Figure 2 shows an actual PLEC containing a 27 x 21 BPE array in full view. Two extra rows of 27 discs overlapped with the straight edges of the DEs. Figure 2(a) shows the PLEC without a voltage bias. The BPE discs appear as white dots under UV illumination. The image is dominated by the bright photoluminescence (PL) from the luminescent polymer, MEH-PPV. Figures 2(b)–2(f) show the PL images of the cell under an applied voltage bias of 200 V. In Figure 2(b), p-doping of similar sizes are visible from the anodic poles of all BPEs. This indicates the electric field within the PLEC was uniform on a global scale. Both BPE doping and DE doping grew in size with time, as shown in Figure 2(c) and Figure 2(d). The magnifying box of Figure 2(d) shows that the top two rows of BPEs are entirely surrounded by p-doping from the top DE. Light shaded BPE n-doping is also visible atop the BPE discs. Although p-n junctions had already formed between the p- and n-doped regions, EL was not yet visible against the strong PL background.

At $t=129$ s, EL became visible at some junctions, as shown in Figure 2(e). In Figure 2(f), EL is visible from nearly all junctions formed between the BPEs. The magnified boxes of Figure 2(f) shows that at the top of the cell, each BPE column is enveloped by a merged n-doped region. Light-emitting p-n junctions are formed at the lower tips of the dark, compact p-doped regions between the BPEs. The space between the n-doped regions are entirely occupied by the dark p-doping. Interestingly, EL is also observed in some sections of the nearly vertical junctions between the merged p- and n-doped regions. These vertical junctions are typically much dimmer than the junctions formed between the BPEs. At the bottom of the cell, the same behavior is observed except that the doping types are reversed. Figure S1 shows the time-lapsed images of a planar PLEC with a 46x36 BPE array under a 300 V bias. Highly uniform doping is once again observed from all BPEs, leading to the formation of bright light emitting junctions nearly mid-way between the BPEs as well as some vertical junctions.

Figure 2. Time-lapsed images of a planar PLEC with a 27x21 BPE array under UV illumination. The images are taken at (a) 0 s, (b) 15 s, (c) 63 s, (d) 93 s, (e) 129 s, and (f) 390 s after a 200 V voltage bias was applied.

Figure 3(a) is a full view of a second planar LEC with a 46x36 BPE array operated at 400 V. The image was taken in the dark when the cell current reached 1.7 mA. The strong EL illuminated

the entire test chamber like a light bulb. Figure 3(b) shows a single-junction control cell also operated under a 400 V bias and imaged with the same camera settings. From these two images, the emitting area as a fraction of the entire device area was calculated to be 36.9% and 4.6%, respectively.

Figure 3(c) shows the time evolution of cell current in four cells. In LECs, the cell current undergoes a sharp increase, or “turn-on” when the light-emitting p-n junction is first formed.^[9] For the multi-junction cells, EL and current turn-on occurred in less than 10 s. For the control cells, the junction was not fully formed until $t=110$ s, as shown in Figure S2. The much faster turn-on of the multi-junction cells is the result of the simultaneous doping reactions induced at the uniformly distributed BPEs. This reduced the effective distance that the doping fronts needed to travel to form a junction to only 0.15 mm. In addition to a faster turn-on, the multi-junction cells also exhibited a peak cell current that was approximately 14 times higher than the control cells, despite a lower initial current.

Figure 3. (a) A planar PLEC with 46x36 BPEs operated at 400 V, 360K, imaged in the dark. (b) A single-junction planar PLEC operated and imaged under identical conditions. (c) Time evolution of cell current of different cells. (d) Time evolution of open circuit voltage of different cells.

After the cell current had peaked, the applied voltage bias was removed and the open-circuit voltage (V_{OC}) was measured. Figure 3(d) shows the time evolution of V_{OC} of several cells. Interestingly, the cell exhibits a giant open-circuit voltage of nearly 35 V that decayed to 0.58 V in 700 s. Two other multi-junction cells with fewer BPEs also exhibited a large initial V_{OC} of 7.8 V and 7.1 V, respectively. The single-junction cells, in comparison, only showed a V_{OC} of 2.15–2.18 V. When the applied voltage bias was removed, the doping ions began to slowly diffuse out of the doping sites, causing the detection of a V_{OC} under the open-circuit condition. The V_{OC} of a single-junction cell is limited to 2.4 V, which is the size of MEH-PPV band gap. The multi-junction cells, however, can exceed this limit due to the formation of multiple junctions in series. An unexpected observation in the 46 x 36 multi-junction cell is an initial increase in V_{OC} for about 3 s after the applied voltage bias was removed. This peculiar behavior is analogous to the enhancement of photovoltaic V_{OC} observed in frozen-junction LECs that were allowed to partially de-dope and then re-frozen. The “controlled doping relaxation” removes microshorts in the junction, causing the LEC junction to exhibit better diode rectification and higher V_{OC} when illuminated.^[25] Here, the V_{OC} increase is likely of the same origin. The de-doping causes

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the temporary increase in V_{OC} due to the formation of less leaky, p-i-n junctions. Eventually, the V_{OC} decreases when the cell become less doped and more resistive.

The results presented above demonstrate that EL in a planar PLEC can be effectively shaped and more importantly, enhanced by introducing patterned arrays of BPEs. Unlike a single-junction LEC, the electrochemical doping in a PLEC containing a large, closed BPE array occurs at all BPEs at once. This greatly speeds up the doping process and increases the number of active junctions formed. The technique is versatile and not limited to square arrays of inkjet-printed Ag-NPs. Figure S3 shows a multi-junction cell made with 2379 evaporated Al disc BPEs arranged in a hexagonal lattice pattern. The cell once again exhibits junction EL between the BPEs. Multi-junction cells were also demonstrated using Aeropress coffee filters as shadow masks for evaporated BPEs or screen-printed BPEs based on a carbon ink. The multi-junction cells demonstrated in this study are similar in concept to "bulk homojunction" LECs containing dispersed conductive particles. Although not explicitly mentioned, the conductive particles such as indium tin oxide (ITO) macro-particles must have functioned as BPEs to form a large number of light-emitting junctions between the driving electrodes. The frozen bulk homojunction LECs also exhibit a giant V_{OC} when operated as photovoltaic cells.^[26] The random distribution of conductive particles and their tendency to aggregate, however, made it impossible to control the size and density of BPE particles.^[27] Printed BPE arrays, on the other hand, allow for the design of optimal BPE side, shape and pattern. A future study will explore micro-fabricated BPE arrays of higher densities and different lattice structures. In particular, a BPE lattice should be designed to avoid an open channel between the DEs in order to minimize DE doping and force the current flow through the junctions formed between the BPEs. Ultimately, the concept demonstrated here will be applied to thick sandwich cells to improve light output at a lower voltage bias.

In conclusion, we have demonstrated planar PLECs with large, closed arrays of inkjet-printed Ag-NP BPEs. The regular arrangement of the BPEs led to highly uniform initial doping and the formation of well over a thousand highly emissive light-emitting p-n junctions. Compared to a single-junction control cell, the multi-junction cells exhibit vastly enhanced peak EL output and 10 times faster turn on response. Moreover, a large open-circuit voltage far exceeding the fundamental limit set by a single p-n junction was detected when the multi-junction cells were allowed to relax/de-dope under open-circuit conditions.

Supporting Information.

Experimental details; PL and EL images of a PLEC with a 46x36 Ag-NP BPE array (Figure S1); PL and EL images of a single-junction control cell (Figure S2); PL and EL images of a PLEC with a thermally evaporated, hexagonal BPE array (Figure S3).

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Keywords: bipolar electrodes • light-emitting electrochemical cell • electroluminescence • electrochemical doping • p-n junction

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Entry for the Table of Contents

Solid-state polymer light-emitting electrochemical cells (PLECs) are demonstrated with over 1,000 individual electroluminescent p-n junctions between the planar driving electrodes. The PLECs contain a large, ink-jet printed array of Ag nanoparticle discs that functioned as bipolar electrodes (BPEs) to induce simultaneous redox doping reactions at their opposite poles. Compared to a control cell without any BPE, the PLECs with a BPE array exhibit a giant open-circuit voltage as well as drastically improved turn-on response and light output.