Fast Response Single-Ion Transport Light-Emitting Electrochemical Cell Based on PPV Derivative

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ABSTRACT: We present the electrical and optical characteristics of a single-ion transport light-emitting electrochemical cell (SLEC) based on poly(*p*-phenylene vinylene) (PPV) derivative containing aryl-substituted oxadiazole in the backbone (MEH-OPPV). Ionized polyurethane–poly(ethylene glycol) (PUI) used as polymer electrolyte is introduced into the active layer of the SLEC. The turn-on voltage of the SLEC is about 3 V according to its current density–voltage (J–V) characteristics. The response time of the SLEC is less than 10 ms, lower than that of normal LECs by two orders of magnitudes roughly. The reasons of the quick response for the SLEC are discussed in the article. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4253–4255, 2006

Key words: PPV and its derivatives; conjugated polymer; light-emitting diodes; light-emitting electrochemical cells

INTRODUCTION

In 1995, Pei et al. invented a new kind of polymer light-emitting device, light-emitting electrochemical cells (LECs), in which an active layer consists of a blend of an emissive, electronic conductive polymer, an ion conductive polymer, and a molecular salt.[1] The advantage of LECs is the low onset voltage for electroluminescence (EL), which is theoretically close or equal to E_g/e, where E_g is the optical energy gap of the emissive polymer and e is the electronic charge. In addition, the quantum efficiencies of LECs do not depend on the Fermi levels of electrodes, and so stable metals can be used as electrodes in LECs. However, because of the different polarities of the generally apolar-conjugated polymer and the polar electrolyte, phase separation strongly influences the performances of LECs.[2] The response time of LECs is too longer, more than 1 s, to be applied in flat panel displays. Therefore, the improvement of the response speed has become an important subject of current investigations for LECs. The response time of LECs has been improved by a frozen-junction approach and addition of a surfactant into the active layer.[3,4] Yin et al. have found that using single-ion transport polymer PUI as polymer electrolyte can effectively enhance the response speed of LECs.[5]

In the study, we present a light-emitting device structured by a blend polymer layer sandwiched with Al and indium tin oxide (ITO) electrodes. The blend layer consists of MEH-OPPV and PUI, whose chemical structures are shown in Figure 1. PUI is employed as polymer electrolyte and MEH-OPPV is used as luminescence polymer in the single-ion transport light-emitting electrochemical cell (SLEC). The turn-on voltage of the SLEC is about 3 V, much lower than polymer light-emitting diode (PLED) structured by ITO/MEH-OPPV/Al. The response time of the SLEC is less than 10 ms, lower than that of normal LECs by two orders of magnitudes roughly.

EXPERIMENTAL

MEH-OPPV was synthesized through the Wittig condensation reaction.[6] The mass average molecular weight of the polymer was measured with gel permeation chromatography and was found to be 16,400 g/mol. The molecular weight of the poly(ethylene glycol) segment was 1000 and the sodium content was 0.63% by weight in PUI, and so the molecular ratio of the CH_2CH_2O moiety to sodium cation is 24 : 1.[5] Cyclic voltammetry measurement of the MEH-OPPV film was performed on an Autolab Electrochemical Analyzer (ECO Chemie, The Netherlands) in a mixture of $LiClO_4$ (20 wt %) and PEO as the supporting electrolyte at a scan rate of 80 mV/s. Platinum wire electrodes were used as both working and counter electrodes, and an Ag/AgCl electrode was used as a reference electrode. The MEH-OPPV film was coated on the Ag/AgCl electrode.

SLEC was prepared as follows: MEH-OPPV (20 mg) and PUI (20 mg) were dissolved in a blend solvent of
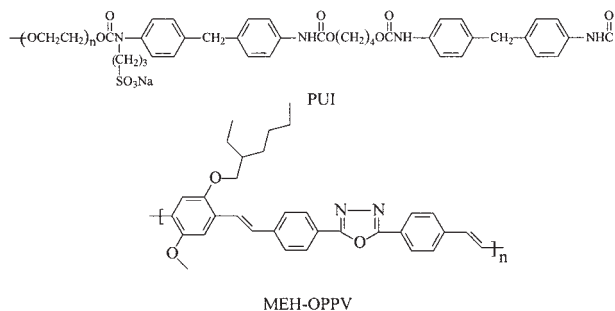
Figure 1 The chemical structures of PUI and MEH-OPPV.

tetrahydrofuran (8 mL) and *N,N*-dimethylformamide (2 mL). The blend film was spin-coated on ITO (50 Ω/□) substrate (thickness ~120 nm). Aluminum was evaporated onto the blend film (2 × 10⁻⁵ Torr) to form a sandwiched structure (ITO/MEH-OPPV : PUI/Al). The PL and EL spectra were carried out on a FluoroMax-2 fluorescence spectrophotometer. Current–voltage characteristics of the devices were measured on an Agilent 4156C Precision Semiconductor Parameter Analyzer. The transient behaviors of the SLEC were detected on a home-made measurement system, which consists of a transient circuit and a photomultiplier tube.

RESULTS AND DISCUSSION

The EL spectrum of the SLEC under a DC bias of 5 V is shown in Figure 2. For comparison, the PL spectrum of the blend film is also plotted in Figure 2. It can be seen that the peak positions are the same in the two curves, but the EL spectrum is wider than the PL spectrum, which is due to Joule heating in the devices at high current contributing to a wide band gap distribution in the materials.[7,8] As a DC bias above the
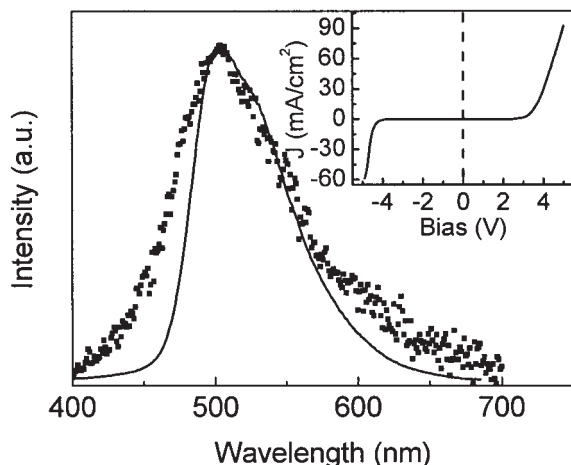

Figure 2 PL spectrum of the MEH-OPPV: PUI film (solid line) and EL spectrum of the SLEC (dotted line), and the inset is the J–V characteristics of the SLEC.
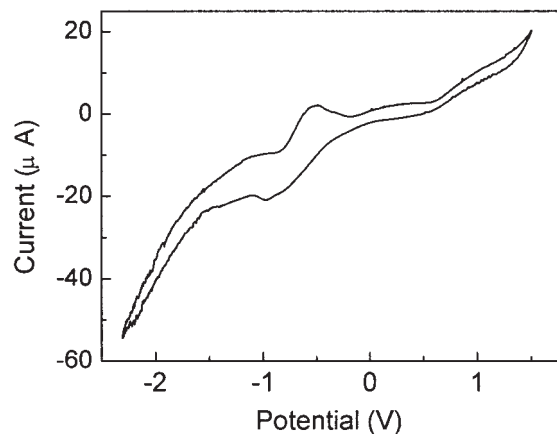

Figure 3 Cyclic voltammogram of the MEH-OPPV film in the solid electrolyte mixture at 80 mV/s scan rate.

onset voltage is added on the device, electrons are injected from cathode to π^*-band of MEH-OPPV and holes from anode to π-band of MEH-OPPV. They encounter in the emitting layer to form excitons, which are trapped in the low energy sites and then radiatively recombine to give out light.

The current density–voltage (J–V) characteristics of the SLEC under positive and negative bias are shown in the inset of Figure 2. The turn-on voltage of the SLEC is about 3 V for ITO electrode acting as anode (positive bias), much lower than that of the PLED without PUI (ITO/MEH-OPPV/Al). Under a DC bias, cations (Na⁺) in the SLEC move to cathode and are congregated at the interface between the polymer film and cathode, and the polymeric anions are left in other side. The presence of ionic charge redistributes the internal electric field of the SLEC towards the electrodes.[9] And then the barrier width of electron injection is reduced to enhance the efficiencies of electron injection. So the efficiency of electron injection is independent of the Fermi level of cathode in SLEC. For the PLED, electron injection must overcome a wide barrier, and so the turn-on voltage of the PLED is higher than that of the SLEC.

It can be seen from the inset of Figure 2 that the J–V characteristics of the SLEC are asymmetrical. In PUI, anions ($-SO_3^-$) are covalently bonded with PUI chains, and so they cannot move to anode under electric field. In this case, the barrier of hole injection strongly affects the onset voltage of the SLEC. To analyze the asymmetrical J–V characteristic of the SELC based on MEH-OPPV, we measured the electrochemical properties of the polymer. Figure 3 shows the cyclic voltammogram of the MEH-OPPV film in a solid electrolyte mixture at 80 mV/s scan rate. The onset potentials of reduction and oxidation were determined to be −1.62 and 0.63 V *versus* Ag/AgCl reference electrode, respectively. This suggests that the presence of one oxadiazole ring per repeat unit in the backbone makes the polymer more suitable for n-doping
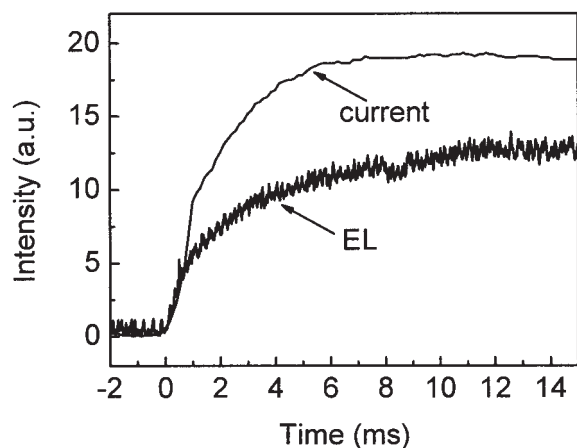
Figure 4 The transient behaviors of the SLEC under a DC bias of 5 V.

than p-doping.[10] By using the standard normal potential of ferrocene/ferrocenium (0.24 V) in this measurement system and its vacuum energy level (4.8 eV), the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital energy levels of MEH-OPPV are estimated to be 5.19 and 2.94 eV, respectively. The corresponding electrochemical band gap is 2.25 eV, which approximately matches with the optical band gap of 2.46 eV.[6] The barrier between the Fermi level of Al electrode (4.3 eV) and the HOMO energy level of MEH-OPPV is 0.89 eV, larger than that (0.29 eV) between the Fermi level of ITO electrode (4.9 eV) and the HOMO energy level of MEH-OPPV, and so the barrier width of hole injected from Al electrode is larger than that from ITO electrode. The different barrier widths of hole injection result in the asymmetrical J–V characteristics of the SLEC under the positive and negative bias.

Figure 4 shows the transient behaviors of the SLEC under a DC bias of 5 V (ITO acting as anode). It can be seen that the EL intensity of the SLEC is similar to its current as the time of the voltage applied on the SLEC increases. It has been found that the efficiency of electron injection depends on the concentration of the cation near the electrode.[11] The cations (Na^+) move to cathode under electric field and congregate at the interface between the blend film and Al electrode to make the electric field in the SLEC redistributed. The electrical field near the electrodes is increased with the congregation of the cations. As a result, the barrier widths of electron and hole injections are reduced to increase their injection efficiencies. The electrons and holes are injected from the cathode and anode, respectively, and they encounter in the active polymer layer to form excitons. The excitons are recombined radiatively to give out light. So, the intensity of light emission from the SLEC is increased with the increasing time of the voltage applied on the SLEC.

The response time of the SLEC is defined as the time during which the EL intensity of the SELC increases to half of its maximum value.[12] It can be seen from Figure 4 that the response time of the SLEC is about 3 ms, much shorter than that of normal LECs (1 s). The response time of the SLEC depends on the speed of cations moving to cathode. It has been reported that the phase separation seriously blocks the ion transport to result in long response times of normal LECs.[2] In the SLEC, the chains of MEH-OPPV and PUI are entwisted each other to improve the phase separation and to form a continuum network in favor of ion transport. On the other hand, the cations moving to cathode are scattered by the anions moving to anode in normal LECs. But in the SLEC, the anions are combined with the chains of PUI by covalent bonds. So the cations are scattered by the fixed anions as they move to cathode through the channels made up of poly(ethylene glycol) segments in PUI. The scatter effect of unmovable anions on cations in the SLEC is weaker than that of movable anions in normal LECs. The weak scatter effect of unmovable anions on cations is contributed to the quick response of the SLEC.

CONCLUSIONS

We have fabricated the fast response SLEC based on MEH-OPPV, whose turn-on voltage is about 3 V. The asymmetrical J–V characteristic of the SLEC is attributed to the different barrier widths for hole injection under the positive and negative bias. The response time of the SLEC is about 3 ms, lower than that of normal LECs roughly two orders of magnitude. The chains of MEH-OPPV and the chains of PUI in the films form a continuous network in favor of ion transport. The weak scatter effect of unmovable anions is also contributed to the fast response of the SLEC.

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