VISUALIZING BIPOLAR ELECTROCHEMISTRY IN SOLID STATE- IN SITU ELECTROCHEMICAL DOPING OF LUMINESCENT CONJUGATED POLYMERS

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Abstract

We use a micro-manipulated vacuum probe station to generate and visualize bipolar electrochemical redox reactions in a solid-state polymer light-emitting electrochemical cell (PLEC). *In situ* electrochemical p- and n-doping of a luminescent polymer is initially induced via a pair of biased metallic probes in direct contact with the luminescent polymer. Subsequently, the biased probes are moved to contact the planar aluminum driving electrodes of the PLEC to activate the device. By analyzing the complex doping patterns generated, we conclude that the doped polymers have functioned as bipolar electrodes (BPEs), from which electrochemical p- or n-doping are induced wirelessly. The potential energy barrier between the polymer BPE and the undoped polymer have played a major role in doping initiation. In a separate planar cell of a smaller gap size, a pair of planar aluminum electrodes was driven in such a way that they functioned as long BPEs to create five coupled and strongly emitting polymer p-n junctions. These results offer vivid visualization of the intriguing bipolar electrochemical phenomena in a solid-state polymer blend. The ability to form a BPE *in situ*, and in the form of a heavily doped polymer offer innovative ways to modify the doping profiles in molecular devices. The all-polymer BPE also expands the realm of bipolar electrochemistry to beyond that of a conventional liquid cell containing metal or carbon electrodes.

Introduction

The simplest two-terminal electrolytic cell consists of a pair of driving electrodes separated by an electrolyte solution. Adding a wireless conductor to the electrolyte creates a bipolar electrode (BPE) that is capable of driving both reduction and oxidation reactions even though it is not directly connected to a power source. The redox reactions preferentially occur at the extremities of the BPE where the potential difference between the BPE and the electrolyte solution is the largest.¹⁻³ Electrochemistry involving a bipolar electrode, or bipolar electrochemistry, has become an increasingly versatile and powerful method with applications in electrodeposition and patterning,⁴ growth of nanotubes and nanoparticles,⁵⁻⁷ fuel cells,⁸ and catalyst screening⁹⁻¹⁰ among others.¹¹⁻¹⁵

Although many of the applications mentioned above are more commonly accomplished with a wired working electrode, a BPE offers distinctive advantages due to its wireless nature. For example, millions of dispersed micro-BPEs can be addressed remotely to generate homogenous electrochemiluminescence in bulk.¹⁶ Suspended, wireless BPEs can have net motion when propelled by bubbles generated asymmetrically at the poles.¹⁷⁻¹⁸ In the direction of the applied field, the solution potential along the BPE is spatially varying. This property of the BPE has been exploited to produce materials with a compositional or doping gradient,^{7, 19-20} and Janus particles in bulk.²¹⁻²²

These bipolar electrochemical systems contain a liquid or gel electrolyte in contact with bipolar electrodes that are either metallic or carbon conductors. Recently, our group demonstrated that bipolar electrochemistry could also be combined with solid-state electrochemistry in a polymer light-emitting electrochemical cell (PLEC).²³ A PLEC was initially demonstrated as an alternative to the common polymer light-emitting diodes (PLED).²⁴ Both PLEC and PLED employ a luminescent conjugated polymer as the light emitter. The PLEC, however, also contains a solid polymer electrolyte (SPE) mixed together with the luminescent polymer. A sufficiently large external voltage bias causes in situ electrochemical p- and n-doping of the polymer next to the driving electrodes. The doping fronts

propagate inward until they meet to form an electroluminescent p-n or p-i-n junction. The PLEC is a solid-state electrochemical cell based on a mixed ionic/electronic conductor.²⁵⁻²⁶

Adding a floating metallic conductor to the PLEC film can cause additional doping if the external bias and/or the size of the conductor are sufficiently large. The electrochemical p- and n-doping originate from the extremities of the floating conductor and propagate in opposite directions. As many as four light-emitting junctions are formed when doping from the floating conductor interacts with doping that originated from the driving electrode. This is an example of bipolar electrochemistry at work in a solid-state device.²³

The solid-state PLEC offers some unique opportunities and advantages to explore the phenomenon of bipolar electrochemistry. For example, the solid PLEC film allows for the facile formation of driving electrodes and BPE on top of the polymer film via conventional vacuum deposition techniques. Cell and BPE geometries can be easily modified with the shadow mask design. The PLEC has two built-in indicators, photoluminescence (PL) and electroluminescence (EL), from which the dynamic bipolar electrochemical processes can be visualized. Finally, the lack of a liquid solvent allows for the probing of transient phenomena without interference from convection, and as the following study demonstrates, the ability of modifying the PLEC film itself to function as bipolar electrodes.

In this study, the electrochemical redox reactions have been visualized with unprecedented clarity via fluorescence imaging. The doping patterns suggest that the potential energy barrier between the polymer BPE and the undoped polymer nearby plays a major role in doping initiation. And the polymer BPE itself is not inert when functioned as bipolar electrodes.

Experimental Methods

In this study we fabricated extremely large planar LECs with an interelectrode gap of over 10 mm, a device configuration pioneered by our group and particularly suited for visualizing

electrochemical and bipolar electrochemical phenomena via optical imaging.²⁷⁻²⁹ The planar LECs had an active layer consisting of three compounds. 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, $M_w=2M$), and the potassium triflate (KTf, 98%) salt, were purchased from Sigma Aldrich and used as received. Cyclohexanone solutions of MEH-PPV (10 mg/ml) and PEO:KTf (20mg:3.85mg/ml) were mixed to create a casting solution of MEH-PPV:PEO:KTf at a weight ratio of 1:1.3:0.25. 100 μ l of the solution was dispensed onto square glass substrate (16 $\times$ 16 mm²) and spun at 2000 rpm. The resulting polymer film had a thickness of 300 nm, as determined with a DektakXT stylus surface profiler. The polymer film was dried at 50°C for at least 5 hours to remove any residual solvent. Aluminum electrodes of 100 nm in thickness were thermally evaporated onto of the polymer film to create a planar LEC with an interelectrode spacing of either 10.7 mm or 2.1 mm. The above device processing steps were carried out in a nitrogen-filled glove box/evaporator system with low levels (<1 ppm) of oxygen and water.

The finished LECs were placed in a sealed glass vial and transferred into Janis ST-500 micron-manipulated cryogenic probe station. The cells were exposed to air briefly (around 1 minute) during the loading process. A small amount of silver thermal paste was applied to the gold plated sample stage to improve thermal contact with the glass substrate and to provide a non-reflective background for imaging. The probe station chamber was then sealed and evacuated to a pressure of approximately 5×10^{-4} torr with an oil-free turbo-pump. Gold and tungsten probes of 100 μ m tip radius were brought into contact with the polymer film or with the aluminum electrodes for testing. A Labview-controlled Keithley 237 high-voltage source measurement unit was used to source voltage bias to the probes and simultaneously measure the resulting current. The planar LECs were imaged with a computer-controlled Nikon D300 digital SLR camera equipped with a Tamron 90 mm 1:1 macro-lens. A UV ring lamp

provides illumination to the polymer film through the quartz window of the sample chamber. The temperature of the sample stage/planar LEC was controlled with a CryoCon temperature controller.

Results and Discussion

As shown in Figure 1 (i), the planar LEC has two aluminum electrodes deposited on top of the polymer film. The PLEC was placed on the sample stage of a micro-manipulated probe station and heated to 340 K under vacuum. The PLEC film was illuminated with a UV ring light from above the quartz widow.

Figure 1. In situ electrochemical doping of MEH-PPV induced with a pair of biased probes. The cell was heated at 340 K under vacuum in a probe station. (i) A schematic of the 10.7 mm planar LEC and biased metallic probes. (ii) Probe current as a function of time at a bias voltage of 60 V. (iii) Time-lapse fluorescence images of the polymer film. The imaging times are 57s, 92s, 212s, 327s, and 362s. These times have been labeled on the probe current vs. time curve in (ii). Note the last image (e) was taken when the applied bias was removed.

The voltage bias, however, was not initially applied to the aluminum driving electrodes. Instead, a pair of metallic probes, biased at 60 V between them (gold probe +, tungsten probe -), was brought

into contact with the polymer film. A running Labview program sampled the probe current every second. Electrical contact with the LEC film was confirmed when a sharp jump in current from the background level of about 30 pA to 13.6 nA at $t=52$ s. Subsequently, the probe current increased rapidly to about 35 μ A at $t=200$ s and eventually reached close to 50 μ A. With the probes fixed in place and a constant voltage bias of 60 V, the probe current increased by more than 3,600 fold!

The enormous increase in probe current is a direct consequence of in situ electrochemical doping. The effect of doping is two-fold. One, it rendered the polymer film between the probes conductive and caused the probe current to increase. Two, it caused strong PL quenching due to the formation of band gap states.³⁰ Figure 1 (iii) provides a visual account of the dynamic doping process by exploiting the optical effect of PL quenching. The strong orange PL between the probes became quenched as soon as the biased probes were brought into contact with the polymer film. The dark p-doped region occupied a larger area than the lighter n-doped region. Both doped regions grew in size. EL is visible in (b)-(d) at the boundaries between the p- and n-doped regions. EL in a PLEC is the result of radiative recombination of injected electrons and holes in the PLEC junction under forward bias. EL disappeared when the applied voltage bias was removed, revealing a sharp boundary between the p- and n-doped regions (e). For convenience and reasons to be explained later, we call these doped regions p- and n-doped BPE regions respectively.

Subsequently, the probes were repositioned to contact the aluminum driving electrodes and a voltage bias of 800 V was applied. This created a unique situation where the PLEC film between the driving electrodes contained regions of doped polymer that were not in direct contact with the driving electrodes. How do these isolated p- and n-doped regions respond to the 800 V applied to the driving electrodes? Figure 2 is a visualization of this intriguing process.

Figure 2 (i) is a schematic showing the new probe positions. Note that the cell orientation in (ii) and (iii) is rotated 90° degrees relative to (i). Figure 2 (iii) (a) depicts the cell just before the 800 V bias

was applied. Comparing this image with Figure 1 (iii) (e) reveals that some de-doping had occurred during the 385 seconds it took to reposition the probes. The

Figure 2. In situ electrochemical doping driven by a pair of aluminum electrodes. (i) Schematic of the 10.7 mm planar LEC showing the positions of the biased probes. (ii) A schematic showing the electronic and ionic charge carriers in the LEC film. (iii) Time-lapse PL images of the cell before (a) and after the application of an 800 V bias across the driving electrodes. The images are taken at 722s, 757s, 772s, 782s, 792s, and 807s.

dedoping caused the doped BPE regions to become lighter in color. A less doped, quasi-intrinsic region with negligible PL quenching is visible where the p-n junction was first formed. The regions near the probe contact points, however, remained heavily quenched in PL. Judging by the degree of PL quenching, the doping in both p- and n-doped BPE regions exhibited a strong doping gradient. The doping concentration decreased radially away from a heavily doped core region. The doped regions had a core/shell structure.

Despite the enormous spacing of 10.7 mm between the driving electrodes, an 800 V bias was sufficient to induce strong doping from both the positive and negative driving electrodes with the cell maintained at 340 K. The p- and n-doping fronts propagated continuously, leaving behind a doped region that grew in size with time.

The presence of the doped BPE regions in the center of the cell did not affect the doping patterns of planar cell. The doped BPE regions, however, underwent changes that are puzzling at first sight. Figure 2 iii (b) shows new, cone-shaped doping originating from both core BPE regions. From the n-doped BPE core, faint doping shot up but became narrower and eventually faded out in (c)-(f). At the same time, new doping from the p-doped BPE core propagated downward and grew in size until it met the n-doping front that originated from the bottom driving electrode.

How do we explain the appearance of new doping from the isolated, doped BPE regions? We learned that a metallic disc deposited between the driving electrodes in a planar PLEC could function as a bipolar electrode to induce doping at its extremities.²³ Since the luminescent polymer MEH-PPV can also be doped metallic, a logical explanation of the new doping is that of a bipolar electrochemical origin. The doped BPE regions had functioned as bipolar electrodes due to their elevated conductivity. Doped polymers are already widely used in PLEDs and PLECs as the hole injection electrode.³¹⁻³⁴ Polymers can also be doped or deposited via a conventional metal bipolar electrode.^{19, 35-37} Here we show that a doped polymer can function as a bipolar electrode itself and can induce redox reactions in the same polymer nearby.

Electrochemical doping of a conjugated polymer such as MEH-PPV involves reduction or oxidation of the polymer and the insertion of counter ions to neutralize the injected electronic charges.³⁸ The counter ions, in the case of a PLEC, are supplied by the polymer electrolyte. Unlike the doping of a conventional, crystalline semiconductor, the counter ions do not become part of polymer chain (i.e. no breaking of covalent bonds). Like chemically doped silicon, a doped polymer is an electrically neutral

material with additional mobile charge carries. Figure 2 (ii) depicts the charge distribution of doped BPE regions under bias. The p-doped BPE region contains equal numbers of mobile holes and anions (CF_3SO_3^-). With the top driving electrode biased positive, new p-doping is induced at the lower half of the p-doped BPE. The n-doped BPE region contains equal numbers of mobile electrons and cations (Li^+). New n-doping is induced to propagate upwards in accordance with the polarity of the applied bias.

Two important facts should be noted. First, the induced doping from both p- and n-doped BPE regions did not originate from the extremities of the large doped shell but rather from the much smaller core regions. This observation confirms that only the more conductive, dark core regions had sufficiently elevated conductivity to function as BPEs. Second, both doped BPEs promoted only one type of doping-p-doping from p-doped BPE and n-doping from n-doped BPE.

Charge neutrality requires that the redox reactions at the BPE to be coupled and balanced. In other words, a reduction reaction (n-doping) on one extremity should be accompanied by an oxidation reaction (p-doping) on the other extremity that occurs at the same rate. It is tempting to regard the two doped BPEs as a single, connected BPE from which both p- and n-doping had indeed been observed. This scenario, however, is highly improbable because the doped BPEs are separated by a less quenched, quasi-intrinsic region. The fact that the new n-doping had nearly disappeared in (f) when the new p-doping was at its maximum size means that they are not balanced through the same BPE. The fast dissipation of the n-doped BPE is consistent with the observations that the n-doped MEH-PPV had a lower conductivity and fast relaxation than p-doped MEH-PPV.^{26, 29}

To rationalize the observations in Figure 2, we need to realize that the BPEs in this study are doped regions of a polymer in contact with the undoped regions of the same polymer. The BPEs are not inert in that they can be reduced or oxidized themselves. Figure 3 uses the p-doped BPE as an example

to illustrate the doping processes involving the p-doped BPE core and the surrounding polymer when the voltage bias was just applied to the driving electrodes.

Figure 3. Schematic representation of the doping processes around a p-doped BPE under bias. The upper portion shows the p-doped BPE with a doping gradient. The white trace is the PL intensity across the entire p-doped BPE though its core. The data were extracted in Matlab. The thick, black dashed line represents the solution potential. The horizontal white dashed line represents the potential of the p-doped BPE core. The lower portion shows the energy level diagrams of the BPE core and its outer regions.

The doped BPE region in Figure 2 (iii) (a) is rotated 90° and shown at the top of the Figure 3. The PL intensity across the p-doped BPE has been extracted from Matlab and shown as the white trace. The presence of heavily quenched core region is obvious from the PL intensity profile. The solution potential is represented by the black dashed line. Note the potential shown scales with the potential energy of electrons and is opposite to the electrostatic potential. The dark core region is assumed to be metallic with a constant potential. The potential of the BPE shell should gradually approaches the solution potential towards the edges of the BPE shell. Here we assume the potential of the BPE shell is the same as the solution potential. Therefore, the largest potential differences, δ^+ and δ^- , occur at the edges of the core and are responsible for driving the redox reactions. The lower portion of Figure 3 shows the energy level diagrams of the BPE region. MEH-PPV has an energy gap of 2.4 eV and a non-

degenerate ground state. Heavy p-doping in the core introduces bi-polaron bands in the energy gap that are empty. The less doped shell contains discrete polaron levels that are singly occupied. These band gap states are responsible for the observed PL quenching in the doped polymer.³⁰

The vertical dashed lines in the energy level diagram represent the boundaries between the core and shell, where redox reactions occur. On the right hand side, the shell loses an electron to the core and is oxidized (this causes the positive polaron to become a positive bipolaron or a neutral polymer to become a positive polaron). A negative counter ion (CF_3SO_3^-) moves in to compensate the positive charge at the site of oxidation. As a result, new p-doping is observed from the RHS of the BPE core. For new n-doping to occur on the left hand side, however, an electron must be injected to the upper polaron level of the shell to create a negative polaron, which is difficult due to the large potential energy barrier that the electron must overcome. A more likely process is for the core BPE to retain the injected electron and eject a negative counter ion across the boundary. This leads to a dedoped polymer on the LHS of the core. In this fashion, the core BPE remains electrically neutral. The counter ion CF_3SO_3^- is also balanced as shown. The overall reaction involves a new oxidation reaction on the RHS that leads to new p-doping and a dedoping process that is the reduction of the BPE core itself. Similar arguments can also be made to explain the fact that only n-doping is observed from the n-doped BPE. The doped polymer BPE induces a doping reaction on one extremity that is balanced by a dedoping reaction on the opposite extremity.

The above explanation is strongly supported by the doping patterns shown in Figure 2. We observe that with time the dark core shrunk to an asymmetric shape due to dedoping that occurred preferentially on the topside for the p-doped core. Eventually the dark core disappeared altogether. The region that used to be the p-doped core even became a lighter shade than the surrounding shell region. This phenomenon was never observed when the doped BPE regions were allowed to dedope without an applied bias. The bipolar electrochemical actions of the doped polymer are responsible for the observed doped patterns.

The p-doping from the p-doped BPE persisted until it made contact with the n-doping from the negative driving electrode, as shown in Figure 2 (iii) (f). However, EL was not observed at the junction formed and the n-doping front kept propagating upwards. EL was only observed when the doping fronts from the driving electrodes had met to form a long and jagged light-emitting p-n junction. This suggests the doping from the BPE was of an insufficient level due to the transient nature of the doped BPE.

The simple device configuration shown in Figure 1 (i) allowed for a different demonstration of bipolar electrochemistry. We note that when a voltage bias was applied to the pair of probes, the aluminum bar electrodes on both sides of the probes were electrically floating and could function as a BPE. However, we did not observe any doping along the inner edges of the aluminum electrodes due to the large gap size between them and the close spacing between the probes. The circular doped region, which stopped growing after 297 second, represented the spatial extent of the region that had a significant electrical field before the doped had occurred. In order to observe any bipolar electrochemical reactions, we need to decrease the separation between the deposited aluminum electrodes and/or increase the separation of the biased probes.

Figure 4. In situ electrochemical doping driven by a pair of gold probes. The planar aluminum electrodes at the top and bottom were not connected. The cell was heated to 390 K and under UV illumination. A 10 V DC bias was applied between the probes. Time elapsed since the voltage bias was applied: (a) 35 sec, (b) 75 sec, (c) 325 sec. The equivalent circuit is shown in (d) corresponding to the cell that is emitting in (c).

In Figure 4, we show a planar LEC with a gap size of 2.1 mm. A pair of gold probes was brought into contact with the polymer film at 2.4 mm apart. A 10 V bias was applied between the probes with the cell heated to 390 K. Under these conditions, we observed strong doping from both probes as well as the inner edges of the aluminum electrodes, as shown in Figure 4 (a)-(b). The polymer regions next to the aluminum electrodes were doped p-type on the left and n-type on the right. The floating aluminum electrodes had functioned as BPEs. The various doped regions expanded and eventually fill up the entire space between the two aluminum electrodes. A total of five, isolated light-emitting p-n junctions were formed (c). The equivalent circuit of the arrangement is shown in (d). Note that the p-doping has a very circular, compact shape, while the n-doping is heavily branched and resembles a fractal. The large work function of the gold electrode makes it more suitable for p-doping and less so for n-doping of the MEH-PPV. This is another example of the importance of the potential energy barrier for doping initiation.

Conclusions

In summary, we studied the electrochemical and bipolar electrochemical doping of a mixed polymer conductor in a solid-state electrochemical cell. The extremely large planar LEC configuration offers unique opportunities to visualize the doping processes. We demonstrated, for the first time, that a doped polymer could function as a bipolar electrode to induce redox doping reactions wirelessly. In the p-doped BPE, electrochemical p-doping is induced on one end which is balanced by a reductive dedoping reaction on the opposite end. In the n-doped BPE, only electrochemical n-doping is observed which is balanced by an oxidative dedoping reaction. In addition, we showed that in a smaller planar LEC, a pair of biased metallic probes at a larger separation could induce both p- and n-doping from the nearby aluminum electrodes, which functioned as BPEs, to form five light-emitting p-n junctions. The solid-state nature of the PLEC as well as its built-in EL and PL indicators make it a very versatile platform for exploring the fascinating phenomena within bipolar electrochemistry as well as the polymer mixed conductor itself.

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