Novel approach for hole-blocking in light-emitting electrochemical cells

Yutaka Majima, Toshiro Hiraoka *, Norio Takami, Shuzi Hayase

Materials and Devices Research Laboratories, Research and Development Center, Toshiba Corporation, 1, Komukai-Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

Abstract

The light emission from solid-state conjugated polymer light-emitting electrochemical cells (LECs) has been studied when a hole-blocking layer was employed. A multilayer LEC consists of an indium–tin oxide (ITO) electrode, an emissive (EM) layer of poly(1,4-phenylenevinylene) (PPV) containing poly(ethylene oxide) (PEO) complexed with lithium trifluoromethanesulfonate, a hole-blocking (HB) layer of PEO complexed with poly(lithium 4-styrenesulfonate) (PSS-Li), and an aluminum (Al) electrode. The light emission intensity and external quantum efficiency of ITO/EM/HB/EM/Al cells were clearly greater than those of ITO/EM/Al cells. These results indicate that holes on the PPV main chain are trapped by immovable PSS anions and that the HB layer is effective for improving light-emitting properties of LECs. © 1997 Elsevier Science S.A.

Keywords: Light-emitting electrochemical cells; Cation-exchange resin; Hole-blocking layer; Poly(lithium 4-styrenesulfonate)

1. Introduction

The effect on light emission from solid-state conjugated polymer light-emitting electrochemical cells (LECs) as a result of incorporating a cation-exchange resin into the LECs was studied. It was found that the resin clearly improved both light emission and external quantum efficiency.

Recently, Pei et al. [1,2] have reported the development of a single-layer LEC consisting of an indium–tin oxide (ITO) electrode, an emissive (EM) layer of poly(1,4-phenylenevinylene) (PPV) admixed with poly(ethylene oxide) (PEO) complexed with lithium trifluoromethanesulfonate (CF_3SO_3Li), and an aluminum (Al) electrode [1,2]. Their explanation of the operating mechanism of the LEC is summarized here. PPV is a luminescent polymer that is responsive to both n-type and p-type electrochemical doping, while PEO complexed with a lithium salt is a polymer electrolyte with relatively high ionic conductivity. When a sufficiently high voltage is applied between ITO and Al, charges are injected from the electrodes into PPV. When the ITO electrode is wired as the anode and the Al electrode as the cathode, the PPV polymer near the ITO is initially oxidized, the polymer near the Al is reduced, and counterions from the electrolytes move to compensate the charges on the oxidized and reduced polymer chains (holes and electrons, respectively). Under

the influence of the applied voltage, the holes in the PPV propagate from the anode toward the cathode, and the electrons propagate from the cathode toward the anode. These holes and electrons meet in the compensated volume between the n-type-doped and p-type-doped regions. This compensated volume defines the electrochemically induced p–n junction. Within this volume, holes and electrons recombine to form neutral charge carrier pairs which radiatively decay to the ground state. The width of the induced p–n junction has been reported to be 1–3 μm within a 15 μm wide region in the surface cell configuration [2]. In the case of the thin film EM layer of an LEC with a thickness of a few hundred nm, the p–n junction should spread across the entire thickness of the single EM layer, and the holes and electrons are expected to reach their respective counterelectrodes. When the carriers reach their counterelectrodes, the carriers are consumed as conduction carriers which do not contribute radiation. As a result of these non-radiative electrochemical reactions of holes and electrons at their counterelectrodes, the quantum efficiency of the LEC is expected to be reduced.

The carrier transport mechanism of LEC has not been clarified, but the conductivities of the anion and cation are thought to affect the mobilities of holes and electrons, respectively. In this paper, we discuss the light-emitting properties of LECs resulting from the incorporation of a cation-exchange resin into the LECs. The cation-exchange resin used in this study was poly(lithium 4-styrenesulfonate) (PSS-Li), and PEO was complexed with PSS-Li to form the hole-blocking (HB)

---

* Corresponding author. Present address: Department of Physical Electronics, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan.

layer. In the HB layer, the PSS anion is fixed, and cation conduction due to the lithium ion only is observed [3]. The HB layer was incorporated because this layer is expected to block only holes and not electrons. The quantum efficiency of the LEC is expected to improve because the number of holes reaching the cathode will decrease and the density of holes between the anode and HB layer will increase.

2. Procedure

The procedure used to fabricate multilayered LECs containing the cation-exchange resin is now outlined. PPV was prepared by the precursor route [4,5]. We prepared the poly(xylylidene-tetrahydrothiophenium) precursor according to Ref. [5]. PEO ($M_w = 4\ 000\ 000$) and $LiCF_3SO_3$ were used without further purification. The PSS-Li ($M_w = 2700$) cation-exchange resin was kindly supplied by TOSOH. The EM and HB layers were prepared by spin-casting. A methanol solution of the EM layer (SA) contained 780 mg of poly-(xylylidene-tetrahydrothiophenium), 350 mg of PEO, and 65 mg of $LiCF_3SO_3$. A methanol solution of the HB layer (SB) contained 300 mg of PEO and 68 mg of PSS-Li. The films were heated in vacuum at 200 °C for 0.5 h to convert the precursor polymer into PPV. It should be noted that a solution mixture of PPS-Li and poly(xylylidene-tetrahydrothiophenium) was not obtained because of the formation of a polyion complex between PPS-Li and poly(xylylidene-tetrahydrothiophenium). The thicknesses of the EM and HB layers per spin-casting were about 17 nm and below 2 nm, respectively. Multilayer LECs were fabricated on ITO-coated glass substrates (purchased from Geomatec). In the case of ITO/EM/HB/EM/Al cells, spin-casting of the SA solution on the substrate was performed three times, and the sample was heated to 200 °C. Then spin-casting was performed once for each SB and SA solution, and the sample was again heated. The Al electrode was evaporated onto the film at a pressure of around 2×10^{-7} Torr. In the case of ITO/EM/Al cells, spin-casting of the SA solution was performed three times followed by heating, and this process was repeated once (spin-casting of the SA solution was performed a total of six times). In the case of ITO/EM/HB/Al cells, spin-casting of the SA solution was performed three times followed by heating, and then spin-casting of the SB solution was performed once followed by heating.

3. Experimental results and discussion

Fig. 1 shows typical current density–voltage (J–V) characteristics of ITO/EM/Al, ITO/EM/HB/Al, and ITO/EM/HB/EM/Al cells. In Fig. 1, the forward voltage bias indicates that the ITO electrode is wired as the anode. Step voltages of 0 to 4 V in increments of 0.1 V were applied to the cells for 2 s each. The current density for ITO/EM/Al was 3.9 and 2.4 times greater than that of ITO/EM/Al and ITO/EM/

HB/EM/Al, respectively, at an applied voltage of 4 V. Also, the voltage where the current densities for ITO/EM/HB/Al and ITO/EM/HB/EM/Al started increasing exponentially was about 2 V greater than that for ITO/EM/Al.

Fig. 2 shows typical light intensity–voltage characteristics of ITO/EM/Al, ITO/EM/HB/Al, and ITO/EM/HB/EM/Al cells. Yellow–green emission was clearly observed from these cells. The light intensity was measured using a photodiode. The photoemission current density J_{ph} is given by

$$J_{ph} = \frac{en_{ph}}{\phi_{pd}S} \qquad (1)$$

Here e is a unit charge, n_{ph} is the number of emitted photons per second from the cell, ϕ_{pd} is the quantum efficiency of the photodiode in the wavelength range of the emission from the cell, and S is the emissive area of the cell. The J_{ph} values for the ITO/EM/HB/Al and ITO/EM/HB/EM/Al cells were
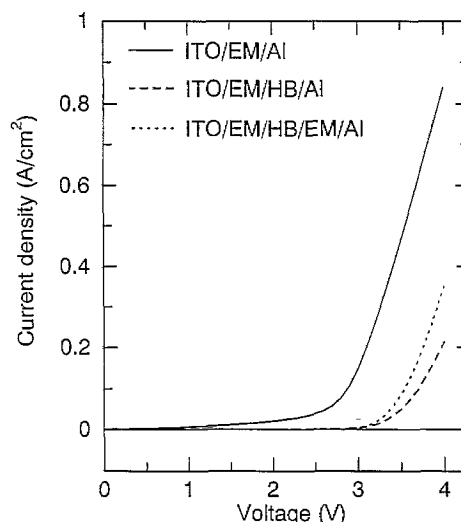

Fig. 1. Current density vs. voltage for ITO/EM/Al, ITO/EM/HB/Al, and ITO/EM/HB/EM/Al cells with the ITO contact wired as the anode.
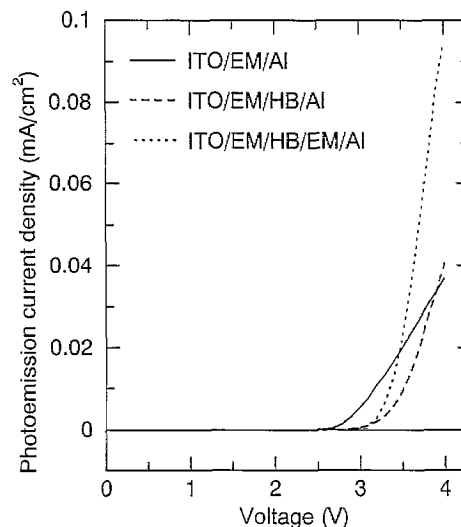

Fig. 2. Photoemission current density vs. voltage for ITO/EM/Al, ITO/EM/HB/Al, and ITO/EM/HB/EM/Al cells.
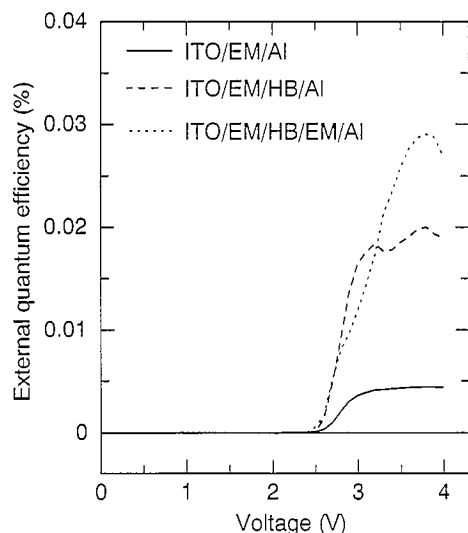
Fig. 3. External quantum efficiency vs. voltage for ITO/EM/Al, ITO/EM/HB/Al, and ITO/EM/HB/EM/Al cells.

respectively 1.1 and 2.5 times greater than that of the ITO/EM/Al cell at an applied voltage of 4 V.

Fig. 3 shows the typical external quantum efficiency–voltage (ϕ–V) characteristics (where $\phi = J_{ph}/J$) of ITO/EM/Al, ITO/EM/HB/Al, and ITO/EM/HB/EM/Al cells. The maximum peak values of ϕ for the ITO/EM/Al, ITO/EM/HB/Al, and ITO/EM/HB/EM/Al cells were 0.0045, 0.020 and 0.029%, respectively. The maximum values of ϕ for the ITO/EM/HB/Al and ITO/EM/HB/EM/Al cells were respectively 4.5 and 6.6 times greater than that of ITO/EM/Al.

The figures also revealed the effects of incorporating the HB layer. In Fig. 1, J decreased as a result of incorporation of the HB layer. When the conduction of electrons is blocked in the same manner as that of holes in the HB layer, J_{ph} should decrease. However, the J_{ph} values for ITO/EM/HB/Al and ITO/EM/HB/EM/Al were respectively 1.1 and 2.5 times greater than that of ITO/EM/Al. These results indicate that, while the number of holes and number of electrons are both reduced by the HB layer, holes and electrons can both cross the HB layer. When the ITO/EM/HB/Al and ITO/EM/HB/EM/Al cells are compared, the J and J_{ph} values for the ITO/EM/HB/EM/Al cell are seen to be respectively 1.6 and 2.3 times greater than those for the ITO/EM/HB/Al cell. When the HB layer and the Al cathode are in contact, the formation of a double layer by the lithium ion at the HB/cathode interface is prevented by the immovable PSS ion. Also, electrons

injected from the Al electrode have to cross the HB layer. The number of injected electrons in the ITO/EM/HB/Al cell is therefore expected to be smaller than that in the ITO/EM/HB/EM/Al cell.

When the number of holes blocked is greater than the number of electrons blocked in the HB layer, the hole density in the region between the ITO electrode and HB layer of the ITO/EM/HB/EM/Al cell will become larger than the hole density in the EM layer of the ITO/EM/Al cell. Also, the radiative recombination rate in the ITO/EM/HB/EM/Al cell is expected to become large as the hole density increases. The increase in J_{ph} in the ITO/EM/HB/EM/Al cell is thought to be caused by the increase in hole density. At this stage, the difference between the number of holes and electrons which cross the HB layer has not been quantified, but the number of holes blocked is expected to be smaller than the number of electrons blocked because the counterion for holes at the EM/HB interface is the PSS ion (which can trap holes effectively). When holes are trapped by immovable PSS ions, the movement of holes on the polymer chain is expected to be restricted. This trapping of holes by PSS ions is expected to make the hopping process of holes difficult.

It should be noted that, although the maximum ϕ value of the ITO/EM/HB/EM/Al cells was only 0.029% in this study, we have already fabricated a cell with a maximum ϕ value of 0.13% by adjusting the thickness of the EM and HB layers. ϕ is expected to improve further if the humidity during storage and the vacuum level during heating are decreased.

In this paper, the effect of the incorporation of an HB layer consisting of PEO complexed with PSS-Li on light emission from LECs was investigated. Both the light emission intensity and the external quantum efficiency were clearly improved by the inclusion of the HB layer. More detailed research, including a study on the fabrication of such a layer using a mixture consisting of a conjugated polymer and PEO complexed with PSS-Li, is now in progress.

References

[1] Q. Pei, G. Yu, C. Zhang, Y. Yang and A.J. Heeger, Science, 269 (1995) 1086.
[2] Q. Pei, G. Yu, C. Zhang, Y. Yang and A.J. Heeger, J. Am. Chem. Soc., 118 (1996) 3922.
[3] L.C. Hardy and D.F. Shriver, J. Am. Chem. Soc., 107 (1985) 3823.
[4] R.A. Wessling, J. Polym. Symp., 72 (1985) 55.
[5] P.L. Burn, D.D.C. Bradley, R.H. Friend, D.A. Halliday, A.B. Holmes, R.W. Jackson and A. Kraft, J. Chem. Soc., Perkin Trans., 1 (1992) 3225.