Chem. Mater. **2000,** *12,* 1853−1856

Single-Ion Transport Light-Emitting Electrochemical Cells: Designation and Analysis of the Fast Transient Light-Emitting Responses

Chun Yin,[†] Yan-zhu Zhao,[‡] Chang-zheng Yang,*[,†] and Shu-yi Zhang[‡]

Department of Polymer Science and Engineering, College of Chemistry and Chemical Engineering; and Laboratory of Modern Acoustics and Institute of Acoustics, Nanjing University, Nanjing, 210093, People's Republic of China

Received February 17, 2000. Revised Manuscript Received April 6, 2000

A single-ion transport light-emitting electrochemical cell (SLEC) was designed. The SLEC is the first LEC-type device that can be driven by ac voltages indicating its fast response speed. The fast light-emitting response of the SLEC was attributed to the single-ion transport property of the device. Because of the easy migration of the cations under the influence of the external electric field, the electron injection from the cathode to the luminescent polymer (with low electronic affinity) was enhanced quickly. The experimental results demonstrate that compared with the ionic conductivity, the transport mode of the ionic species is a more sensitive factor that dictates the response speed of LECs. A color-shifting effect was also observed in the SLEC, the EL spectrum was greatly blue-shifted and expended (from orange to whitish). It possibly resulted from the interaction between naked and immobilized SO_3^- in the bulk of the polymer layer and the excitons in MEH−PPV.

Introduction

Polymer light-emitting electrochemical cells (LECs) have brought about much activation in the area of polymer electroluminescence (EL).[1−7] With the involvement of ionic species in the luminescent layer, LECs exhibit many unique light-emitting behaviors different from conventional polymer light-emitting diodes (LEDs). Various properties of the LECs (such as low turn-on voltage; high quantum efficiency; dual light emission; etc.), are based on the improved and nearly balanced carrier injection with the aid of the accumulated ionic species near electrodes. Doping theory was proposed to account for the mechanism.[1] However, it is a common phenomenon that the response speed of LECs is much slower than that of LEDs. A typical response time of the conventional LECs is in the range of second,[1,8] or even slower.[2] Since fast response speed is essential for LEC-type devices to find practical applications in large-area dynamic display, research work in this aspect is important and meaningful. Low ionic conductivity of the electrolytes used in LECs is one of the reasons that lead to the slow response speed, but detailed mechanism has not been fully elucidated. One way to improve the ionic conductivity is to add some organic additives into the electrolyte; and the response speed of the LECs was greatly improved through this way.[8] At present, only biionic transport electrolytes were used in the LECs. Alternately, we explore the relationship between the response speed and the ionic transport mode of the LEC-type devices in this paper. A novel, single-ion transport light-emitting electrochemical cell (SLEC) was fabricated, and its transient response properties were investigated. For the first time, the SLEC was demonstrated to be driven by ac (alternating-current) input voltages. In addition, a color-shifting phenomenon was also observed in this new device.

Experimental Section

Preparation of the Single-Ion Transport Electrolyte. The single-ion transport electrolyte is an ionized polyurethane−poly(ehtylene glycol) copolymer (PUI). The chemical structure of PUI was shown in Chart 1. It was synthesized by a two-step solution polymerization. Detailed synthesis and purification was reported in our previous work.[9] The molecular weight of the poly(ethylene glycol) segment is 1000, and the sodium content is 0.63 wt % in PUI. About 15.7% of the nitrogen has been ionized, such that the molecular ratio of the CH_2CH_2O moieties in PUI to sodium cation is about 24:1. The ionic conductivity of PUI is about 10^{-8}S cm^{-1} at room temperature measured by complex impedance spectrum.

Preparation of MEH−PPV. MEH−PPV was synthesized through an improved Gilch route to avoid gelation.[10−12] The

---

[†] Department of Polymer Science and Engineering.

[‡] Laboratory of Modern Acoustics and Institute of Acoustics.

(1) Pei, Q.; Yu, G.; Zhang, C.; Yang, Y.; Heeger, A. J. *Science* **1995**, *269*, 1086.

(2) Pei, Q.; Yang, Y. *J. Am. Chem. Soc.* **1996**, *118*, 7416.

(3) Pei. Q.; Yang, Y.; Yu, G.; Zhang, C.; Heeger, A. J. *J. Am. Chem. Soc.* **1996**, *118*, 3922.

(4) Yu, G.; Cao, Y.; Zhang, C.; Li, Y.; Gao, J.; Heeger, A. J. *Appl. Phys. Lett.* **1998**, *73*, 111.

(5) Yang, Y.; Pei, Q. *Appl. Phys. Lett.* **1997**, *70*, 1926.

(6) Huang, F.; Wang, H. L.; Feldstein, M.; MacDiamid, A. G.; Hsieh, B. R.; Epstein, A. J. *Synth. Met.* **1997**, *85*, 1283.

(7) Campbell, I. H.; Smith, D. L.; *Appl. Phys. Lett.* **1998**, *72*, 2565.

(8) Cao, Y.; Yu, G.; Heeger, A. J.; Yang, C. Y. *Appl. Phys. Lett.* **1996**, *68*, 3218.

(9) Xu, H. S.; Yang, C. Z. *J. Polym. Sci.: Part B: Polym. Phys.* **1995**, *33*, 745−751.

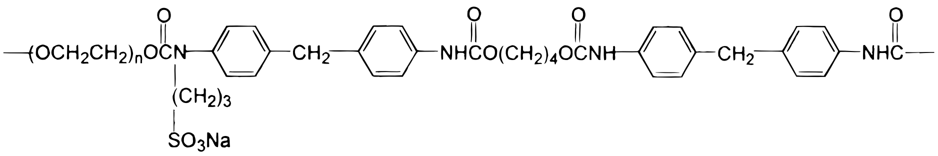
(10) Wudl, F.; Srdanov, G. U.S. Patent 5,189,136, 1993.

(11) Hsieh, B. R.; Yu, Y.; Vanlaeken, A. C.; Lee, H. *Macromolecules* **1997**, *30*, 8094.

(12) Yin, C.; Yang, Chang-zheng *J. Appl. Polym. Sci.*, submitted for publication.

10.1021/cm0001408 CCC: $19.00

Chart 1. Chemical Structure of PUI



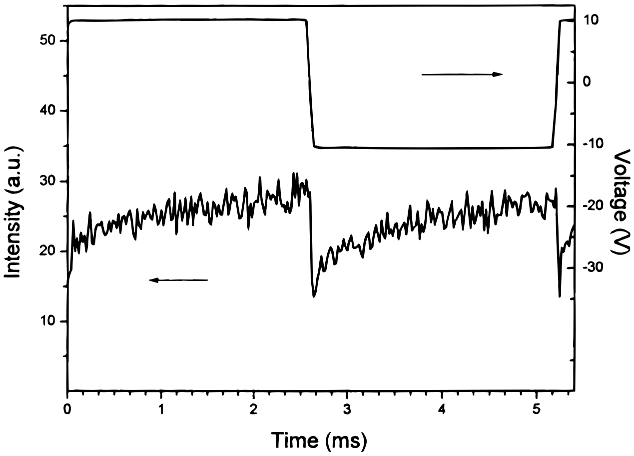


Figure 1. The EL response of the SLEC under ac square-wave voltage (191 Hz).

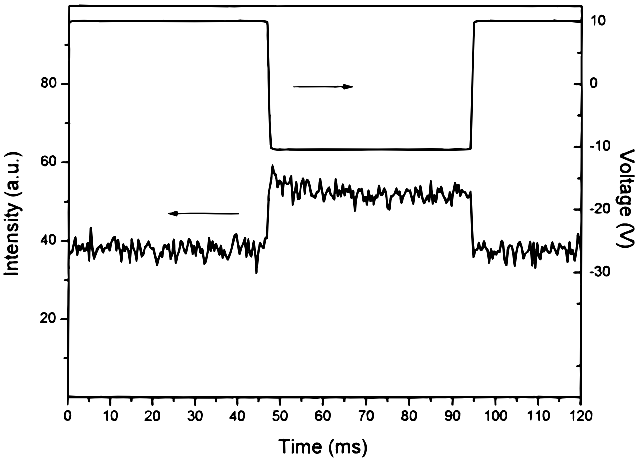


Figure 2. The EL response of the SLEC under ac square-wave voltage (10 Hz).

molecular weights of the synthesized MEH−PPV measured by GPC are $M_w = 7.82 \times 10^5$ and $M_n = 1.84 \times 10^4$. The elemental analysis data are as follows: C, 77.65; H, 9.13, in good agreement with that (C, 78.42; H, 9.29) calculated for $[C_{17}H_{24}O_2]$. FT-IR (film): 703, 860, 968, 1039, 1203, 1253, 1351, 1413,1461,1504, 2857, 2925, 2956, 3056 (cm^{-1}).

Device Fabrication. The fabrication of the SLEC was carried out as follow: 20 mg of PUI and 20 mg of MEH−PPV was dissolved in 8 mL of THF; a small amount of methanol (160 μL) was added to make the mixture uniform and improve the dual light-emitting performance of the cell. A thin film of this polymer blend (~100 nm) was spin-cast onto ITO (indium tin oxide) substrate (50Ω/□). Aluminum (~100 nm) was then vacuum evaporated (10^{-5} Torr) onto the polymer film. The area of a light-emitting spot is 2 mm × 4 mm. A control device was fabricated according to the similar procedure, but an additional 0.25 mg of $LiClO_4$ was added into the MEH−PPV/PUI solution.

Characterization of the SLEC. The transient light-emitting response was measured according to the method described below. The emission was detected by a photomutipiler (Toshiba MS-9S), a storage oscilloscope (300 MHz, Hewlett-Packard 54510B) was used as the recorder, and the ac voltages were applied by a pulse generator (Tektronix CFG280). The PL and EL spectra were measured by a Fluoro Max-2 luminescence spectrometer.

Results and Discussion

AC Light-Emitting Responses. The SLEC was the first LEC-type device that could response under ac voltages. When an ac voltage (with an absolute V_{max} more than 7 V) within a wide frequency range (up to 10 kHz) was applied, light emission from the SLEC was clearly observed by eyes in a dim room. Figures 1 (191 Hz) and 2 (10 Hz) showed two typical ac light-emitting responses. In Figure 1, a fast increase of the emission was observed at the beginning of each half-cycle before the complete decay of the light from the previous half-cycle, such that the emitted light became continuous during the whole period. Following the fast increase, the increase of the emission became slow and less evident. It was obvious in Figure 1 that the light emission had exceeded its half-saturated brightness at the end of each half-cycle. Hence it was evaluated that the ac rise time (the time needed for achieving the half-saturated brightness as defined in ref 8) of the SLEC in this case was no more than a half-cycle of the applied voltage (about 2.6 ms). The response behavior at lower frequency (Figure 2) virtually reflected the situation when the device worked at a static condition. The light intensities at the two half-periods were saturated and comparable. It is clear from both Figures 1 and 2, that this new device is a real LEC-type device, since the dependence of the carrier injection (both for holes and electrons) on work functions of the electrodes disappeared, and nearly balanced carrier injection was achieved.[1] It is interesting to compare the ac light-emitting responses between the SLEC and the ac LEDs.[13,15] However, in those ac LEDs that were made from those luminescent polymers that have low electron affinity, the "reverse" emission was usually much weaker than the "forward" emission (ITO wired as the anode),[13] but the efficiency of the SLEC was low. Possibly, it resulted from the overinteraction between naked anions and electronic carriers. In principle, only in the case that both balanced carrier injection and efficient recombination and radiative decay of the injected carriers were achieved could strong dual light emission from the LEC-type devices be warranted.[14] The schematic diagram that depicted the ionic distribution of the SLEC under a bias was shown in Figure 3. Obviously, unlike conventional biionic transport LECs, there existed dissociated and immobilized anionic species in the bulk of polymer layer. An additional and possibly harmful interaction between these naked anions and the electronic species in the recombination

---

(13) Pal, A. J.; Osterbacka, R.; Kallman, K.-M.; Stubb, H. *Appl. Phys. Lett.* **1997**, *70*, 2022 and references therein.

(14) Cao, Y.; Pei, Q.; Andersson, M. R.; Yu, G.; Heeger, A. J. *J. Electrochem. Soc.* **1997**, *144*, L317.

(15) Wang, Y. Z.; Epstein, A. J. *Acc. Chem. Res.* **1999**, *32*, 217.

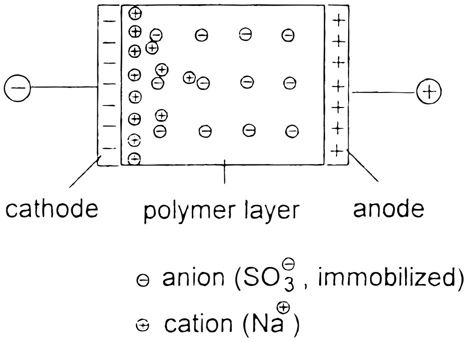


Figure 3. The schematic distribution of the ionic species in the SLEC under a bias.

region might be responsible for poor light-emitting performances.

There are two problems to be elucidated to the transient light-emitting responses of the SLEC. First, why can the SLEC maintain dual light emission with only cations mobile? Second, why can the SLEC respond so fast to the point that it can respond under ac voltages with a low ionic conducting electrolyte incorporated in the emitting layer?

As is known, MEH−PPV and most of the luminescent polymers have low electronic affinity. For the light-emitting devices made from these polymers, the hole injection from anode to the polymer layer is easy, but the electron injection from cathode is more difficult due to the existence of a high barrier between the work function of the cathode and the LUMO of the luminescent polymer. Therefore, it is usually necessary to enhance the electron injection for achieving balanced carrier injection. For LED-type devices, this is usually realized by choosing metals with low work function such as Ca as the cathode, or by addition of an electron transport layer sandwiched between cathode and the emitting layer. On the other hand, in LECs, the carrier injections (both holes and electrons) are enhanced through an electorchemical mechanism (for example, doping mechanism). With the aid of accumulated ionic species near the electrodes under the influence of the external electric field, the barriers at the electrode/polymer interfaces were substantially decreased and balanced carrier injection is easy to achieve. But obviously, since hole injection has been easier when a polymer with low electronic affinity was used as the emitter in LECs, in fact only the enhancement of electron injection from cathode is essential. This is just the case in the SLEC. Since only cations can be effectively accumulated near cathode under a bias, the electron injection from the cathode is thus preferably enhanced (possibly by n-type doping according to the doping mechanism). It is similar to a LED with an electron transport layer between the cathode and the luminescent polymer layer to enhance the electron injection, but the physical mechanism between the two is completely different.

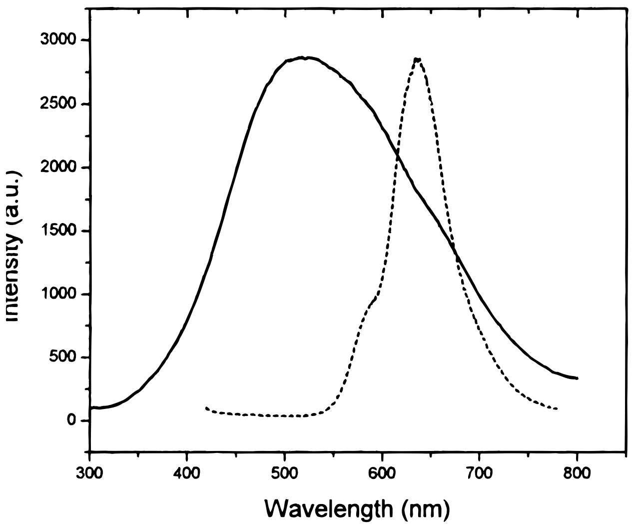


Figure 4. EL spectrum of the SLEC (solid line) and PL spectrum (dashed line) of a thin free-standing film of MEH−PPV (the excitation wavelength $\lambda_{ex} = 400$ nm).

The fast response of the SLEC clearly shows that the response speed of LEC-type devices is not simply limited by the low ionic conductivity of electrolyte used in the device. The electron injection is sensitively influenced by the accumulation of cations other than anions; however, the transport number of the cations (t_+) in common biionic transport electrolytes is usually smaller than that of the anions,[16] $t_+ = 0.2-0.5$, sometime even lower than 0.1. This is because the transport process of cations was greatly slowed by the aggregated anions under a bias. When these biionic transport electrolytes are used in LEC-type devices, more time is needed to achieve efficient and stable improvement of the electron injection due to the slowed accumulation of the cations. In contrast, the cationic transport number of the single-ion transport electrolyte is nearly unity;[9] the migration of the cations is much easier due to the lack of the hysteresis that results from the aggregated anions under the influence of the external electric field, and the electron injection is thereof more easily enhanced. It was confirmed that the single-ion transport characteristic was the precondition of the ac light-emitting response of the SLEC by comparing the performance of the SLEC and the control device (with $LiClO_4$ added into the MEH−PPV/PUI blend). The later was returned to being a biionic transport device, and no light response was detected under ac voltages despite the fact that bright light emission was observed under a forward or reverse dc bias.

Color-Shifting Effect. As is known, the emitting color of MEH−PPV is orange, but the light color directly observed by eyes from the SLEC is whitish. The EL spectrum was greatly blue-shifted and extended compared with PL spectrum (Figure 4), and covered the whole visible spectrum region. It was obvious that the excitation states of the luminescent polymer were greatly changed, and mainly elevated. The influence of the anionic species should be considered once again. Just as mentioned above (see Figure 3), when part of Na^+ cations were dissociated and moved away from their immobilized counterparts under the influence of the external electric field, there would be equivalent naked anionic charges left and distributed across almost the whole polymer layer. The interaction between these anions and electronic species (holes, electrons, and excitons) would probably not only decrease the efficiency of the radiative decay of the excitons, but also change the energy states of the excitons, leading to the change

---

(16) Sun, J.; Liu, C. *Polym. Bull. (Beijing)* **1997**, *4*, 219−225.

of the EL spectrum. We noticed the color-variable symmetrically configured ac light-emitting (SCALE) devices reported by Wang and Epstein in which the color of emitted light in the SCALE was determined by the characteristics of the interfaces.[15] Whether there is any similarity in mechanism between the two color-shifting effects is under further discussion. But these color-shifting effects provide a new approach to achieving different emitting colors from limited luminescent polymers and are meaningful for the investigation on the interaction between the electronic and ionic carriers in these devices.

Conclusions

A novel single-ion transport light-emitting electrochemical cell was designed. The SLEC is the first LEC-type device that can be driven by ac voltages indicating its fast response speed compared with conventional biionic transport LECs. It was clearly demonstrated from the transient light-emitting responses of the SLEC that the transport behavior of cations, not the ionic conductivity was the most sensitive factor that dictated the response speed of LECs when a luminescent polymer with low electronic affinity was employed in the active layer. A color-shifting effect was also observed in SLEC which turned the emitting color of MEH−PPV from orange to whitish.

Acknowledgment. We thank Dr. Zhong-ning Zhang for technical support in the measurement of transient light-emitting response. This work was supported by the National Natural Science Foundation of P. R. China.

CM0001408