Efficient, fast response light-emitting electrochemical cells: Electroluminescent and solid electrolyte polymers with interpenetrating network morphology

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The device performance of light-emitting electrochemical cells is improved by adding a bifunctional liquid additive into the light-emitting layer. Because of the surfactant-like character of the additive, the light-emitting layer exhibits a high surface area bicontinuous three-dimensional network morphology. The semiconducting polymer forms a continuous network phase enabling electronic transport of injected electron and holes: the electrolyte forms a continuous network phase enabling fast ion transport; the nm length scale of the phase separated network enables rapid, effective transport of the ions into the conducting polymer during electrochemical doping. © *1996 American Institute of Physics.* [S0003-6951(96)01323-X]

Pei *et al.*[1] described a light-emitting device utilizing solid state electrochemical cells in which a blend of conjugated luminescent polymer and solid electrolyte serves as the active layer. The operating mechanism proposed for the polymer light-emitting electrochemical cell (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 E_g/e where E_g is the π-π^* energy gap of the semiconducting polymer and *e* is the electronic charge; (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. From this 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 nonpolar 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 phase separate. 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 counterions 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 optimzed 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 this letter, 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 bifunctional (surfactantlike) liquid compound with high boiling point as an 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 bifunctional with an A-B molecular structure, where A is a polar moiety and B is a nonpolar 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.[2] 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. In addition to the improving ionic conductivity, these additives act as bifunctional ''surfactants'' to facilitate formation of an interpenetrating network morphology within the electroactive layer.

LEC devices were fabricated on indium–tin oxide (ITO) coated glass substrates. The device structure was similar to that in Ref. 1: Thin films of the blend of poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene], MEH-PPV, prepared according Refs. 3 and 4, PEO containing Li triflate (lithium trifluoromethanesulfonate) and additive were used as the active light-emitting layer between ITO and aluminum electrodes. The typical composition was as follows: 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 then

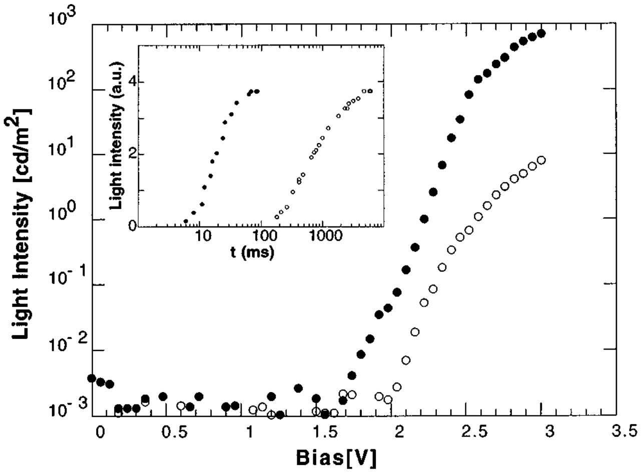

FIG. 1. Comparison of light output vs voltage and turn-on voltage for ITO/MEH-PPV+PEO(Li$^+$)+OCA/Al light-emitting electrochemical cell, with ITO wired as the anode; solid dots with OCA; open dots without OCA. The turn-on response data are shown in the inset; the solid dots (with OCA) were obtained at 5 Hz (190 ms on/10 ms off); the open dots (without OCA) were obtained at 0.05 Hz (19 s on/1 s off).

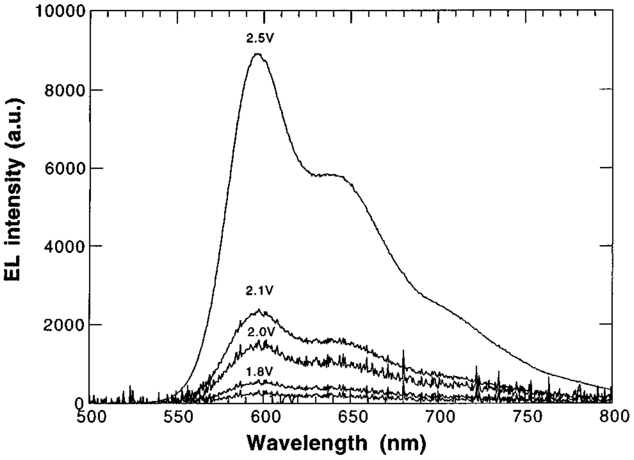

FIG. 2. Emission spectra at various bias voltages from LEC fabricated with OCA additive, i.e., ITO/MEH-PPV+PEO(Li$^+$)+OCA/Al. The bottom curve (weakest signal) was obtained just above thresohld at 1.7 V.

heated to 65 °C on a hot plate for 12 h. The thickness of the polymer layer was typically 2000–4000 Å. The aluminum layer (≈1000 Å) was evaporated onto the polymer film at pressures around 1×10^{-6} Torr and used as backelectrode. The active area of the devices was 12 mm^2.

Based upon the requirements listed above, a number of commercially available compounds were screened as functionalized additives for the polymer LEC, including octylcyanoacetate, N,N-diethyldodecanamide, stearamide, dodecanolactone, 2-tert-butylcyclohexanone, and N-dodecylpyrrolidinone. All these compounds have a nonpolar (long chain alkyl group) on one end and a polar group on the other end. Of these, octylcyanoacetate OCA, gave the best results.

Figure 1 compares light output versus voltage for ITO/MEH-PPV+PEO(Li$^+$)/Al devices in the presence of OCA as an additive. The brightness of these devices is around 1000 cd/m^2 at 3.0 V, dramatically improved over identical devices (same composition and thickness) without the additive (~10–20 cd/m^2 at 3 V). 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.

LECs made from MEH-PPV without additives turn-on at a bias voltage approximately equal to the measured optical gap, $V_{\mathrm{on}}\approx2.1$ V, as expected for a *p-n* light-emitting junction created *in situ* by electrochemical doping.[1,5] For LEC devices made with OCA as an additive, however, the onset of emission moved to a significantly lower voltage, $V_{\mathrm{on}}\approx1.5$–1.7 V. Thus, in the presence of OCA, $eV_{on}<E_g$. Even for voltages below 2 eV the spectrum is characteristic of MEH-PPV. The emission spectra for various bias voltages are shown in Fig. 2; the spectrum at 1.7 V (eV$<E_g$) is identical to that at 2.5 V ($eV>E_g$). Moreover, the absorption spectrum of thin MEH-PPV/PEO-Li films with or without OCA, show no difference in the onset of π-π^* absorption.

A possible explanation for the reduced turn-on voltage involves the *in situ* doping process. For example, the doping could be initiated via a subgap state at the surface of the MEH-PPV, i.e., a charge-transfer state formed between the MEH-PPV and electronegative polar end of OCA. The onset of electrochemical doping would then occur when the applied voltage spans the electrochemical difference between the charge-transfer state and the electron-hole pair state (in the π-π^* system MEH-PPV). Since the spectrum of the emitted light is close to that from the pure polymer, the electronic structure of the polymer away from the interface is unchanged. Thus, after the initiation of electrochemical doping (*n* type on one side and *p* type on the opposite side, as described previously), the resulting carriers will move within the π and π^* bands during transport to the *p-n* junction region. The unexpected lowering of the turn-on voltage provides a possible route to even lower voltage turn-on of the LEC. Careful examination of the curve of the light output versus bias for devices with OCA in Fig. 1 indicates a second threshold point at E_g/e, i.e., at about 2.1–2.2 V, consistent with the explanation proposed above. Experiments designed to clarify the mechanism of the reduced turn-on voltage are in progress.

The turn-on response of the ITO/MEHPPV +PEO(Li$^+$)/Al cell at a bias of 3 V was measured using a square wave drive voltage. The data are shown in the inset of Fig. 1; the solid dots (with OCA) were obtained at 5 Hz (190 ms on/10 ms off); the open dots (without OCA) were obtained at 0.05 Hz (19 s on/1 s off). For the device using PEO+Li triflate as an electrolyte, the rise time (to 1/2 saturated brightness) is ≈1 s. For the device fabricated with the same composition but with OCA, the response time decreased to ≈20 ms.

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 (octylcyanoacetate) in the ratio of 1:1:1 was spin cast from the solution and subsequently dried at 70 °C. For TEM studies, the blend films were overcoated with a thin carbon layer (~10 nm thickness), floated on water, and picked up on gold TEM grids with the carbon

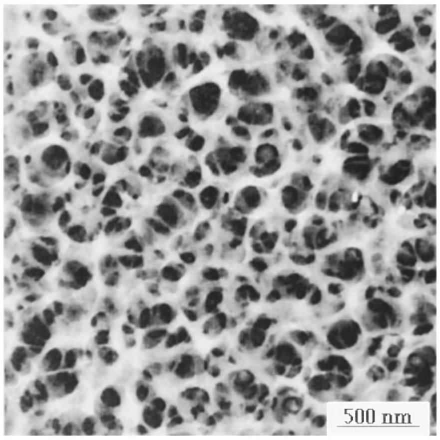

FIG. 3. TEM micrograph of (MEH-PPV+PEO(Li $^+$)+OCA) composite film.

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 for several hours. The extracted films were shadowed by Pt/Pd from the bottom side. Pure MEH-PPV films were also examined for comparison purpose. The pure MEH-PPV films were uniform, and no contrast was observed after this treatment.

The TEM micrographs, as shown in Fig. 3, demonstrate 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 of 10–100 nm. Because of the bifunctional, surfactantlike nature of the additive (A-B, polar–nonpolar), the blend phase separates with a high surface area bicontinuous network morphology.

Devices made with the bifunctional additive exhibit improved operating life; at 300 cd/m^2 (initial), the brightness decreased less than 20% after continuous operation for more than 100 h. For LECs without OCA, the typical operating life (defined as the time at which the brightness has decreased to 50% of the initial value) is 6–10 h. A possible explanation of the improved operating life is that the bifunctional additive stabilizes the bicontinuous network morphology and prevents large scale phase segregation of MEH-PPV and Li/PEO caused by self-heating during continuous operation.

The bicontinuous network morphology is ideal for the light-emitting electrochemical cell for the following reasons: (i) The semiconducting polymer froms 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 electrochemical doping.

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 surfactantlike 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, and lower turn-on voltage than identical devices made without the bifunctional additive.

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[2] See, for example, M. Alamgir and K. M. Abraham, in *Lithium Batteries–New Materials, Developments and Perspectives*, edited by G. Pistoia (Elsevier, Amsterdam, 1994), pp. 93–136.

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