

Abstract

Influence of several operating conditions on luminance decay in a green organic light-emitting diode with tris (8-hydroxyquinoline) aluminum (Alq3) has been investigated by the analysis of its luminance decay curves. The conditions varied were operating current mode (DC or pulse) and environmental temperature (25–120 °C). The decay curves measured were analyzed by fitting the curves to stretched exponential ones. The analysis results showed that the curves measured under both operation modes well fit to the stretched exponential ones, and that the curves measured under the pulse mode were closer to simple exponential curves than those measured under the DC mode. A rapid decline in the initial

stages of operation appeared in the DC mode, though it was not clearly observed in the pulse mode. Thus, the luminance decay was divided into two major components: a simple exponential during operation and a rapid decline in the initial stages of operation. The simple exponential decline was due to a chemical degradation of Alq3, while the rapid decline is probably due to the generation of an internal electric field. The results also showed that the environmental temperature has little effect on the shape of the decay curves, suggesting that the relative contributions of the two decay components are independent of temperature.

Keywords

Organic light-emitting diode, Degradation mechanism, Luminance decay, Stretched exponential, Lifetime, Half life

1. Introduction

The multilayer organic light-emitting diode (OLED), which was reported by Tang and Van Slyke,¹⁾ has exhibited a great potential for the development of flat panel displays. The first reported multilayer OLED had a half-life of only few hundred hours.¹⁾ Lifetimes of OLEDs are governed by various factors, such as electrochemical or thermal instability of the materials,^{2, 3)} the charge balance between the injected holes and electrons,⁴⁾ instabilities of the interfaces,^{5, 6)} and local electric breakdown or thermal dissipation.⁷⁻⁹⁾ Many approaches have been performed to control these factors in the last decade. Generally, OLEDs have a hole transport layer (HTL) and an emitting electron transport layer (ETL) which are sandwiched between an indium-tin-oxide (ITO) electrode (anode) and a metal electrode (cathode). The introduction of a buffer layer, like copper phthalocyanine (CuPc), between the ITO electrode and the HTL has lowered the injection barrier at the ITO/HTL interface and improved the stability of the interface.¹⁰⁾ Adding an emissive dopant to the emitting layer has improved electroluminescent (EL) efficiency.^{11, 12)} Thermal stability has been improved by using materials with high glass transition temperatures (T_g s).¹⁰⁾ Encapsulation of the device in inert gas has controlled the growth of non-emissive spots.^{8, 13, 14)} By the accumulation of these findings, a lifetime of longer than 10000 h has been achieved in each of red, green, and blue color emissive OLEDs.¹⁵⁾

In spite of such an extension of the lifetime, mechanisms of degradation leading to luminance decay have never been clarified. Recently, Aziz et al. proposed a degradation mechanism in which the long-term luminance decay is based on the formation of unstable cationic tris (8-hydroxyquinoline) aluminum (Alq3) species.¹⁶⁾ This mechanism successfully explained the effects of several approaches, such as addition of an emissive dopant to the emitting layer and introducing a CuPc layer at the ITO/HTL interface.

It is well-known that environmental temperature and initial luminance accelerate the luminance decay.¹⁷⁾ However, the influence of these parameters on the decay mechanisms remains incompletely

understood. The operating current mode (DC or pulse) also varies the lifetime. Thus, we explored the influence of these operating conditions on the decay mechanisms by analyzing luminance decay curves. In order to analyze the curves, we employed two comparison methods.

2. Analysis of luminance decay curves¹⁸⁾

We measured the time dependence of luminance for green OLEDs composed of materials with T_g s of higher than 130 °C. The devices were driven at 25, 85, and 120 °C. The OLEDs with a multilayer structure of ITO/CuPc(10 nm)/triphenylamine tetramer(TPTE)(40 nm)/1.0%-dimethylquinacridone (MEQA)-doped Alq3(20 nm)/non-doped Alq3(40 nm)/LiF(0.5 nm)/Al(150 nm) were fabricated using a standard vacuum evaporation process. The TPTE used as a hole transport layer has a T_g of higher than 130 °C.¹⁹⁾ The ITO substrates were cleaned by plasma exposure prior to the deposition of CuPc. The devices were encapsulated with some desiccants in nitrogen atmosphere after the fabrication.

The devices had an active area of 3×3 mm and were driven at a constant DC current density of 59 mA/cm² in order to obtain an initial luminance of 4800 cd/m² in an oven controlled at 25, 85, or 120 °C. The time dependence of the luminance was monitored with a luminance meter through the window of the oven.

Figure 1 shows the luminance decay curves measured under the above operating conditions.

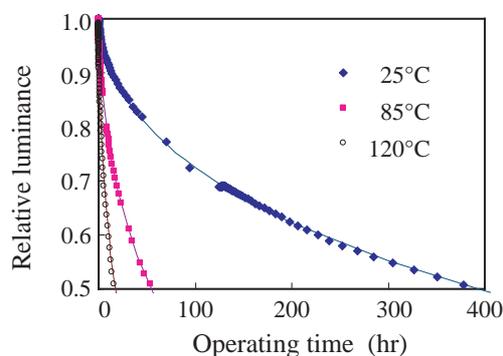


Fig. 1 Relative luminance decay curves of devices operated at 25, 85, and 120 °C. The initial luminance was 4800 cd/m². The solid lines are stretched exponential fits to the decay curves.

Although this figure clearly indicates that the environmental temperature accelerates the luminance decay, it does not tell us the difference in mechanism among the three decay curves. It is a general idea that luminance decays proceed under multiple mechanisms operating in parallel.¹⁷⁾ The temperature may change the relative contributions of the different mechanisms. Thus, we compared the shapes of the luminance decay curves to investigate the influence of temperature on the decay mechanisms. To compare the shapes of the curves, we employed two methods.

One of the two is to redraw the decay curves on a time scale normalized by half-life. **Figure 2** shows the decay curves obtained by redrawing the curves in Fig. 1. Redrawing in this way makes it possible to compare the curves with widely different half-lives. In this case, all three curves, measured at 25, 85, and 120 °C, have almost the same shape. This shows that the environmental temperature under the T_g s of the organizational materials hardly changes the relative contribution of the different degradation mechanisms.

The comparison of decay curves by redrawing using a normalized time scale is a simple and easy method. It is, however, difficult to check for slight differences in shape, because the normalized decay curves meet inevitably at the starting point (the

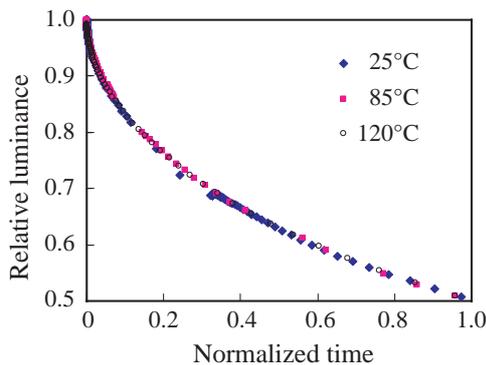


Fig. 2 Relative luminance decay curves redrawn on a time scale normalized by each half life obtained from the devices operated at 25, 85, and 120 °C.

initial time) and the end point (the normalized time 1). Thus, another method was employed to analyze the decay curves. The measured decay curves were fitted by using the following stretched exponential equation:

$$L(t)/L_0 = \exp[-(t/\tau)^\beta] \dots\dots\dots(1)$$

where $L(t)$ is the luminance at time t , L_0 is the initial luminance, τ corresponds to the decay time, and β is called dispersion factor, which expresses the shape of the curve.

The solid lines in Fig. 1 are the stretched exponential fits to the measured decay curves. The stretched exponential fits traced the experimental data accurately. **Table 1** shows the parameters obtained from the fits. Since the shape of the decay curves is expressed by β , β is compared to check the differences between the shapes. Table 1 indicates that almost the same value of β is obtained from the decay curves measured at 25, 85, and 120 °C. This confirms that the three decay curves have the same shape.

3. Influence of operating conditions on luminance decays

The comparison of the decay curves demonstrated that the environmental temperature had little effect on luminance decay mechanisms. There are, however, several cases in which the shape of a luminance decay curve is significantly changed by operating conditions. As an example, we compared the decay curve of the device operated under a pulse current stress with that under DC constant current operation. Under the pulse mode stress, the device was operated at a pulsed current with a frequency of

Table 1 Parameters obtained from the stretched exponential fits to the luminance decay curves in Fig. 1.

	τ	β
25	757	0.56
85	102	0.59
120	31.8	0.57

153 Hz and duty cycle of 1.6 %. The luminance decay curves obtained under the two operating conditions are shown in **Fig. 3**. The initial luminance was 300 cd/m². It is clearly seen that the shape of the decay curve under pulse current operation is different from that under DC operation. The solid lines in the figure are the stretched exponential fits to the plotted data. **Table 2** shows the parameters extracted from the fits. The value of β obtained from pulse current operation is closer to 1 than that from DC current operation. This indicates that the pulse current operation brings the decay curve close to a simple exponential one. The shape difference between the simple exponential curve and

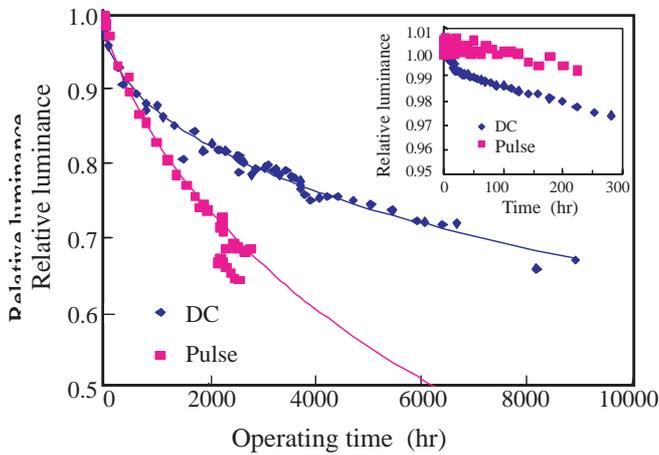


Fig. 3 Relative luminance decay curves of devices operated at pulse and DC current stress. The solid lines are stretched exponential fits to the decay curves. The inset is the enlargement of the early degradation stage.

Table 2 Parameters obtained from the stretched exponential fits to the luminance decay curves in Fig. 2.

	τ	β
DC	60400	0.48
Pulse	10300	0.72

the decay curve obtained from DC current operation is due to the appearance of rapid decay in the initial stages of DC operation, as shown in the inset of Fig. 3. In the case of DC current operation, the exponential luminance decay and the rapid one probably proceed in parallel. The mechanisms of the simple exponential decay and the rapid decay are discussed below.

4. Mechanisms of luminance decay

4.1 The exponential decay mechanism

In this section, we discuss the simple exponential decay, that is, the case of $\beta = 1$ in Eq. (1). As a model of degradation, we suppose a reaction scheme that a light emitting species A is excited to A^* and A^* returns to A again, as shown in **Fig. 4**. In the scheme, if the generation rate of a non-emissive species B is expressed as r_B , the concentration of A , C_A , is given by the following expression:

$$C_A/C_A^0 = (1-r_B)^n \dots\dots\dots(2)$$

where C_A^0 is the initial concentration of A and n is the number of the reaction times. Assuming that $r_B \ll 1$ and $n \rightarrow \infty$, Eq. (2) is transformed into the following expression:

$$C_A/C_A^0 = \exp(-r_B n). \dots\dots\dots(3)$$

As an analogy between this equation and Eq. (1) with $\beta = 1$, the exponential decay of luminance can be explained by the reaction model. As a more concrete reaction model, we can adopt the degradation model proposed by Aziz et al. in which

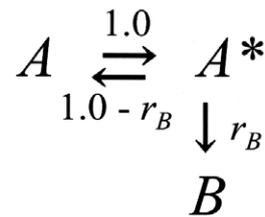


Fig. 4 A Scheme of a degradation reaction. A is a light emitting species, A^* is an excited state of A , and B is a non-emissive species produced as a result of degradation. The generation rate of B is presented by r_B .

the long-term luminance decay is based on the formation of the unstable cationic Alq3 specie,¹⁶⁾ because the reaction scheme can be substituted for the redox reaction of Alq3 as shown in **Fig. 5**. Although the reaction model in Fig. 4 could certainly be replaced by another model that is expressed by a first-order reaction, the reaction model shown in Fig. 5 is at least consistent with the exponential luminance decay.

4. 2 Rapid luminance decay in the initial stages of operation

The device operated at a DC constant current exhibited the luminance decay curve fitted by the stretched exponential expression with β of less than 0.5. Even though the device was operated by a pulsed current, the value of β obtained from the fitting was still less than 0.8. The main difference between these measured decay curves and the simple exponential curve is the appearance of the rapid decay in the initial stages of operation, as mentioned above.

The two likely causes have been proposed for the rapid decay. One of the two is that an internal electric field is generated due to mobile ions or polarization of some organic molecule.²⁰⁾ The internal electric field decreases the effective electric field. The other is the morphological change in an organic film induced by heat.¹⁷⁾ We consider the former as a plausible explanation for the rapid decay because it successfully explains the experimental result that the pulse drive hindered the rapid decay. In the case of the pulse operation there are long

intervals with an applied voltage of zero. It is most likely that the intervals reduce the internal electric field. As a result, the rapid decay is reduced by the pulse drive.

On the other hand, Hung et al. reported that modification of the ITO surface by polymerized CFX films improved the rapid luminance decay in the initial stages of operation.²¹⁾ This suggests that the stability of the ITO/HTL also affects the rapid decay. A combination of several mechanisms probably results in the rapid decay.

5. Summary

The influence of environmental temperature and operating current mode (DC or pulse) on luminance decay in OLEDs was investigated by the analysis of luminance decay curves. The curves measured were analyzed by fitting the curves to stretched exponential ones. The results showed that the curves well fit to the stretched exponential ones, and that the environmental temperature hardly changed the shape of the decay curves. The results also showed that the curves measured under the pulse mode were closer to simple exponential curves than those measured under the DC mode. A rapid decline in the initial stages of operation appeared in the DC mode, though it hardly appeared in the pulse mode. Thus, the luminance decay was divided into two major components: a simple exponential during operation and a rapid decline appearing in the initial stages of operation. The exponential luminance decay was explained in terms of a certain chemical degradation reaction. The rapid decline is probably due to the generation of an internal electric field. The temperature-independent shape of the decay curves suggests that the environmental temperature has little effect on the relative contributions of the two decay components.

References

- 1) Tang, C. W. and Van Slyke, S. A. : Appl. Phys. Lett., **51**-12(1987), 913
- 2) Scott, J. C., Kaufman, J. H., Brock, P. J., DiPietro, J. R. and Goitia, J. A. : J. Appl. Phys., **79**-545(1996), 27
- 3) Fenter, P., Schreiber, F., Bulivic, V. and Forrest, S. R. : Chem. Phys. Lett., **277**(1997), 521
- 4) Vestweber, H. and Rieß, W. : Synth. Met., **91**(1997), 181

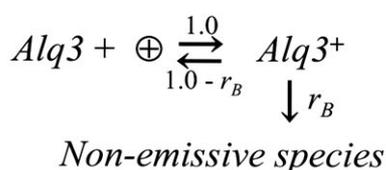


Fig. 5 A redox reaction scheme of Alq3.
 \oplus represents a hole.

- 5) Lee, S. T., Gao, Z. Q. and Hung, L. S. : Appl. Phys. Lett., **75**-10(1999), 1404
- 6) Gautier, E., Lorin, A., Nanzi, J. M., Schalchli, A., Benattar, J. J. and Vital, D. : Appl. Phys. Lett., **69**-8 (1996), 1071
- 7) Liao, L. S., He, J., Zhou, X., Lu, M., Ziong, Z. H., Deng, Z. B., Hou, X. Y. and Lee, S. T. : J. Appl. Phys., **88**-5(2000), 2386
- 8) McElvain, J., Antoniadis, H., Hueschen, M. R., Miller, J. N., Roitman, D. N., Sheats, J. R. and Moon, R. L. : J. Appl. Phys., **80**-10(1996), 6002
- 9) Savvate'ev, V. N., Yakimov, A. V., Davidov, D., Pogreb, R. M., Neumann, R. and Avny, Y. : Appl. Phys. Lett., **71**-23(1997), 3344
- 10) Van Slyke, S. A., Chen, C. H. and Tang, C. W. : Appl. Phys. Lett., **69**-1(1996), 2160
- 11) Shi, J. and Tang, C. W. : Appl. Phys. Lett., **70**-13 (1997), 1665
- 12) Tang, C. W., Van Slyke, S. A. and Chen, C. H. : J. Appl. Phys., **65**-9(1989), 3610
- 13) Cumpston, B. H., Parker, I. D. and Jensen, K. F. : J. Appl. Phys., **81**-8(1997), 3716
- 14) Burrows, P. E., Bulovic, V., Forrest, S. R., Sapochak, L. S., McCarty, D. M. and Thompson, M. E. : Appl. Phys. Lett., **65**-23(1994), 2922
- 15) Sakaguchi, Y., Tada, H., Tanaka, T., Kitazume, E., Mori, K., Kawashima, S. and Suzuki, J. : Soc. for Inform. Display 2002 Int. Symp. Digest of Tech. Pap., **33**(2002), 42.3
- 16) Aziz, H., Popovic, Z. D., Hu, N. X., Hor, A. M. and Xu, G. : Science, **283**(1999), 1900
- 17) Parker, I. D., Cao, Y. and Yang, C. Y. : J. Appl. Phys., **85**-4(1999), 2441
- 18) Ishii, M. and Taga, Y. : Appl. Phys. Lett., **80**-18 (2002), 3430
- 19) Tokito, S., Tanaka, H., Noda, K., Okada, A. and Taga, Y. : IEEE Trans. Electron Devices, **44**-8(1997), 1239
- 20) Zou, D. and Tutsui, T. : J. Appl. Phys., **87**-4(2000), 1951
- 21) Hung, L. S., Zheng, L. R. and Mason, M. G. : Appl. Phys. Lett., **78**-5(2001), 673

(Report received on Apr. 1, 2003)



Masahiko Ishii

Year of birth : 1960

Division : Frontier research group VIII

Research fields : Materials and device structures in organic light-emitting diode, Organic transistors, Colloidal crystals

Academic degree : Dr. Eng.

Academic society : Jpn. Soc. Appl. Phys.