JOURNAL OF APPLIED PHYSICS **99**, 064505 (2006)

Optical and electrical properties of single-ion transport light-emitting electrochemical cells

F. Kong, X. L. Wu,[a] Y. Zheng, C. G. Ou, and R. K. Yuan
National Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, People's Republic of China and Department of Physics, Nanjing University, Nanjing 210093, People's Republic of China

C. Z. Yang
College of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, People's Republic of China

Paul K. Chu
Department of Physics and Materials Science, City University of Hong Kong, Kowloon, Hong Kong, China

(Received 16 September 2005; accepted 21 January 2006; published online 21 March 2006)

We present electrical and optical characteristics of single-ion transport light-emitting electrochemical cells (SLECs) based on a blend film of poly(*p*-phenylene vinylene) derivative with ion-conducting side groups and ionized polyurethane-poly(ethylene glycol). The turn-on voltage of the SLECs is lower than 4 V. The response time of the SLECs is less than 10 ms, which is approximately two orders of magnitude faster than that of conventional bi-ionic transport light-emitting electrochemical cells. The quick response can be explained on the basis of both good compatibility between the two polymers and weak scattering behavior of the counter ions. In addition, according to the transient current and electroluminescence characteristics, we reveal that the electrical field is close to zero in the inner of the SLEC under the condition of steady state. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2180452]

I. INTRODUCTION

In 1995, Pei *et al.*[1] introduced polymer electrolyte into polymer light-emitting diodes (LEDs), inventing 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 an molecular salt. The salt ions are separated spatially after applying a sufficiently large bias to the LEC. The cations and anions will, respectively, drift toward the cathode and anode and then aggregate near the two electrodes, which improves electron and hole injections. Pei and co-workers[1–3] have stated that the salt ions dope the luminescence polymer *p* type near the anode and *n* type near the cathode and an electrochemical *p*-*n* junction is thus formed between the *p*- and *n*-doped regions. The *p*-*n* junction model is oppugned by deMello and co-workers[4,5] who have claimed that the accumulation of ionic space charge in the vicinity of the electrodes gives rise to large electric field that reduces the barrier widths to facilitate electron and hole injections. Recently, Dane *et al.*[6] directly obtained the images of the *p*- and *n*-doped regions in extremely large planar LECs. The electrochemical doping of a conjugated polymer is achieved by the oxidation (electron injection) or the reduction (hole injection) in the presence of spatially separated ions.

The LECs have some advantages, such as low operating voltage, high quantum efficiency, and the use of air stable electrodes.[1–3] However, phase separation tendency of the polymer blends strongly limits the response time and stability of the LECs due to different polarities of the generally apolar conjugated polymer and the polar electrolyte.[7,8] In order to overcome the tendency associated with the phase separation, a useful way is to introduce grafting ion-conducting side groups into luminescent polymers.[3,8] Other similar polymers, with a poly(*p*-phenylene vinylene) (PPV)-based backbone, have also been reported for application in the LECs.[9,10] In an ideal concept, the active layer consists of an interpenetrating network of ion and electron conducting polymer blends with a homogeneous distribution of ionic species.[11] Cao *et al.*[7] added a bifunctional liquid additive into the light-emitting layer of the LEC to form a bicontinuous network and prevent large scale phase segregation, but the response time of the fabricated LECs is too long (more than 1 s) to be applied in flat panel displays. This can be improved by adding a surfactant into the active layer or using crown ether as a solid electrolyte.[7,12] A frozen-junction approach is effective to realize the fast response of the LECs.[13,14] Yin *et al.*[15] introduced an ionized polyurethane-poly(ethylene glycol) [polyurethane intermediate (PUI)] into the active layer of polymer light-emitting device to fabricate a single-ion transport light-emitting electrochemical cell (SLEC). The SLEC can be driven by ac voltage due to its fast response speed compared with conventional bi-ionic transport LECs.

In this work, we study optical and electrical properties of the SLECs. Poly[2,5-bis(triethoxy)-*p*-phenylene vinylene-alt-phenylene vinylene] (BTEO-PPV-alt-PPV) was used as a luminescence polymer and PUI as a polymer electrolyte in the device. The chemical structures of the two polymers are shown in Fig. 1. We found that the turn-on voltage of the

---

[a] Author to whom correspondence should be addressed; electronic mail: hkwuxl@nju.edu.cn

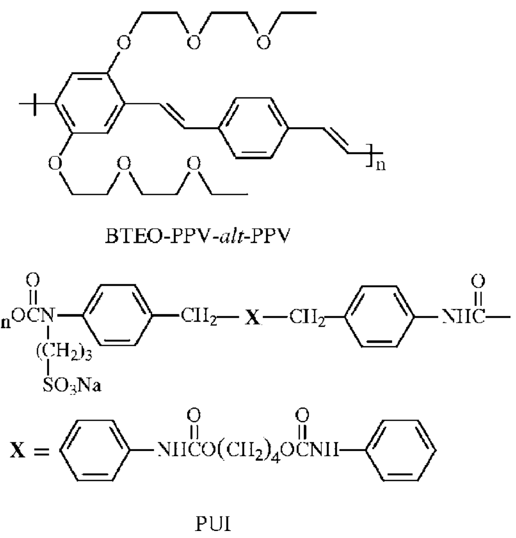

FIG. 1. Chemical structures of BTEO-PPV-alt-PPV and PUI.

SLEC is lower than 4 V according to the current-voltage and electroluminescence-voltage characteristics. The response time of the device is less than 10 ms, which is approximately two orders of magnitude lower than that of conventional bi-ionic transport LECs. We attribute the fast response speed of the SLEC to the good compatibility between the two polymers and weak scattering of the counter ions.

II. SAMPLES AND EXPERIMENTS

BTEO-PPV-alt-PPV was synthesized via a Wittig condensation reaction.[16] The mass average molecular weight of the polymer was measured with gel permeation chromatography (GPC) to be $\sim 5 \times 10^5$ g/mol. The molecular weight of the poly(ethylene glycol) segment was 1000, and the sodium content was 0.63% by weight in PUI. Thus, the molecular ratio of the CH_2CH_2O moiety to sodium cation is about 24:1. The SLEC was prepared as follows: BTEO-PPV-alt-PPV (20 mg) and PUI (20 mg) were dissolved in a blend solvent of tetrahydrofuran (8 ml) and *N*,*N*-dimethylformamide (2 ml). The blend film was spin coated (5000 rpm) on a patterned indium tin oxide, (ITO, $50\ \Omega/\square$) substrate, and then aluminum was evaporated onto the blend film (2×10^{-5} Torr) to form a sandwich structure. The thickness of the blend film was ~ 120 nm. The size of the patterned SLEC is $2 \times 5\ \text{mm}^2$. The atomic force microscopy (AFM) images of the blend film were obtained on a Nanoscope IIIa scan probe microscope of Digital Instruments under tapping mode. Photoluminescence (PL) and electroluminescence (EL) spectra of the devices were taken on a FluoroMax-2 fluorescence spectrophotometer. Current-voltage (*I*-*V*) characteristics of the devices were measured on an Agilent 4156C precision semiconductor parameter analyzer. Transient EL and electrical characteristics of the SLECs were measured on a homemade measurement system, which consists of a transient circuit and a photomultiplier tube. All the measurements were performed at room temperature.

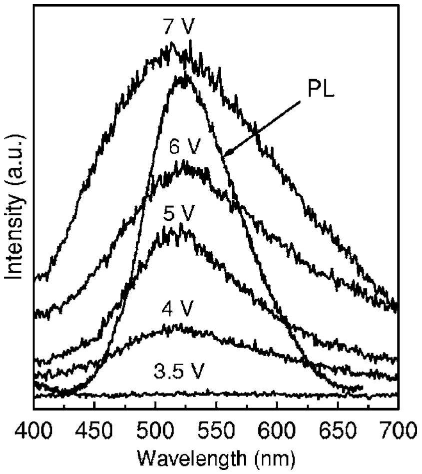

FIG. 2. EL spectra of the SLEC obtained at 3.5, 4, 5, 6, and 7 V (ITO acting as the anode) and PL spectrum of the blend polymer film. The PL spectrum was taken under excitation with the 380 nm line of a Xe lamp.

III. RESULTS AND DISCUSSIONS

The EL spectra of a typical SLEC at different biases are shown in Fig. 2. For comparison, the PL spectrum of the blend film is also plotted in this figure. It can be seen that no emission is detected for the SLEC at 3 V and the EL intensity goes up as the bias is higher than 4 V. The result indicates that the turn-on voltage of the SLEC is lower than 4 V. The peak positions of all the EL spectra are around 520 nm, which is the same as that of the PL spectrum. However, the EL spectra are wider than the PL spectrum since Joule heating at high current contributes to a wide band gap distribution in the devices.[17,18] As a bias above the turn-on voltage is applied to the device, electrons are injected from the cathode to π^* band and holes from the anode to π band of BTEO-PPV-alt-PPV. Excitons are formed in the emitting layer and trapped in the low energy sites and then radiatively recombine to give out light. The energies of the excitons generated by electrical injection are the same as those of the excitons by photoexcitation.

The *I*-*V* characteristics of the SLEC under positive (ITO acting as the anode) and negative biases (ITO acting as cathode) are shown in Fig. 3. The turn-on voltage of the SLEC is lower than 4 V for ITO acting as the anode and is much less than that of the device without PUI (ITO/BTEO-PPV-alt-PPV/Al).[19] Unlike the bi-ionic transport LECs, only dissociated cations (Na^+) drift toward the

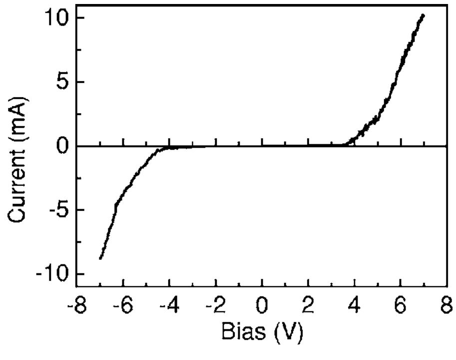

FIG. 3. Current-voltage characteristics of the SLEC.

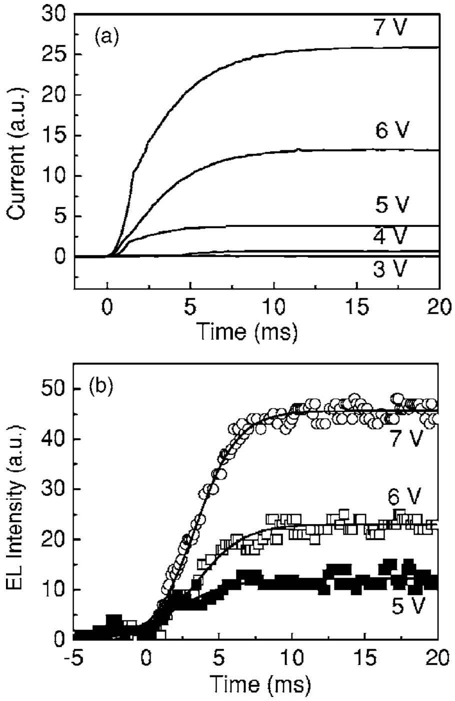

FIG. 4. (a) Transient current and (b) transient EL characteristics of the device at different biases.

cathode and aggregate at the polymer film/cathode interface, and then the unmovable anions are left in the other side as a bias is applied to the SLEC. Currently, it is unclear whether electrochemical doping occurs in the SLEC, but the cation aggregation near the cathode is beneficial to electron injection.[20] Since the electron injection is not sensitive to the Fermi level of the cathode in the SLEC, stable metals such as Al and Au can be used as the cathode in the device.[21]

Since there are several kinds of carriers in the SLEC system, such as electron, hole, and cation, it is important to measure and analyze the transient EL and electrical properties of the device for understanding the work mechanism of the SLEC. Figure 4(a) shows the transient current characteristics of the SLEC under different biases. No current is detected for the applied bias below 3 V. The current through the SLEC increases with time as the applied voltage is equal or higher than 4 V. It is approximately 10 ms for the current of the SLEC to attain its maximum (response time). Figure 4(b) shows the transient EL characteristics of the SLEC under the applied voltages of 5, 6, and 7 V, respectively. It is also ~10 ms to reach the maximum EL intensity for the device under different voltages. The rise time (to 1/2 saturated brightness) for the SLEC is only 3 ms, whereas it is ~1 s for the LECs using poly(ethylene oxide) (PEO)+Li triflate as an electrolyte.[1–3,7] The response time of the SLEC depends on the speed of the cations drifting toward the cathode, which is determined by the mobility of the cations. In the bi-ionic transport LECs,[3,7] it was disclosed that the phase separation largely weakens the performance of the cations and reduces their response speed. The PEO segments in the polymer electrolyte provide a favorable pathway for the ion transport. However, since the ions must overcome the barrier at the phase boundary, the phase separation between the conjugated polymer and the polymer electrolyte destroys the pathway and blocks the ion transport. The current phase separation can be suggested from the surface morphology of the film.[11,22] Figure 5 presents the tapping-mode AFM image of the blend film. The film has a smooth appearance (the surface roughness is less than 10 nm), indicating that there is no obvious phase separation. This can be attributed to an enhanced compatibility between BETO-PPV-alt-PPV and PUI because ion-conducting side groups are grafted on the luminescence polymer.[3,8,9] The chains of PUI and BETO-PPV-alt-PPV interpenetrate to form a favorable ion transport network, reducing the effect of phase separation on the ion transport. The scattering of the counter ions can depress ion transport in polymer electrolyte. In the SLEC, the cations are scattered by the unmovable anions covalently bonded in PUI as the cations drift toward the cathode through the channel formed by poly(ethylene glycol) segments, but in the bi-ionic transport LECs the cations are scattered by the anions moving to the anode. The effect of the scattering from the unmovable anions on the cations in the SLEC is obviously less than that in the bi-ionic transport LECs.

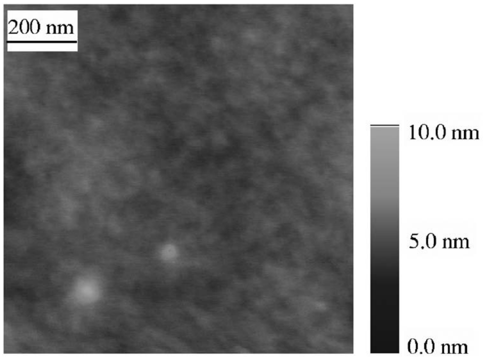

FIG. 5. Tapping-mode AFM image of the blend film.

The tunneling current depends on the width of a triangular barrier according to the Fowler-Nordheim theory.[23] The barrier width for electron injection is related to the concentration of the cations near the cathode and therefore can be controlled.[4,24] The concentration increase of the cations near the cathode depends on the motion speed of the cations which is proportional to the electric field in the SLEC. It can be seen from Figs. 4(a) and 4(b) that the current and EL intensity of the SLEC increase quickly at the beginning of several milliseconds and then the increase rate becomes slow as a bias is applied to the SLEC. The result indicates that the speed of the cations is high at the beginning of applying a bias and then decreases after several milliseconds. This means that the electrical field is gradually reduced in the inner of the SLEC within the response time.

It can also be seen from Fig. 4 that the maxima of the current and EL intensity of the SLEC increase with the applied bias, but the response time remains constant (10 ms). This can be explained as follows: The speed of the cations moving to the cathode is faster at the beginning of applying a higher bias. The cations quickly aggregate near the cathode to result in the redistribution of the electric field in the SLEC. In such a case, the inner electric field decreases quickly to reduce the speed of the cations; as a result, the

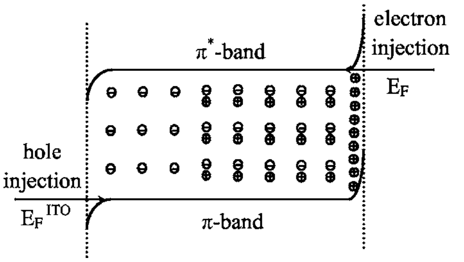

FIG. 6. Schematic representation of the charge injection mechanism for the SLEC: ⊖ anion (–SO$_3^-$, immobilized) and ⊕ cation (Na$^+$).

response time of the SLEC is not sensitive to the applied bias. The results indicate that no noticeable time difference exists for the cations moving from the anode to the cathode under different biases. The cation motion is strongly affected by the scattering of both anions and cations. The change of the electric field in the SLEC makes the cation motion very complex. As discussed above, the speed of the cations acutely decreases with time as a high bias is applied on the SLEC, which leads to an almost constant time for the cations to reach the cathode under different biases. For the SLEC in a steady state, the concentration of the cations aggregating near the cathode increases with the applied bias, which leads to the enhancement of electron and hole injections. As a result, the current and EL intensity of the device increase.

According to the above experimental results and discussions, we schematically plot an electron-injection model and ionic distribution in the SLEC operating in a forward bias in Fig. 6. The cations move and aggregate to one side (the cathode) and the unmovable anions are left in the other side at the beginning of a bias applied on the SLEC. The spatially separated ions cause a redistribution of the electric field in the SLEC.[4,24] The decreased inner electric field leads to the reduction of the motion speed of the cations, but the cations still continue to aggregate near the cathode with increasing time. The barrier width for electron injection depends on the concentration of the ions near the electrode. An increase of the concentration of the cations near the cathode reduces the barrier width to facilitate electron injection. As a result, the current and the EL intensity of the SLEC increase. After 10 ms, the inner electric field is reduced to be close to zero. Therefore, no more cations move to the cathode and the concentration of the cations near the cathode attains its maximum. In this case, a stable state of the SLEC appears, as shown in Fig. 6. For the bi-ionic transport LECs, the ions become spatially separated. A *p-n* junction forms and the current begins to flow as an applied bias is above the threshold voltage for junction formation. The threshold voltage depends on the energy gap of the used polymer, the dissociation free energy of the salt, and the density of the added salt. The applied voltage partially falls in the contact region to establish the junction by electrochemical doping and partially falls across the junction.[25,26] For the SLEC at a certain applied bias, the cations are dissociated from the anions in PUI and drift toward the cathode. No matter whether the electrochemical doping occurs, the spatially separated ions will lead to a redistribution of the electric field in the SLEC. The inner electric field in the SLEC gradually decreases with the cation aggregation. At the steady state, no electric field acts on the ion pairs. Electrons and holes injected from the electrodes diffuse into the blend film to form neutral electron-hole pairs (excitons) and then radiatively recombine to emit light.

IV. CONCLUSIONS

We have fabricated the SLEC based on a blend film of PPV derivative with ion-conducting side groups and PUI. The operating voltage of the device is much lower than that of the polymer LED without PUI. The response time of the SLEC is less than 10 ms, which is roughly two orders of magnitude lower than that of the bi-ionic transport LECs. The chains of BTEO-PPV-alt-PPV and PUI form a continuous network in favor of ion transport. Quick response of the SLEC has been observed and considered to be due to weak scattering effect of the unmovable anions. The electric field in the inner of the SLEC is close to zero for the device at the steady state.

ACKNOWLEDGMENTS

This work was supported by the Grant Nos. 10225416 and 604210038 from the National Natural Science Foundations of China and the LAPEM. Partial support was also from Jiangsu Planned Projects for Postdoctoral Research Funds and the Major State Basic Research Project No. G001CB3095 of China and City University of Hong Kong Direct Allocation Grant 9360110.

[1] Q. Pei, G. Yu, C. Zhang, C. Y. Yang, and A. J. Heeger, Science **269**, 1086 (1995).
[2] Q. Pei, Y. Yang, G. Yu, C. Zhang, and A. J. Heeger, J. Am. Chem. Soc. **118**, 3922 (1996).
[3] Y. Yang and Q. Pei, J. Appl. Phys. **81**, 3294 (1997).
[4] J. C. deMello, N. Tessler, S. C. Graham, and R. H. Friend, Phys. Rev. B **57**, 12951 (1998).
[5] J. C. deMello, Phys. Rev. B **66**, 235210 (2002).
[6] J. Dane, C. Tracy, and J. Gao, Appl. Phys. Lett. **86**, 153509 (2005).
[7] Y. Cao, G. Yu, A. J. Heeger, and C. Y. Yang, Appl. Phys. Lett. **68**, 3218 (1996).
[8] Q. Pei and Y. Yang, J. Am. Chem. Soc. **118**, 7416 (1996).
[9] C. Huang, W. Huang, J. Guo, C. Z. Yang, and E. T. Kang, Polymer **42**, 3929 (2001).
[10] J. Morgado, F. Cacialli, R. H. Friend, B. S. Chuah, H. Rost, and A. B. Holmes, Macromolecules **34**, 3094 (2001).
[11] F. P. Wenzl *et al.*, Adv. Funct. Mater. **14**, 441 (2004).
[12] Y. Cao, Q. Pei, M. R. Andersson, G. Yu, and A. J. Heege, J. Electrochem. Soc. **144**, L317 (1997).
[13] J. Cao, G. Yu, and A. J. Heeger, Appl. Phys. Lett. **71**, 1293 (1997).
[14] G. Yu, Y. Cao, M. Andersson, J. Cao, and A. J. Heeger, Adv. Mater. (Weinheim, Ger.) **10**, 385 (1998).
[15] C. Yin, Y. Z. Zhao, C. Z. Yang, and S. Y. Zhang, Chem. Mater. **12**, 1853 (2000).
[16] D. Xiang, Q. D. Shen, S. Y. Zhang, and X. Q. Jiang, J. Appl. Polym. Sci. **88**, 1350 (2003).
[17] D. Braun, D. Moses, C. Zhang, and A. J. Heeger, Appl. Phys. Lett. **61**, 3092 (1992).
[18] L. Ding, Z. Lu, D. A. M. Egbe, and F. E. Karasz, Macromolecules **37**, 10031 (2004).
[19] F. Kong *et al.*, Synth. Met. **137**, 1083 (2003).
[20] T. W. Lee, O. O. Park, L. M. Do, T. Zyung, T. Ahn, and H. K. Shim, J. Appl. Phys. **90**, 2128 (2001).

[21] J. K. Shen *et al.*, Synth. Met. **137**, 1085 (2003).
[22] C. H. Yang, Q. J. Sun, J. Qiao, and Y. F. Li, J. Phys. Chem. B **107**, 12981 (2003).
[23] I. D. Park, J. Appl. Phys. **76**, 1656 (1994).
[24] T. W. Lee and O. O. Park, Adv. Mater. (Weinheim, Ger.) **13**, 1274 (2001).
[25] D. L. Smith, J. Appl. Phys. **81**, 2869 (1997).
[26] E. Moderegger, F. P. Wenzl, S. Tasch, G. Leising, U. Scherf, and K. O. Annan, Adv. Mater. (Weinheim, Ger.) **12**, 825 (2000).