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<http://hdl.handle.net/2324/19442>

出版情報 : Applied Physics Letters. 66 (20), pp.2679-2681, 1995-05-15. American Institute of Physics

バージョン :

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Molecular design of hole transport materials for obtaining high durability in organic electroluminescent diodes

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(Received 19 December 1994; accepted for publication 20 March 1995)

The molecular design of hole transport materials (HTMs) for producing high durability in organic layered electroluminescent (EL) diodes was elucidated. The durability tests were examined using fourteen hole transport materials in the cell structure of an anode/hole transport layer (HTL)/emitter layer (EML)/cathode. The ionization potential (I_p) of HTLs was found to be the dominant factor for obtaining high durability in organic EL devices. The formation of the small energy barrier at the interface of a HTL/anode was required for high durability. Moreover, no straightforward relations between melting point, glass transition temperature of the HTMs, and durability of the EL devices were observed. The EL device using the HTM having a low I_p (5.08 eV) showed an especially remarkable stability. In this case, the half-life period of the initial luminance was beyond 500 h.

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After Tang's report on the multilayered organic electroluminescent (EL) diode,¹ the development of organic EL devices focused on the optimization of cell structures for obtaining high luminance^{2,3} and the development of organic materials for obtaining a wide variety of emission colors.⁴⁻⁷ Concerning the optimization of EL cell structures, three types of EL cell structures were proposed.⁸ Using various kinds of EL cell structures, a variety of fluorescent dyes could be used for emitter materials. The key point for obtaining high luminance was found by controlling the movement of charge carriers and molecular excitons and to realizing the confinement in the emitter layers. A variety of emission colors were also obtained by the doping of highly fluorescent molecules into the host emitter layers based on the idea of a host-guest system.^{9,10} Thus, it was revealed that the organic EL devices possess high quantum efficiency (3%) and high energy conversion efficiency (10 lm/w) with various emission colors.¹¹

From a practical point of view, another significant subject is to increase the durability of the EL devices. There have been several studies on EL devices with the aim of achieving high durability under continuous operation. In particular, VanSlyke demonstrated the insertion of a phthalocyanine layer between an anode/HTL interface, which resulted in a significant improvement in durability.¹² Recently, Shirota demonstrated that the multilayered EL device consisting of double hole transport layers of triphenylamine derivatives exhibits significant durability.¹³ At this stage, however, the factors affecting the durability of the EL devices remained uncertain.

In this study, we focused on the energy barrier of hole injection and examined the durability tests using fourteen hole transport materials (HTMs) in the cell structure of an anode/hole transport layer (HTL)/emitter (EML)/cathode. We also measured the ionization potential (I_p) of the HTLs and the melting point (T_m) and glass transition temperature (T_g) of the HTMs. We mention the molecular design of

HTMs for obtaining high durability in organic EL diodes.

Figure 1 shows the EL cell structure used in this study. In Fig. 1 the organic materials, the HTMs, and the emitter material are also shown. We used fourteen aromatic amines as the HTL and tris(8-quinolinolato) aluminum as an emitter. Organic layers were deposited on a precleaned indium-tin-oxide (ITO) glass substrate and a cathode MgAg alloy (10:1, atomic ratio) layer was deposited on an EML by codeposition in a 6×10^{-6} Torr vacuum at room temperature. The thickness of the ITO layer was 1700 Å and the sheet resistance was about 20 Ω/\square (Asahi Glass Co., Ltd. sputtered film). The deposition rate for organic layers was about 2 Å/s. The thickness of the organic layers was fixed at 500 Å. The durability tests were performed under the nitrogen atmosphere at a constant current density of $J = 30$ mA/cm². The luminance was measured with a luminance meter, Topcom BM-7. The ionization potential of the organic layers and an ITO layer was determined using a Riken-Keiki AC-1. The thermal analysis of the HTMs was measured using a Rigaku TAS100.

Table I summarizes the durability characteristics (initial luminance, and luminance after 10, 100, and 500 h) of EL cells with fourteen HTMs. In each EL device, the light emission gradually decreased with time, and the durabilities depended on the chemical structures of the HTMs. In particular, excellent performance was obtained using the HTM1 and HTM10. In the HTM1, the initial luminance was 790 cd/m² and the luminance of a 438 cd/m² was still maintained after 500 h of continuous operation. Also, similar result was obtained in the HTM10. On the contrary, the half-life period of the initial luminance was less than 10 h in the HTM3, HTM4, HTM5, and HTM11. Furthermore, the time for the half-decay of the luminance was a few hours in the HTM2, HTM6, HTM7, HTM8, HTM9, HTM13, and HTM14.

Figure 2 shows the relation between the ionization potential of the HTLs and L_{10}/L_0 . L_0 denotes the initial luminance and L_{10} indicates the luminance maintained after 10 h of continuous operation. Thus, a large L_{10}/L_0 value expresses high durability of the EL devices. Though the I_p of HTLs ranged widely from 5.0 to 5.8 eV depending on the

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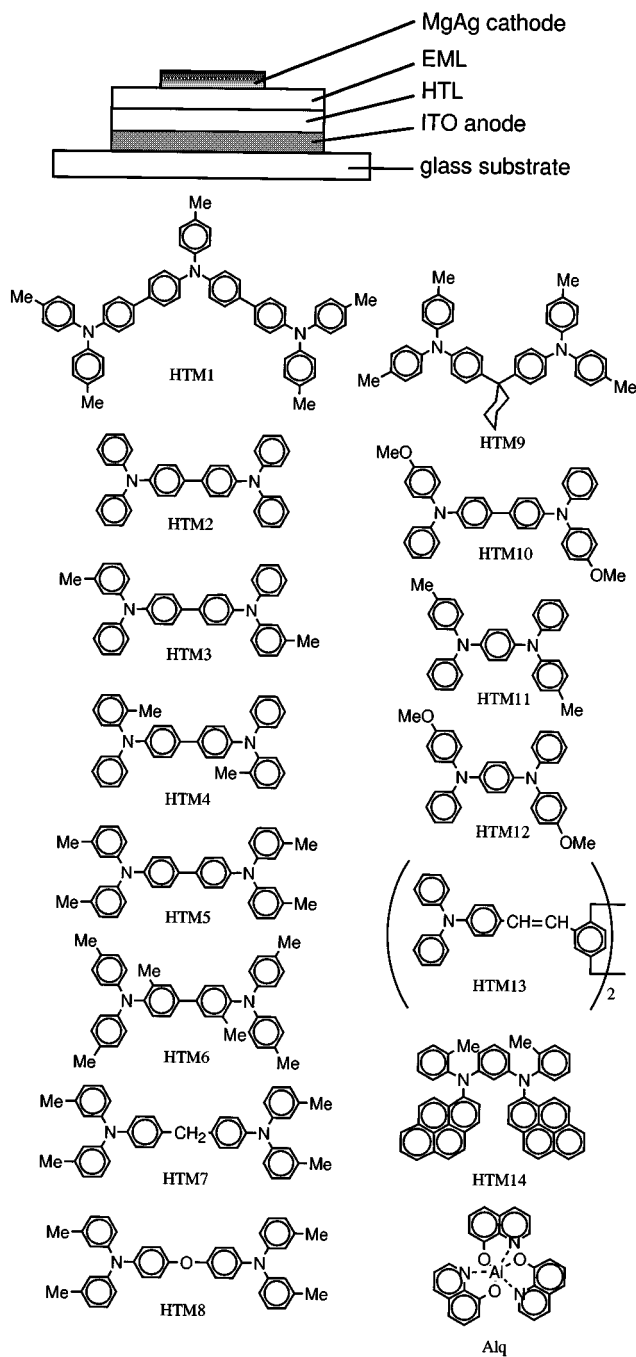


FIG. 1. The EL cell structure and fourteen hole transport and emitter materials used in this study.

substituent groups and the conjugated system of the HTMs, we can recognize that the durability of EL devices (L_{10}/L_0) is closely related to the I_p of the HTLs. The HTL1 having a low I_p value (5.08 eV) showed a high L_{10}/L_0 value, whereas HTL7 having a high I_p value (5.60 eV) showed a low L_{10}/L_0 value. In addition, we observed that the initial voltage of each device was closely correlated with the I_p of the HTLs. The HTL having a low I_p value resulted in a low initial driving voltage. Thus, we can recognize that the formation of the small energy barrier for hole injection at the interface of an ITO/HTL resulted in high durability and low drive voltage, because the I_p of the ITO layer used in this

TABLE I. The initial luminance L_0 , initial voltage (V_0), and the luminance after 10, 100, and 500 h of continuous operation (L_{10}, L_{100}, L_{500}) in the fourteen EL devices.

HTM	Initial luminance L_0 /cd/m ²	Initial voltage V_0 /V	Luminance/cd/m ²		
			L_{10}	L_{100}	L_{500}
1	790	8.1	547	476	438
2	790	10.6	260
3	920	13.7	350	180	...
4	860	12.2	390	250	...
5	790	12.3	343	140	...
6	1240	12.0	300
7	276	18.0	0
8	350	15.3	18
9	750	11.7	38
10	685	9.6	433	310	200
11	470	9.3	250
12	157	8.0	133
13	566	15.8	164	94	...
14	600	11.8	48

experiment was 5.0 eV and the I_p of the Alq emitter layer was 5.7 eV.

We also must take into account the thermal characteristics of the HTMs for the discussion of durability. As all HTMs used in this experiment form amorphous films by vacuum deposition, the gradual growth of crystallites in an amorphous film induced by joule heat are thought to be one of the important degradation factors. Figure 3 shows the relation between the L_{10}/L_0 term and the T_m of the HTMs, and Fig. 4 shows the relation between the L_{10}/L_0 term and the T_g of the HTMs. However, in each case, we observed no direct relationships between L_{10}/L_0 and the thermal characteristics. Thus, simple improvement in the thermal properties of the HTMs is insufficient to enhance the durability of the EL devices.

We will now discuss one of the possible degradation mechanisms. When a large energy barrier of hole injection at the interface of the ITO/HTL exists, large joule heat is produced at the interface. The produced heat gradually causes the local aggregation of molecules such as dimerization and crystallization of an amorphous HTL. These states then form sites for hole traps and a part of the injected hole carriers builds up a space charge. Simultaneously, the same number

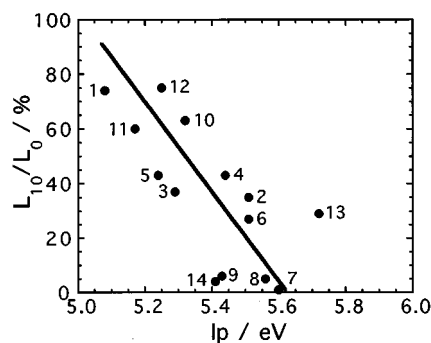


FIG. 2. The relation between the normalized luminance (L_{10}/L_0) and the ionization potential (I_p) of the hole transport layers (HTLs). The numbers in this figure refer to the HTMs listed in Fig. 1. L_0 : the initial luminance, L_{10} : the luminance after 10 h of continuous operation.

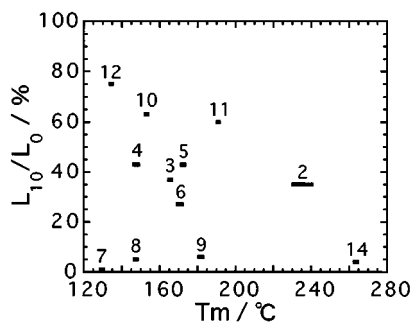


FIG. 3. The relation between the normalized luminance (L_{10}/L_0) and the melting point (T_m) of the hole transport materials (HTMs). The numbers in this figure refer to the HTMs listed in Fig. 1. In the case of the HTM1, a melting point was not observed.

of electron carriers accumulates inside an emitter near the HTL/EML interface, because the HTL has the ability to block electron injection.⁹ In other words, a capacitor is formed in the EL device. These excess electrons interact with the molecular exciton created by the recombination of a hole and an electron at the interface. This leads to the nonradia-

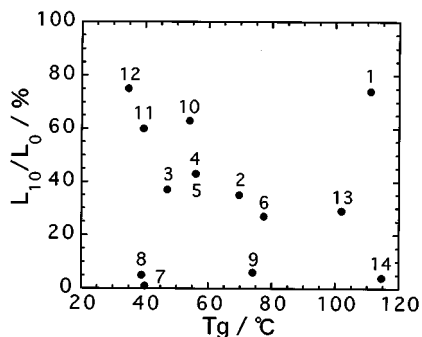


FIG. 4. The relation between normalized luminance (L_{10}/L_0) and the glass transition temperature (T_g) of the hole transport materials (HTMs). The numbers in this figure refer to the HTMs listed in Fig. 1.

tive destruction of excitons¹⁴ and the resulting decrease in luminance.

In conclusion, we elucidated the molecular design of HTMs for obtaining high durability. The formation of small energy barriers between an anode HTL interface was required for high durability. We observed no straightforward relations between the T_m , the T_g of HTMs, and the durability of EL devices. The same way to reduce the energy barrier of electron injection is another important subject for further improvement of organic EL devices. We also must clarify the detailed degradation mechanism.

We would like to acknowledge T. Shimada, M. Sasaki, and M. Ohta for the preparation of hole transport materials.

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