RECENT PROGRESS ON POLYMER LIGHT-EMITTING ELECTROCHEMICAL CELLS

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A polymer light-emitting electrochemical cell (LEC) is a bipolar p-n junction device; when biased, a dynamic light-emitting *p-n* junction is created. The active layer of an LECs is a blends of conjugated polymers and solid electrolytes. Significant progress have been made since the invention of the LEC. Device turn-on speed and quantum efficiency are significantly improved. Novel device characteristics are also discovered. In this paper, we summarize these progress.

1. Introduction

Recently, we developed a new type of light-emitting device: the light-emitting electrochemical cells (LECs) which combine the novel electrochemical properties of conjugated polymers with the ionic conductivity of polymer electrolytes.[1,2] The operating mechanism proposed for the polymer LEC involves the following steps:

(i) Electrochemical p- and n-doping in the regions adjacent to anode and cathode, respectively, upon application of voltage greater than the bandgap energy;

(ii) Formation, in situ, of a p-n junction within the active layer.

(iii) Radiative recombination of p- and n-type carriers within the compensated p-n junction.

This novel approach enable the use of air stable metals as electrodes and, in the meantime, achieve efficient and balanced charge injection. In principle, device with high quantum efficiency and low turn-on voltage are expected.

Since its invention, significant progress have been achieved in improving device performance [3], and novel device configuration has also been demonstrated [4]. In this paper, we summarize these recent progresses.

2. Interpenetrating Networks for Improved LEC Performance

From the LEC mechanism, it is obvious that the speed of p- and n-type doping and the speed of formation of p-n junction will depend on the ionic conductivity of solid electrolyte. Because of the generally non-polar character of luminescent polymers like poly(phenylene vinylene), PPV, and its soluble derivatives and the polar character of solid electrolytes, the two components within

the electroactive layer will be phase-separated. Thus, the speed of the electrochemical doping and the local density of electrochemically generated p- and n-type carriers will depend on the diffusion of counter-ions from the electrolyte into the luminescent semiconducting polymer. Consequently, the response time and the general performance of the LEC device will depend on the ionic conductivity of the solid electrolyte and the phase behavior of the electroactive composite comprising electroluminescent polymer and solid electrolyte. Because the physical/chemical properties of this composite layer were not optimized in early studies [1], the efficiency of the initial LEC devices was generally lower than corresponding LED devices and the response was relatively slow.

In the first part of this paper, we demonstrate a methodology for increasing the ionic conductivity within the layer and, simultaneously, for controlling the morphology of the phase separated microstructure of the electroluminescent polymer - solid electrolyte composite. The idea is to use a bi-functional (surfactant-like) liquid compound with high boiling point as additive to facilitate the phase separation and to ensure maximum interfacial surface area between these two phases, and ideally, to support the formation of an interpenetrating network of electroluminescent polymer in the composite. If these additive compounds have, in addition, a relatively high dielectric constant, the ionic conductivity will also be enhanced. Liquid compounds for use as additives in the active layer in the LEC should fulfill following requirements:

- The compound should be bi-functional with an A-B molecular structure, where A is a polar moiety and B is a non-polar moiety;

- The polar moiety (B) should have moderate to high dielectric constant;

• The compound must be miscible with the solvent from which the electroactive layer is processed;

• The compound should have high boiling point.

The addition of low molecular weight liquids with high dielectric constant (for example ethylene carbonate or g-butyrolactone) to the polymer electrolyte as plasticizers to enhance both the mobility and the concentration of ionic charge carriers is well known from studies in the field of polymer electrolytes. [5] Our approach builds upon this earlier work on gel-like polymer electrolytes; the difference, however, that in the electroactive material for LECs, the additive compound must serve two purposes at the same time. In addition to the improving ionic conductivity, these additives act as bifunctional "surfactants" to facilitate formation of an interpenetrating network morpholgy within the electroactive layer.

Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene), MEH-PPV, was prepared using the general synthesis described elsewhere. [6] Poly(ethylene oxide), PEO, (molecular weight 400,000) was purchased from Polysciences. Lithium trifluoromethanesulfonate (Li triflate) was purchased from Aldrich. Li trifluoromethanesulfoimide (Li imide) was kindly supplied by 3M Specialty Chemical Division.

LEC devices were fabricated on transparent, indium-tin oxide (ITO) coated glass substrates. The geometric structure was similar to that in ref. [1]. Thin films of the blend of MEH-PPV, PEO containing Li triflate and additive were used as the active light-emitting layer between ITO and aluminum electrodes with the following typical composition: MEH-PPV: PEO: additive = 1 : 1 : 1. The molar ratio of lithium triflate to PEO was 1:20. The composite polymer film was spin-cast from cyclohexanone solution inside a controlled atmosphere box onto the ITO substrate, and thermal evaporated aluminum layer was used as back electrode. The active area of the devices was 12 mm^2.

We have chosen octylcyanoacetate, OCA, as the additive for this study. [3] The ITO/MEH-PPV + PEO(Li$^+$)/ Al devices performance was dramatically improved. The brightness of these devices exceeds 1,000 cd/m^2 at 3.0 V, dramatically improved over identical device without the additive (ca. 10 cd/m^2 at 3V). The external quantum efficiencies of the ITO/MEH-PPV + PEO(Li$^+$)/ Al devices with OCA are in the range 1-2.5% photon per electron, similar to

light-emitting diodes made with the same MEH-PPV.

The turn-on response of the ITO/MEHPPV + PEO(Li$^+$)/ Al cell is shown in Figure 1; the response time is remarkably improved by the OCA additive. For the device using PEO + Li triflate as electrolyte, the response time is in the range of seconds. For the device fabricated at same composition and conditions but with OCA as additive the response time improved to tenth miliseconds. We succeeded in further increase the response speed to millisecond range by using combination of Li imide + PEO + OCA as electrolyte. The response speed in this case is already compatible with typical value for LCD display.
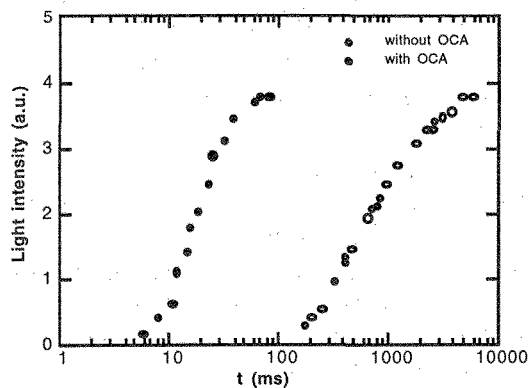

Figure 1. Current and light output versus voltage for ITO/MEH-PPV + PEO(Li$^+$)+ OCA/Al light-emitting electrochemical cell, with ITO wired as the anode.

To characterize the role of the additive in controlling the morphology of the composite, a thin film (1000-2000 Å) of MEH-PPV + PEO/Li + Additive (OCA) in the ratio of 1:1:1 was spin cast from solution and subsequently dried at 70° C. For TEM studies, the blend films were overcoated with a thin carbon layer (approx. 10 nm thickness)), floated on water and picked up on gold TEM grids with the carbon layer on top. In order to enhance the contrast, the PEO was dissolved out of the blends by immersing the films (on the grids) in water. The extracted films were shadowed by Pt/Pd from bottom side. Pure MEH-PPV films were also examined for comparison purpose.

The TEM micrographs, as shown in Figure 2, show that the morphology of the phase separated composite material is that of a bicontinuous three-dimensional interpenetrating network. The open immobile network of semiconducting

polymer (MEH-PPV in this case) is filled with PEO/Li with typical dimensions in the range 10-100 Å. Because of the bifunctional, surfactant-like nature of the additive (A-B, polar-nonpolar), the high surface area bicontinuous network morphology self-assembles.
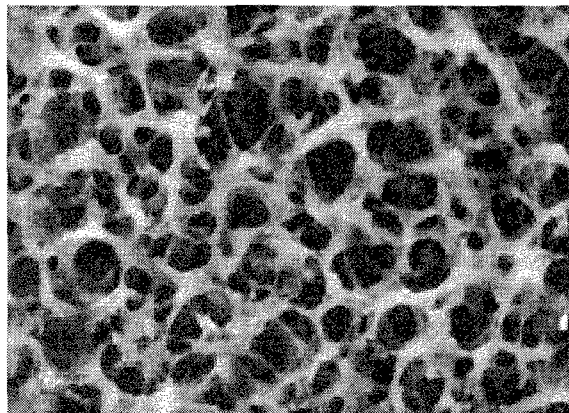

Figure 2. TEM micrograph of (MEH-PPV + PEO(Li$^+$) + OCA) composite film (1.5 cm = 500 nm)

The bicontinuous network morphology is ideal for the light-emitting electrochemical cell for the following reasons:

(i) The semiconducting polymer forms a continuous network phase enabling electronic transport of injected electrons and holes.

(ii) The electrolyte forms a continuous network phase as a relatively high dielectric constant medium (due to the polar end of the additive) enabling fast ion transport.

(iii) The intimate intermixing of the bicontinuous network at nm length scales enables relatively rapid transport of ions from the electrolyte into the semiconducting polymer during electro-chemical doping.

3. Two-color LEC

Confirmation of the LEC operating mechanism came from the direct observation of the light-emitting p-n junction in LECs fabricated in a planar electrode configuration.[1,2] Figure 3 shows an optical microscope photograph of the planar structure LEC. The light-emitting junction is a narrow region with width only a fraction of the total spacing between electrodes. As shown in the photo, when the inter-electrode spacing is 15 μm, the p-n junction width is only about 2 μm. Due to the asymmetry of the active conjugated polymer (e.g. possibly resulting from different mobilities for electrons and holes, different densities of states versus energy in the π and π^* bands, etc.), the junction is off center and closer

to one electrode. When the polarity of external bias changes, the position of this junction will also change and shift closer to the opposite electrode.
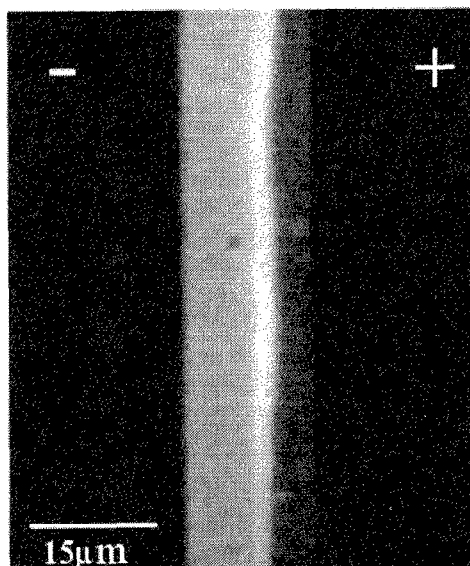

Figure 3. Optical microscope photograph of an operating polymer LEC in the planar electrode configuration. With 4 volts bias applied across the pair of electrodes, the emission light from the dynamically formed p-n junction can be clearly seen.

The two color LEC was fabricated in the sandwich configuration. Since the radiative recombination of electrons and holes only occurs within the light-emitting junction, the light-emitting species inside the p-n junction determines the emission color. For single layer LECs, the emitted color is insensitive to the precise position of the junction. However, for LECs consisting of a polymer bilayer as the active medium, i.e. two layers of different luminescent polymers, the p-n junction can be placed in either one of the two layers, depending on the bias. Note that the thickness of the p-n junction is dependent on the boundary conditions; in the sandwich configuration, the width of the junction must be less than the device thickness (and much less than the 2 μm width in the planar configuration of Figure 3). In the second part of this paper, we report a bilayer light-emitting electrochemical cell, which emits two distinct colors of light when operated at different polarities of external bias.

The polymer bilayer consists of a PPV layer and a MEH-PPV layer. Indium tin-oxide (ITO) and aluminum (Al) were chosen as the two electrodes. Both PPV and MEH-PPV layers were blended with an electrolyte consisting of PEO and lithium trifluoro-methanesulfonate.

Acetonitrile was chosen as the solvent for the PPV precursor blend, and cyclohexanone for the MEH-PPV blend. In each of the layers, the ratio of the luminescent polymer to PEO was 1:1 (weight ratio), and the ratio of PEO to Li salt were 5.6:1 (weight ratio). PPV precursor blends were first spin-cast onto the ITO substrates in air. The spin-cast films were then transferred into a controlled atmosphere (nitrogen) dry box, and converted to PPV by heating to 200 °C for three hours. MEH-PPV films were spin-cast onto the PPV films in the dry box. The PPV and MEH-PPV layers were each ~1500Å thick.
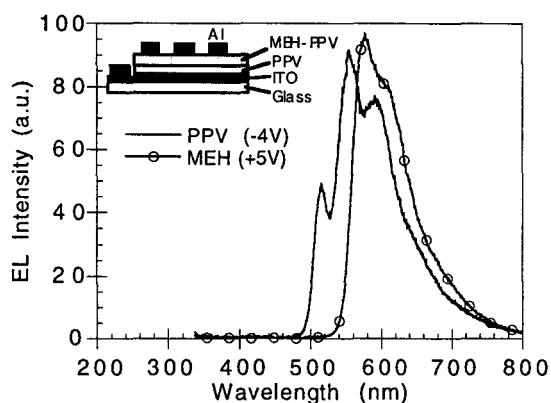

Figure 4. Electroluminescent spectra from the bilayer LEC under forward and reverse bias conditions. Inset shows the schematic diagram of the bilayer device structure.

The electroluminescence spectra of the bilayer LEC are shown in Figure 4 for forward and reverse bias. The characteristic EL spectra from either MEH-PPV or PPV when the device is biased indicates that the light-emitting p-n junction is completely inside the MEH-PPV or PPV layer, respectively. Moreover, the junction width is much less than the thickness of the MEH-PPV or the PPV layer. This information confirms that the junction width is a function of the total thickness of the film (or the inter-electrode spacing in the case of the planar device configuration). While the junction width is ~2 μm for a 15 μm anode-to-cathode spacing, the width is much less than 1500Å in the case of a 3000Å anode-to-cathode spacing. In fact, we have fabricated planar electrode configuration LECs with 10 μm and 30 μm gaps, and the junction width was 1 μm and 2.5 μm respectively. Details of the junction formation are under investigation.

4. Summary

In summary, we have shown that the device performance of light-emitting electrochemical

cells can be significantly improved by adding a bifunctional liquid additive into the light-emitting layer. The surfactant-like character of the additive within the light-emitting layer causes a high surface area bicontinuous three-dimensional network morphology. The resulting LECs have higher brightness, faster turn-on response, lower turn-on voltage and better stresslife than identical devices made without the bifunctional additive.

In addition, a voltage confrolled, two color, light emitting electrochemical cell has also been successfully demonstrated. This two color LEC consists of a polymer bilayer structure, PPV/MEH-PPV, sandwiched between two electrodes. Due to the asymmetry of electron and hole injection and transport, the dynamic light-emitting p-n junction is closer to one of the electrodes (the cathode). Therefore, when the electrode at the MEH-PPV side is wired as negative, the LEC emits the red-orange light from the MEH-PPV layer. On the other hand, when the electrode of the PPV side is wired as negative, the bilayer LEC emits the green light of PPV. The two distinct emission colors are identical to the EL colors obtained from single-layer LECs made from MEH-PPV and PPV, respectively. This is an indication that the light-emitting p-n junction of this bilayer device is completely within one polymer layer, and the width of the junction is less than the thickness of that polymer layer.

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