

ORGANIC ELECTROLUMINESCENT DEVICES WITH BRIGHT BLUE EMISSION

*Yuji HAMADA, Chihaya ADACHI[†], Tetsuo TSUTSUI[†],
and Shogo SAITO[†]*

Functional Materials Research Center, SANYO Electric Co., Ltd.
1-18-13, Hashiridani, Hirakata, Osaka 573

[†]Department of Materials Science and Technology
Graduate School of Engineering Science, Kyushu University
Kasuga-koen 6-1, Kasuga-shi, Fukuoka 816

(Received 28 February 1992; accepted for publication 23 April 1992)

Reprinted from

OPTOELECTRONICS—*Devices and Technologies*—

mita

PUBLISHED BY MITA PRESS
TOKYO, JAPAN

ORGANIC ELECTROLUMINESCENT DEVICES WITH BRIGHT BLUE EMISSION

Yuji HAMADA, Chihaya ADACHI[†], Tetsuo TSUTSUI[†],
and Shogo SAITO[†]

Functional Materials Research Center, SANYO Electric Co., Ltd.
1-18-13, Hashiridani, Hirakata, Osaka 573

[†]Department of Materials Science and Technology
Graduate School of Engineering Science, Kyushu University
Kasuga-koen 6-1, Kasuga-shi, Fukuoka 816

(Received 28 February 1992; accepted for publication 23 April 1992)

Abstract Ten newly synthesized oxadiazole derivatives have been examined as the emitter in organic electroluminescence (EL) devices, and it has been found that eight compounds show blue fluorescence. Most of the EL devices that use the new oxadiazole derivatives have luminance above 100 cd/m² at less than 20 V. Especially significant is the EL device with 1, 3-bis [5-(*p*-dimethylaminophenyl)-1, 3, 4-oxadiazol-2-yl] benzene (OXD-8) which yields bright blue emission having intensity of 1000 cd/m².

The stability of device performance has also been investigated; no remarkable change in the blue emission has been observed after 40 days' standing at ambient temperature.

The durability of the blue EL device under continuous driving conditions is also examined. The luminance falls to half its initial level after 0.25 hours at room temperature. At the temperature of liquid nitrogen, however, only a 20% decrease from the initial luminance is found even after 5 hours' driving. One of the main causes of luminance reduction is assumed to be Joule heat in the EL devices.

1. Introduction

Recently, with the accelerated promotion of the "information society," much attention has been focused on flat panel displays that consume less electric power and occupy less space than cathode-ray tubes (CRTs). Liquid crystal display is a typical example of current flat display technology. Now, a self-luminescent EL device which provides a clear display is drawing special attention.

EL devices can be classified as either inorganic or organic, depending on their constituent materials. Inorganic EL devices have already been put to practical use, although they need to be driven with a high voltage because they are of the so-called "impact excitation" type. This leads to an increase in the cost of peripheral devices. In contrast, organic EL devices can be driven with low voltage because they are injection-type devices.

The application of organic EL devices to new flat display has been expected since C. W. Tang reported high brightness organic EL devices with an 8-hydroxyquinoline aluminum emitter, and C. Adachi proposed stable organic EL devices

Key Words Organic electroluminescent device, organic materials, blue emission, oxadiazole derivatives.

with three-layer structure [1], [2].

These EL devices consist of a hole transport layer (HTL), an electron transport layer (ETL) and an emitter layer (EML), sandwiched between a cathode and an anode. The mechanism of organic electroluminescence is such that holes and electrons, respectively injected from a cathode and an anode, recombine on the interface of the EML and HTL (or ETL), as well as inside the EML, and the recombination of holes and electrons produces light.

One of the most interesting advantages of organic materials is the possibility of a wide range of emission colors for organic EL devices, as a result of the molecular design of organic materials. For example, 8-hydroxy-quinoline aluminum, phthaloperinone derivatives [3] and perylene derivatives [3] are green, yellow and red emitting materials, respectively. However, blue emitting materials, which have stable and high brightness emission, have not yet been developed.

We propose newly synthesized oxadiazole derivatives (OXD) as emitter materials for organic EL devices because they exhibit blue fluorescence. In this paper, we report the characterization of blue emitting EL devices that use new oxadiazole derivatives as the emitter.

2. Experiment

2.1 Samples The new oxadiazole derivatives were synthesized as described by F. N. Hayes [4]. The reactions are shown in Fig. 1. The structures of the oxadiazole derivatives were divided into three types: A, B, and C (Fig. 2). These

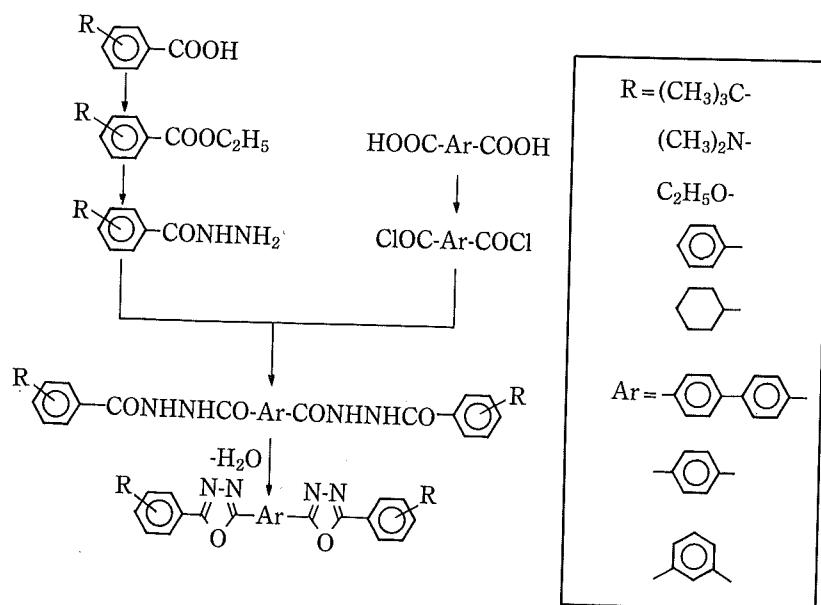


Fig. 1.

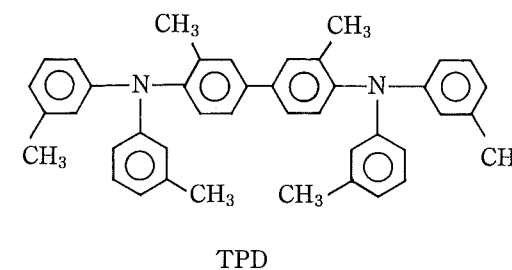
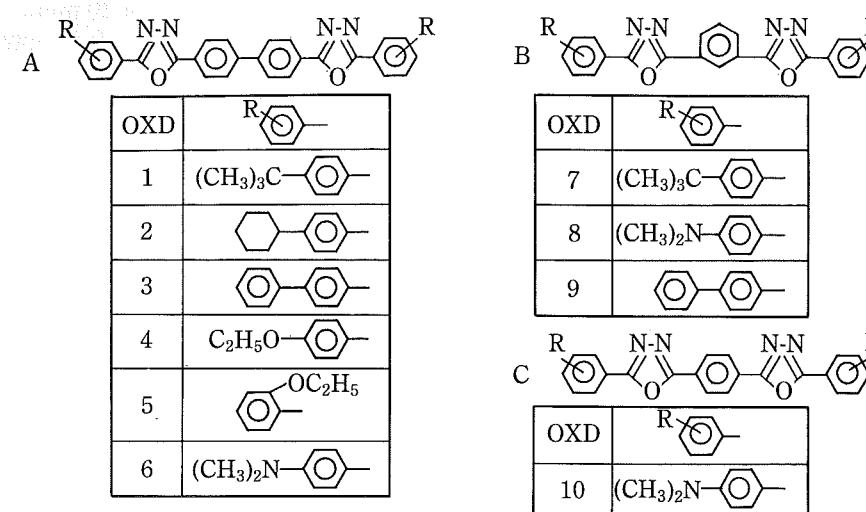


Fig. 2. Chemical structures of new oxadiazole derivatives and diamine derivatives.

compounds were purified by the train sublimation method [5].

OXD-7 was used as the electron transport material in the organic EL devices, because the energy of excited OXD-7 is higher than that of other oxadiazole derivatives. (The PL peak wavelength of OXD-7 was 374 nm, while that of other oxadiazole derivatives was longer).

The structure of the diamine derivative (TPD) used as the hole transport material is also shown in Fig. 2.

2.2 Fabrication of EL devices The substrate was indium-tin-oxide (ITO) coated glass (sheet resistance: 20 Ω/□) purchased from Asahi Glass Co. The ITO coated glass was cut into chips (12 × 45 mm) with a glass cutter. The thickness of the ITO layer was about 1000 Å. The ITO layers were etched with stripes (width: 2 mm) using aquaregia and used as the anodes.

The cleanliness of the substrates was found to be an important factor governing the performance of the organic EL devices. First, ultrasonication in detergent

(0.5% aqueous solution), acetone and ethyl alcohol was carried out for 20 minutes, successively. Then the substrate was boiled with ethyl alcohol for 5 minutes, removed carefully with tweezers and allowed to dry naturally.

The EL devices were fabricated by conventional vacuum vapor deposition in a vacuum of 1×10^{-6} Torr. The organic materials were evaporated from tantalum boats onto an ITO glass substrate at room temperature. The deposition rate for the organic layers was typically 2.0–3.5 Å/sec. The source–substrate distance was usually maintained at 25 cm.

The upper electrode (cathode) was a 2000 Å-thick MgAg (10:1) alloy layer, which was formed as stripes (width: 2 mm) across the ITO stripes. The emitting area in the EL device was 2 × 2 mm. MgAg alloy was deposited from two metal sources which were controlled independently. The deposition rate for magnesium was typically 4 Å/sec, and that for silver, 0.4 Å/sec.

Three types of EL device structure were used in our study (Fig. 3):

Type SH-A [ITO/HTL (TPD) 600 Å/EML (OXD) 400 Å/MgAg 2000 Å]
 Type SH-B [ITO/EML (OXD) 500 Å/ETL (OXD-7) 500 Å/MgAg 2000 Å]
 Type DH [ITO/HTL (TPD) 600 Å/EML (OXD) 100 Å/
 ETL (OXD-7) 300 Å/MgAg 2000 Å]

2.3 Samples for PL spectra measurement The oxadiazole derivatives were vacuum-deposited on non-fluorescent slide glass (cleaned, size: 12 × 45 mm). The thickness of the deposited films was about 500 Å. Measurement of the PL spectra was carried out by fluorescent meter (Hitachi, model 650-60).

2.4 Measurement of EL characteristics The luminance-voltage characteristics were measured using a luminance meter (Topcon BM-8, measuring field: 2°) and a photon counter (Hamamatsu Photonics, model C767) connected to a

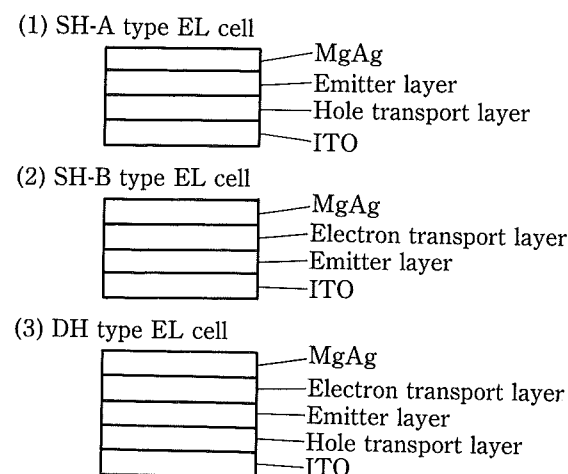


Fig. 3. Configuration of EL devices.

photomultiplier (R649), an electrometer (Takeda Riken, TR-8651) and a power supply (Metronix, DMR200-02). The EL spectra were obtained using a monochromator (Jasco, CT-10) and photoncounter. All measurements were carried out at a vacuum of 10^{-3} Torr in a cryostat.

3. Results and discussion

3.1 Photoluminescence peak wavelengths in oxadiazole thin films

Figure 4 shows the photoluminescence (PL) peak wavelengths of A, B and C type oxadiazole derivative thin films. A type oxadiazole derivatives had PL peak wavelengths ranging from 410 nm (OXD-1) to 510 nm (OXD-6). It was found that the PL peak wavelengths of these compounds, which had stronger donor substituent, became longer.

B type PL peak wavelengths were usually 30–40 nm shorter than those of the A type. The reason for this was that the contrast of π electron conjugation in the benzene ring was collapsed because of the displacement of two oxadiazole rings (electron acceptors) in the meta position of the benzene ring. C type (OXD-10 only) PL peak wavelengths were longer than those of both A type (OXD-6) and B type (OXD-8).

Consequently, it was found that eight in ten oxadiazole derivatives exhibited blue fluorescence (less than 500 nm).

3.2 Luminance characteristics of EL devices The luminance-voltage characteristics of EL devices (SH-A structure) with A type oxadiazole as the emitter

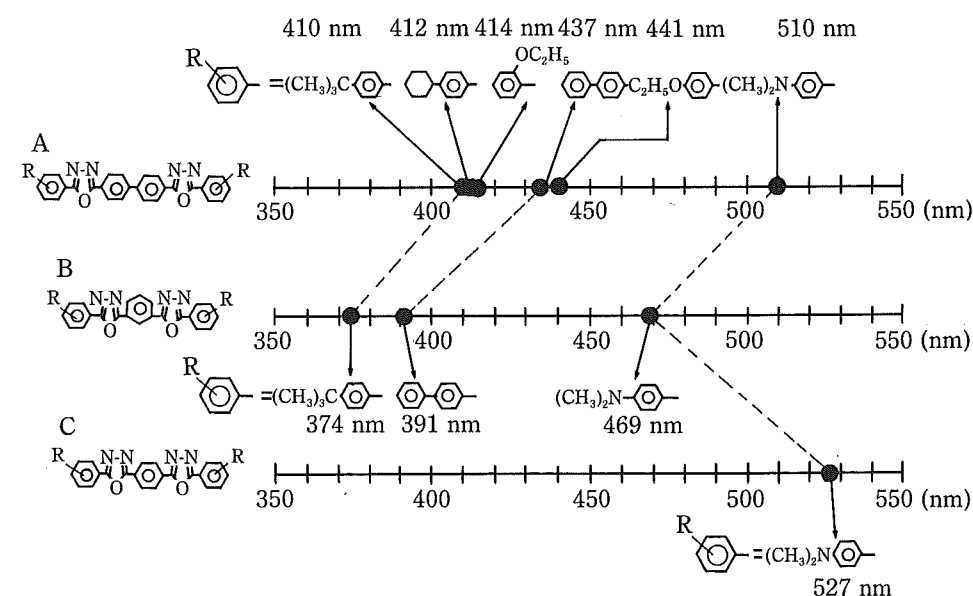


Fig. 4. Photoluminescence (PL) peak wavelengths of ten oxadiazole derivatives in vacuum-deposited films.

are shown in Fig. 5, while those for the B and C types are shown in Fig. 6. The PL and EL peak wavelengths and maximum luminances of the EL devices (SH-A structure) are shown in Table 1.

All of these devices (except OXD-5) achieved a luminance of more than 100 cd/m^2 at less than 20 V. Especially significant were EL devices with OXD-6, 8, and 10, which had a high luminance of 1000 cd/m^2 . Only the EL device with OXD-5 had low luminance, because the OXD-5 thin film was of poor quality and adhered badly to the MgAg alloy.

Blue emissions were observed in EL devices using six of the new oxadiazole derivatives (OXD-1, 2, 5, 7, 8 and 9). The EL device with OXD-8 showed the highest luminance of the six oxadiazole derivatives. Although those EL devices with OXD-6 and 10 showed more than 2000 cd/m^2 , their emission colors were green.

Careful inspection of Table 1 reveals that there were 2 groups of blue EL materials, in which the difference between the EL and PL peak wavelengths was either large or small. The EL peak wavelengths of OXD-1, 2, 5, 7 and 9 were longer than the PL peaks by 70~90 nm. However, the EL peak wavelength of OXD-8 was only 11 nm longer. It is thought that oxadiazoles form exciplexes with TPD on the interface, causing the EL peak wavelength to become longer in consequence. However, OXD-8 had poor ability to form exciplexes with TPD, and so only EL devices with OXD-8 could obtain a high blue colored luminance of 1000 cd/m^2 .

The luminance characteristics of the other device structures were examined in order to study the electrical properties of the blue emitting oxadiazoles. In this

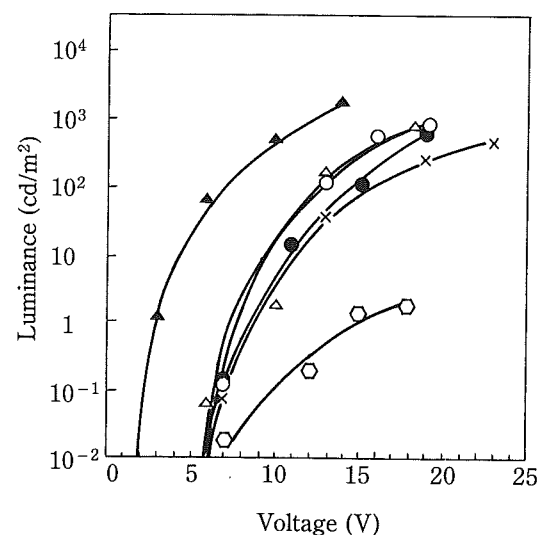


Fig. 5. Luminance-voltage characteristics of EL devices with A type oxadiazole derivatives as the emitter. (Device structure; SH-A, \circ OXD-1, \bullet OXD-2, \times OXD-3, Δ OXD-4, \square OXD-5, \blacktriangle OXD-6)

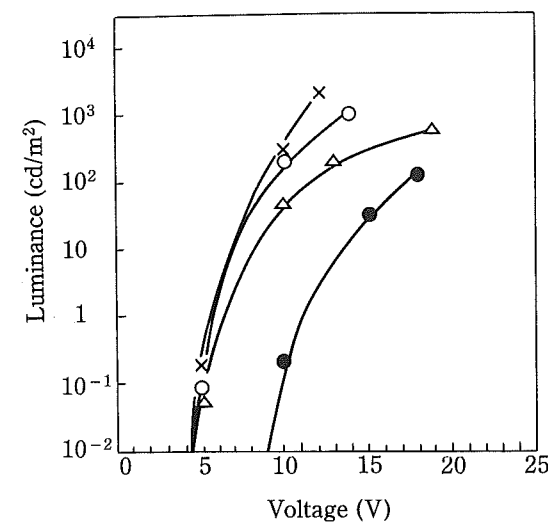


Fig. 6. Luminance-voltage characteristics of EL devices with B and C type oxadiazole derivatives as the emitter. (Device structure; SH-A, Δ OXD-7, \circ OXD-8, \bullet OXD-9, \times OXD-10)

Table 1. The EL and PL peak wavelengths and maximum luminances of EL devices with ten oxadiazole derivatives as the emitter

OXD	PL (nm)	EL (nm)	Colors	Maximum luminance
1	410	487	B	750 (cd/m^2)
2	412	485	B	550
3	437	505	BG	410
4	441	505	BG	730
5	414	492	B	2
6	510	525	G	2200
7	374	465	B	600
8	469	480	B	1000
9	391	465	B	130
10	527	524	G	2200

B: Blue, BG: Blue-Green

experiment, the device structures (the SH-A and SH-B structures) were examined. OXD-1 was selected from the group with a large difference between the PL and EL peak wavelengths. SH-A and SH-B structures with OXD-1 as the emitter

were made, and their luminance-voltage characteristics are shown in Fig. 7. The SH-A structure produced a maximum luminance of 750 cd/m^2 at 19 V, whereas the SH-B structure showed a maximum luminance of only 0.24 cd/m^2 at 22 V. It is thought that OXD-1 only has electron transport properties and cannot act as an emitter with hole transport properties in the SH-B structure. Therefore, OXD-1 can form exciplexes with TPD in the SH-A structure because of its stronger electron withdrawing, and the difference between the EL and PL peaks becomes larger.

DH, SH-A and SH-B structures with OXD-8 as the emitter were also made, and the luminance-voltage characteristics are shown in Fig. 8. Both SH-A and SH-B achieved a high luminance of 1000 cd/m^2 . Therefore, we conclude that OXD-8 has both hole transport and electron transport properties, and does not form exciplexes with TPD.

3.3 Storage test A storage test for the blue EL device was carried out on the DH structure (ITO/TPD/OXD-8/OXD-7/MgAg). When a current density of 10 mA/cm^2 was applied, the initial luminance was measured with a luminance meter. The EL device was then placed in a desiccator at ambient temperature and stored in a vacuum. It was removed from the desiccator at intervals and subjected to the same current densities, and changes in luminance were monitored (Fig. 9). The decrease in luminance for the EL device was recorded over the first 4 days following production. On the fourth day, the luminance had fallen to half the initial luminance measurement. However, measurements over the next 40 days indicated no further decrease in luminance. It was not observed that the EL device was broken by growth of crystals in the organic layers. It is thought that OXD-8 and OXD-7 thin films show good stability and are difficult to grow in crystalline form, respectively.

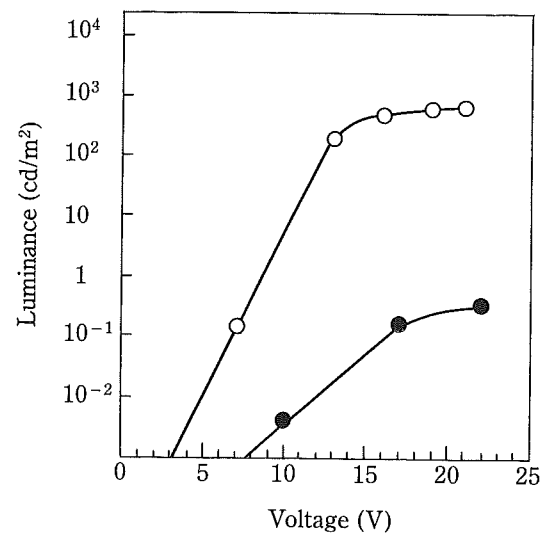


Fig. 7. Luminance-voltage characteristics of SH-A and SH-B devices with OXD-1 as the emitter. (○SH-A, ●SH-B)

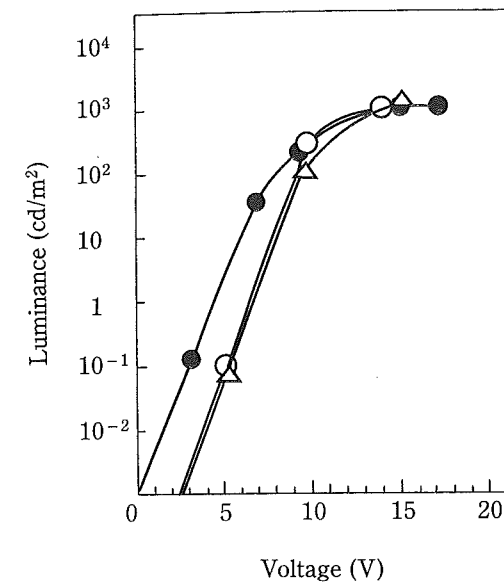


Fig. 8. Luminance-voltage characteristics of SH-A, SH-B and DH devices with OXD-8 as the emitter. (○SH-A, ●SH-B, △DH)

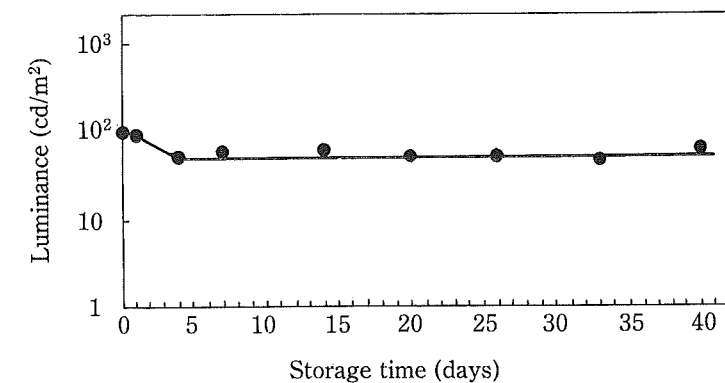


Fig. 9. The storage durability of the blue EL device.

3.4 Continuous driving test The durability of the blue EL device (DH type; ITO/TPD/OXD-8/OXD-7/MgAg) under continuous driving conditions was examined. A fixed current density of 10 mA/cm^2 was applied to the EL device during continuous driving at room temperature, and luminance decrease was

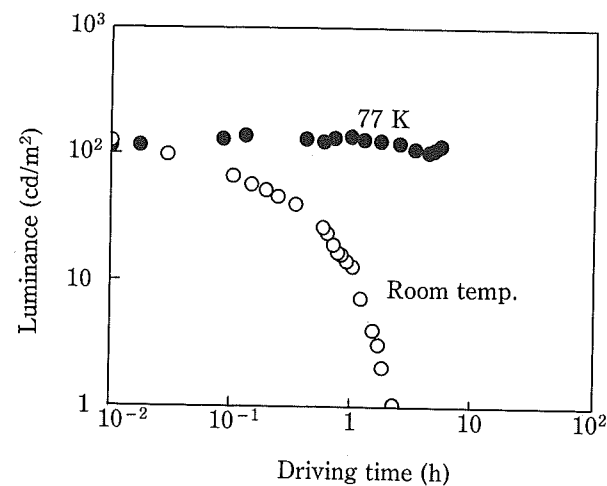


Fig. 10. The durability of the blue EL device under continuous driving conditions. (○Room temperature, ●77 K)

checked (Fig. 10). After 0.25 hours, the luminance had decreased to half the initial luminance of 115 cd/m². After the EL device had emitted continuously for 2.5 hours, its luminance had fallen to 1 cd/m².

However, there was only a 20% decrease in the initial luminance, even after 5 hours' continuous driving, when the device was driven at the temperature of liquid nitrogen (77 K).

One of the main causes of the decrease in luminance was assumed to be degradation at the interface contacts between the organic layers and electrodes due to Joule heat production. Although there remain some unsolved problems regarding durability under continuous driving, much progress has been made on the long-term stability of blue EL devices.

4. Conclusion

Newly synthesized oxadiazole derivatives were examined as the emitter in organic EL devices. The findings are as follows:

- (1) The new compounds had PL peak wavelengths ranging from 374 to 527 nm, and eight of these compounds exhibited blue fluorescence (less than 500 nm).
- (2) All EL devices using oxadiazole derivatives (except OXD-5) as the emitter produced a luminance of more than 100 cd/m² at less than 20 V. EL devices containing six of the oxadiazoles produced blue color emissions. Especially significant was the EL device with OXD-8, which had a high luminance of 1000 cd/m².
- (3) OXD-6, 8 and 10 exhibited both hole and electron transport properties in EL devices, whereas the other oxadiazole derivatives showed only the electron transport property. EL devices with the other oxadiazole derivatives showed a difference between the EL and PL peak wavelengths because they could form exciplexes with the hole transport layer in the

SH-A structure.

- (4) The blue EL devices had long-term stability when allowed to stand at ambient temperature. The luminance fell to half the initial value after 4 days, but measurements taken over the next 40 days indicated no further decrease in luminance. It is thought that OXD-8 and OXD-7 thin films show good stability.
- (5) The durability of the blue EL device under continuous driving conditions was examined. The luminance decreased to half its initial level after 0.25 hours at room temperature. At the temperature of liquid nitrogen, however, only a 20% decrease in the initial luminance was found even after 5 hours' driving. One of the main causes of luminance decrease was assumed to be Joule heat in the EL device.

References

- [1] C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51** (1987) 913.
- [2] C. Adachi, S. Tokito, T. Tsutsui, and S. Saito, *Jpn. J. Appl. Phys.*, **27** (1988) L713.
- [3] C. Adachi, M. Morikawa, T. Tsutsui, and S. Saito, *Chemistry of Functional Dyes*, Mita Press, Tokyo (1989) 583.
- [4] F. N. Hayes, B. S. Rogers, and D. G. Ott, *J. Am. Chem. Soc.*, **77** (1955) 1850.
- [5] H. J. Wagner, R. O. Loutfy, and C. K. Hsiao, *J. Mater. Sci.*, **17** (1982) 2781.