

Reliability and Degradation of Small Molecule-Based Organic Light-Emitting Devices (OLEDs)

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Invited Paper

Abstract—Studies of degradation mechanisms in small molecule-based organic light-emitting devices (OLEDs) are reviewed. A special emphasis is given to OLEDs based on tris (8-hydroxyquinoline) aluminum (AlQ₃), an emitter and electron transport material used in the majority of OLEDs emitting from the green to the red part of the spectrum. Different strategies used for increasing device stability are addressed and the models proposed to explain experimental observations related to OLED operational stability are discussed. Although none of the presently proposed models can explain all experimental observations, the largest body of experimental evidence appears to be consistent with a model based on the instability of cationic AlQ₃ species, produced by the injection of holes into the AlQ₃ electron transport and emitter layer. Other models may be of importance in explaining degradation behavior on different time scales. Models based on redistribution of space charge appear to be responsible for reversible short-term degradation, while a model based on indium migration may be important for degradation on very long time scales.

Index Terms—Aging, AlQ₃, degradation, OLED, organic light-emitting devices, reliability, stability.

I. INTRODUCTION

IN THE LAST DECADE, a new technology has emerged based on electroluminescent organic materials. The electroluminescence in organic materials has been known for a long time. In 1960s, it was discovered that anthracene single crystals can be made to emit light when provided with proper electrodes and external bias [1]. These devices, however, required very high operating voltages, on the order of hundreds of volts, which, together with difficulties of producing large anthracene single crystals, made them unsuitable for practical applications. In the following two decades, organic electroluminescence remained a field of purely academic interest. Anthracene devices based on evaporated amorphous films were demonstrated [2], but their light output decayed catastrophically in a few minutes. Electroluminescence in a polymer was first observed in polyvinylcarbazole (PVK), but like anthracene, light emission decayed very quickly [3].

The situation changed in 1987, with the seminal publication by Tang and Van Slyke in which they described a two layer organic thin-film structure based on tris (8-hydroxyquinoline)

aluminum (AlQ₃), an emitter and electron transport material, and a hole transport material (tertiary amine) [4]. The devices were produced by vacuum evaporation of organic small-molecule materials and a metallic cathode on a conductive substrate. The half-life (time of operation elapsed before luminance decreases to 50% of its initial level) of these devices was measured in hundreds of hours, many orders of magnitude larger than any organic thin-film devices reported previously. Soon after, in 1990, another important development followed. Burroughs *et al.* reported observation of electroluminescence in a single layer device made of a polymer polyphenylenevinylene (PPV), made by a spin coating process [5]. These two developments were seeds of a new technology of organic light-emitting devices (OLEDs). In many respects, these two directions, small-molecule and polymer based OLEDs, developed independently. Until about 1998, the small molecule based devices had significant performance advantages over polymeric devices. Recently, this gap has significantly narrowed and it appears now that both approaches are feasible for practical applications. However, there are still many problems to be overcome, ranging from improving device stability and color purity to devising economical and robust manufacturing processes.

A basic requirement in any emissive technology is providing adequate device stability for intended applications. In case of displays, it is generally assumed that a half-life of at least 10 000 h, at initial display brightness (luminance) of 100 cd/m², is needed. For some specialized applications where the usage duty cycle is low, a shorter device half-life may be adequate. In this paper, device half-life is sometimes also referred to as device lifetime or simply device life.

In this review, the discussion of stability and degradation in OLEDs will be limited to small molecule based devices. In general, degradation in OLEDs, which appears in the form of a decrease in device luminance, proceeds through two independent and visually distinct degradation modes. The first, associated primarily with degradation at the device electrodes, occurs through the formation of nonemissive regions, usually referred to as dark spots, that lead to a decrease in device luminance as a result of losses in the emissive area of a device [6], [7]. The second degradation mode is reflected in a long-term “intrinsic” decrease in the electroluminescence efficiency of the emissive area of a device [7]. Dark spot degradation phenomena will not be discussed in this review, as they are reasonably well understood and their control is successfully accomplished by proper

Manuscript received December 11, 2001; revised February 4, 2002.

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Publisher Item Identifier S 1077-260X(02)03762-0.

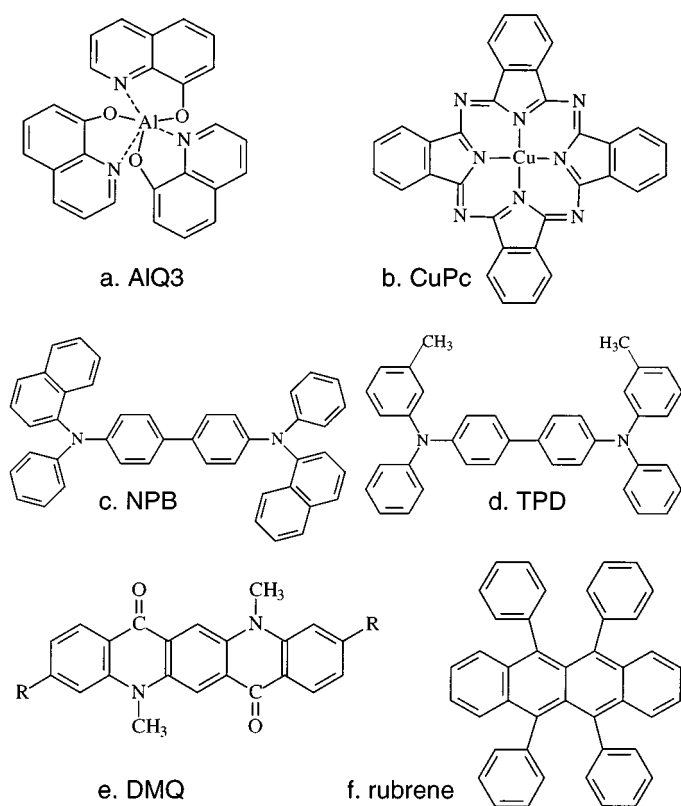


Fig. 1. Chemical structures of some of the materials commonly used in small molecule based OLEDs. Chemical names for these molecules are given in the text.

device encapsulation, which eliminates water and oxygen from the immediate OLED environment [6]–[12]. Our focus will be on the intrinsic degradation, in which device brightness, at constant current bias, decreases in time without any obvious change in device appearance.

Many different materials are used in small molecule based OLEDs. The molecular structures of some frequently used materials, which will be referred to often in this paper, are shown in Fig. 1. AlQ₃ [Fig. 1(a)] is the most frequently used emitter and electron transport molecule (ETM). Copper phthalocyanine (CuPc) [Fig. 2(b)] is commonly used in a buffer layer contacting the hole injecting anode. *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) and *N,N'*-di(naphthalene-1-yl)-*N,N'*-diphenyl-benzidine (NPB) [Fig. 1(c) and (d)] have been the most frequently used hole transport materials (HTMs). For control of emission color, various dopants have been identified. Two typical dopants are dimethyl quinacridone (DMQ), and 5,6,11,12-tetraphenyl naphthacene (rubrene), which produce green and yellow emission, respectively [Fig. 1(e) and (f)]. Transparent indium thin oxide (ITO) is almost exclusively used as a hole injecting anode. A Mg:Ag alloy (9:1 by volume) is usually utilized as an electron injecting cathode, because of its efficient electron injection into AlQ₃. However, other cathode materials (Ca, Al:Li alloy, etc.) are also used. To facilitate further discussion and introduce some common acronyms, Fig. 2 shows a schematic diagram of a typical OLED structure. Often ITO is first covered

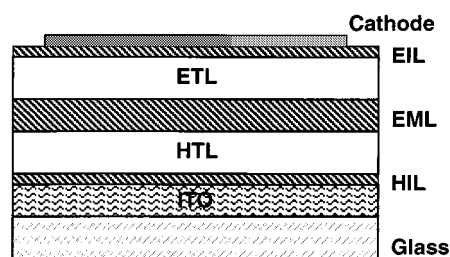


Fig. 2. A typical OLED device structure. The function of different layers and the meaning of acronyms is given in the text.

by a buffer layer (sometimes also referred to as a hole injection layer or HIL), followed by a hole transport layer (HTL), emitter layer (EML), electron transport layer (ETL), optional electron injection layer (EIL), and finally a cathode. Specific device designs may be lacking some of these layers or may have additional layers to further improve device performance.

For a long time it had been believed that morphological instability of the hole transport layer is responsible for OLED degradation [13], [14]. That notion resulted in a significant body of research that focused on the synthesis of high T_g (glass transition temperature) HTMs [15]–[17]. This research led to the design and synthesis of a number of important OLED materials. Although the incorporation of high T_g HTMs in OLEDs realized an increased resistance to device damage that would usually result from brief exposures to elevated temperatures, and certainly enhanced device shelf life, it did not impact device operational stability, even when operated at room temperature [18], [19]. Therefore, in this review, studies on high T_g HTMs will not be discussed in much detail, but only to the extent where they influenced increased device life.

At the present time, OLED intrinsic degradation is usually explained in terms of one of three models that have been proposed relatively recently. According to the first model, device degradation is attributed to the notion that cationic AlQ₃ species are unstable and that their degradation byproducts lead to a decrease in device electroluminescence [20]. In the second model, degradation is believed to be associated with the migration of indium from the ITO anode into the organic layers, and the subsequent quenching of luminescence in the emission zone [21]. The third model proposes that electric field redistribution due to presence of mobile ions in the device is responsible for device degradation [22]. The first model can explain a wide range of experimental observations; nevertheless, there are some phenomena that still cannot be understood within the framework of unstable cationic AlQ₃ species hypothesis. Experimental evidence for the possible role of indium migration and electric field redistribution due to the presence of ionic species in device aging is less broad. Therefore, all three models can explain some of the experimental observations, but so far none can explain all.

In this review, we will highlight results from earlier studies on OLED stability and discuss models proposed to explain degradation phenomena. In the following section, some important results, with a focus on successful approaches for improving device stability, are reviewed in a historical perspective. In Section

III, the degradation model based on the instability of cationic AlQ_3 species is discussed. In Section IV, the two other proposed degradation models are addressed. In both of these sections, phenomena supporting the respective model together with observations that cannot be explained are presented. In the discussion and conclusion section, the main points will be summarized, and possible future research directions will be discussed.

II. APPROACHES FOR IMPROVING OLED STABILITY

The initial thin-film OLED device described by Tang and Van Slyke, consisted of a diamine hole transport layer and AlQ_3 sandwiched between an ITO anode and a magnesium-silver cathode [4]. Its half life was short, only about 100 h at an initial luminance of about 100 cd/m^2 .

In 1994, Shirota *et al.* demonstrated that introduction of a dual hole transport layer significantly improved device stability under operating conditions [23]. They speculated that the good film forming properties and better energy level alignment between ITO and the starburst hole transport molecule [23], placed between ITO and the TPD layer, lead to increased device stability. This hypothesis was investigated in detail by Adachi *et al.*, who studied OLEDs with 14 different hole transport materials in conjunction with AlQ_3 . They found no correlation of device life with glass transition temperature, but established a reasonable correlation with the ionization potential of different HTMs [19]. They concluded that small barrier for hole injection from ITO into the hole transport layer was responsible for improved device performance.

In 1995, Hamada *et al.* [24] combined the dual hole transport zone (starburst amine in contact with ITO overcoated with TPD) proposed by Shirota *et al.* [23] in conjunction with AlQ_3 and also a related electron transport and emitter material BeBq_2 (bis(dydroxybenzo[h]quinolinato)beryllium). They found that doping of the TPD layer with rubrene significantly improved device half life, compared to devices where the electron transport layer was doped with the same material. The half life of the best devices exceeded 3500 h at 500 cd/m^2 initial luminance. It was concluded that the change of emission site from the electron transport to the hole transport material was responsible for improved device performance.

In 1996, Van Slyke *et al.* [25] introduced a thin ($150 \text{ \AA}$) copper phthalocyanine (CuPc) buffer layer between ITO and a new hole transport molecule NPB. Using a $600 \text{ \AA}$ NPB hole transport layer and a $750 \text{ \AA}$ AlQ_3 electron transport and emitter layer, half life of about 4000 h was obtained, at an average current density of 20 mA/cm^2 and initial luminance of 510 cd/m^2 . Such remarkable performance was accomplished without the use of any dopants in either the electron or hole transport layer. This work also established a scaling law for accelerated OLED testing stating that degradation was essentially a coulombic process and depended only on the total charge flowing through the device. As light output is proportional to device current, this scaling law can be expressed by the simple formula

$$L_{(\text{initial})}T_{1/2} = \text{constant} \quad (1)$$

stating that the product of initial luminance $L_{(\text{initial})}$ and device half life $T_{1/2}$ is constant. The law enabled the use of accelerated

half life measurements where testing at high current (resulting in a high luminance) can be used to predict expected half life at typical currents and luminance needed for display applications. According to this scaling law, at typical display brightness level of 100 cd/m^2 their device half life would exceed 20 000 h. Applied to the rubrene doped TPD device described in the previous paragraph, the scaling law would predict half life in excess of 16 000 h.

The remarkable stability of devices based on NPB HTM and CuPc buffer layer was attributed to the higher glass transition temperature of NPB (95°C) compared to TPD (65°C), and to the presence of CuPc buffer layer, whose role was not quite clear. The devices were also driven using an ac biasing scheme, with a reverse bias equal or exceeding the forward device bias, which was believed to result in a reduction of space charge accumulation as the reverse bias was “sweeping out” the charges trapped in the device. The ac bias may also provide the additional benefit of burning device shorts in the reverse bias cycle. Shi and Tang [26] reported further improvement of the performance of this type of device by doping one half of the AlQ_3 layer with DMQ green emitter at different concentration levels. The use of a doped emission zone lead to the increase of both device life and brightness. For optimum dopant concentration of 0.8%, at 20 mA/cm^2 , the device brightness was 1462 cd/m^2 , and half life was 7340 h. Using the scaling law described previously, that would translate to a half life in excess of 100 000 h for an initial brightness level of 100 cd/m^2 . Improvements in OLED stability as a result of using CuPc buffer layer and doping of the emitting layer was also demonstrated by several other groups [27]–[31].

Matsumura and Jinde [32] in 1997, and Sato *et al.* [31] in 1999, compared performance of devices containing different cathodes, such as, Mg:Ag, Li:Al, In and Al. For the same device current, the more efficient electron injecting cathodes (Mg:Ag, Li:Al) required significantly lower operating voltage than devices with an In or Al cathode. In addition, good electron injectors showed significantly improved device half life. A similar behavior was observed by Wakimoto *et al.* [33] who used thin electron injection layer consisting of alkaline metal compounds and Al capping as cathodes, leading to the conclusion that efficient electron injection improves device life.

In 1998, Popovic *et al.* investigated in depth the influence of mixing of hole and electron transport materials on device performance [34]. The study was motivated by the suggestion that interlayer diffusion could be causing device degradation [35]. They used NPB and AlQ_3 as the hole and electron transport materials, respectively. Various OLED structures were investigated including devices with only a single mixed layer, devices with a hole transport layer and a mixed layer, devices with a mixed layer and an electron transport layer, and devices with hole transport layer, mixed layer, and an electron transport layer. The last device structure showed the best performance, demonstrating a half life that was at least an order of magnitude longer than that of conventional bilayer devices. In 1999 Choong *et al.* studied devices containing a CuPc hole injection layer, quinacridone (DMQ) doped NPB: AlQ_3 mixed emitter layer, an undoped mixed layer as ETL, and LiF–Al cathode. This device structure also demonstrated significantly

increased half life (70 000 h at 100 cd/m^2 initial luminance), when compared to conventional bilayer devices (11 000 h at 100 cd/m^2 initial luminance), which used the same materials [36]. In their work, they referred to the mixed layer as BTEL for “bipolar transport and emitting layer” and attributed the significant improvement in device performance to the absence of the heterojunction between the hole and electron transport material.

The above were the most important results reported until the beginning of 1999. A number of different, seemingly unrelated, approaches were found to be successful in increasing OLED stability. These approaches were: 1) doping of the hole transport layer; 2) introducing a CuPc buffer layer inbetween the ITO and the HTL; and 3) using mixed emitter layers composed of hole and electron transport materials. However, the explanations offered for their effectiveness or the underlying degradation mechanisms were essentially speculative in nature and often contradictory. In addition, improved stability devices required cathodes with low injection barriers and also special cleaning procedure for the ITO anode using either UV ozone or oxygen plasma. The use of dopants to modify device emission color and increase efficiency also influenced device life when used in conjunction with these three methods.

III. OLED DEGRADATION MECHANISM BASED ON UNSTABLE AlQ_3 CATION

Our studies on understanding the mechanism of degradation of OLEDs during prolonged operation was motivated by the existence of the above seemingly unrelated approaches, described in the previous section, which all led to substantial improvements in device stability. In this section, we will closely follow the argument which our group first published to explain the origin of long-term degradation of OLEDs based on AlQ_3 electron transport and emitter material [20]. Some more recent results, which provide additional insights into the degradation process, will also be discussed.

The finding that doping of HTL or introducing a CuPc buffer layer between ITO and the HTL could result in a substantial increase in device life suggested that the problem somehow lied in the hole transport layer. But contrary to this assumption, studies on devices with mixed layers of hole transport and electron transport materials showed that neither CuPc buffer layer nor HTL doping were necessary for devices to have increased half life [20], [34]. This remarkable enhancement of stability as a result of introducing the mixed layer, in spite of not having a doped HTL or a buffer layer at the hole injecting contact, suggested that, contrary to what was believed before, device aging was not caused by morphological changes in the HTL [13], [14] or degradation at the ITO–HTL interface [25]. The fact that the stability of the OLEDs was enhanced by altering the HTL– AlQ_3 interface, in this case by means of inserting a mixed layer in between, indicated that aging in OLEDs was mainly caused by degradation at (or near) that interface.

To investigate the mechanism for the enhanced stability, we studied OLEDs of various structures, including ones with a CuPc buffer layer at the ITO contact, or rubrene-doped HTLs. The J – V and L – J characteristics of these devices are

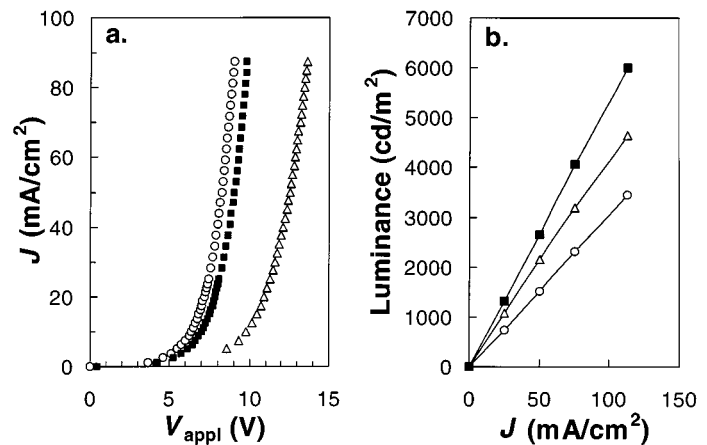


Fig. 3. Current-voltage characteristics (a) and luminance-current curves (b) for different devices. (○) Bilayer device NPB– AlQ_3 . (■) Device containing a doped hole transport layer NPB:rubrene (0.95:0.05)– AlQ_3 . (△) Device containing the buffer layer, CuPc–NPB– AlQ_3 . All devices had an ITO anode and Mg:Ag cathode.

shown in Fig. 3. To follow a control experiment approach, the characteristics of standard bilayer OLEDs, made from the same materials and fabricated on the same substrates during the same vacuum cycle, were taken as a reference. Clearly, introducing a layer of CuPc (15 nm thick) at the ITO contact enhanced the electroluminescence efficiency (equal to the slope of the L – J relationship and measured in cd/A) of the OLEDs ($\sim 4.2 \text{ cd/A}$ for OLEDs with the CuPc layer compared to $\sim 3.1 \text{ cd/A}$ for standard bilayer OLEDs). Because introducing the CuPc layer caused a shift in the J – V characteristics to higher voltages, it was concluded that the CuPc impeded the injection of holes into the HTL. The higher electroluminescence efficiency was, therefore, attributed to the role of the CuPc in achieving more balanced electron and hole injection processes by impeding the injection of holes into the NPB layer. Doping the HTL with rubrene also led to a shift in the J – V characteristics to higher voltages, in agreement with the findings of Vestweber *et al.* [37]. This shift pointed to the role of the dopant molecules in forming hole traps, thus reducing their mobility in the HTL [38]. Similar to the case of OLEDs with a CuPc layer, doping the HTL also led to a higher electroluminescence efficiency. However, unlike the case of CuPc, where the higher efficiency could be solely attributed to a more balanced electron/hole ratio, the role of dopant molecules in enhancing the efficiency was extended to include their contribution to the generation of light. The fact that the shift in the J – V characteristics was much more pronounced in case of introducing the CuPc layer than in case of doping the HTL could be attributed to the different nature of the hole-impeding processes in both cases. The CuPc layer impeded the injection of holes into the HTL, whereas the dopant molecules reduce their mobility inside the HTL [39]. The shift of the J – V characteristics to higher voltages in case of introducing the CuPc layer or doping the HTL did not contradict the fact that these stabilizing agents may seem to lower the luminance turn-on voltage of the OLEDs due to the efficiency enhancement. Based on these results, a common feature in the role of these two approaches to improve OLED's stability was to slow down the transport of holes to the HTL– AlQ_3 interface, where they get injected into the AlQ_3

layer. Therefore, the injection of holes into the AlQ₃ layer appeared to be the main factor responsible for the long-term degradation in OLEDs. This postulate was consistent with the results of Papadimitrakopoulos *et al.* [40], which showed from cyclic voltammetry on AlQ₃ in solutions, that the oxidation of AlQ₃ was irreversible. However, one should keep in mind that solution electrochemistry is not a reliable tool for predicting solid state properties as the environment of organic molecules in the two cases is very different. Therefore, this type of correlation should be taken only as a guide and not as a proof of the degradation mechanism.

To investigate the validity of the hypothesis that cationic AlQ₃ species in the solid state are unstable, photoluminescence (PL) measurements were employed to monitor changes in the PL quantum efficiency of a 5-nm-thick AlQ₃ sandwiched between two thick NPB layers and equipped with ITO anode and Mg:Ag cathode. Under positive ITO bias, charges driven through the AlQ₃ layer would be predominantly holes. Although the shape of the photoluminescence spectra did not change in time on prolonged current flow, a gradual decrease in the peak height of the AlQ₃ photoluminescence spectra was observed, revealing a continuous decrease in the photoluminescence quantum efficiency of the AlQ₃ on prolonged current flow [20], [41]. The decrease in the photoluminescence quantum efficiency of the AlQ₃ pointed to its degradation as a result of hole transport, thus revealing that cationic AlQ₃ species were unstable and that their degradation products were fluorescence quenchers. The establishment of a correlation between fluorescence decay and device aging was attempted before on bilayer devices containing an HTL and AlQ₃ electron transport and emitter layer [42]. However, these attempts did not produce conclusive results as the PL was dominated by the component originating from the bulk of the thick AlQ₃ layer, rather than the interfacial region with the hole transport layer.

It is important to point out that the transport of electrons through AlQ₃, being itself an excellent electron transport material [43], should not be expected to cause degradation. In order to prove the validity of this assumption, devices containing 5-nm-thick AlQ₃ layers sandwiched between two tetraphenyl-triazine (TPT, insert in Fig. 4) electron transport layers were also studied. Like NPB, TPT has the absorption cutoff around 400 nm, and therefore, allowed unobstructed photo-excitation of AlQ₃ in photoluminescence measurements. These devices, where only electron transport was allowed, did not show any decrease in the photoluminescence quantum efficiency of AlQ₃ under similar testing conditions [44]. The results of relative integrated photoluminescence measurements on samples where AlQ₃ was subjected to predominantly hole or electron flow are shown in Fig. 4. While significant photoluminescence decrease is observed in the case of transporting holes into AlQ₃, the photoluminescence stays remarkable constant in case of transporting electrons. These results, therefore, provided strong evidence that injection of holes into the AlQ₃ layers of the OLEDs was a main factor in device degradation.

In view of the above results, the role of doping the HTL or introducing a thin buffer layer of CuPc at the hole-injecting contact in improving OLEDs stability was explained in terms of their effect in slowing down the hole transport to the HTL–AlQ₃

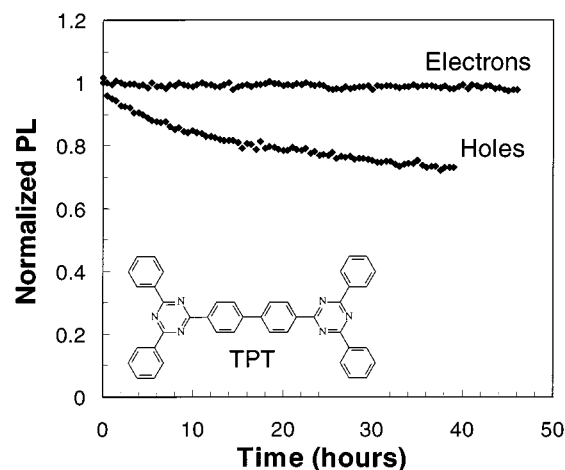


Fig. 4. Integrated fluorescence as a function of time from AlQ₃ sandwiched between two hole transport layers NPB–AlQ₃–NPB, which allow only hole transport, and between two electron transport layers TPT–AlQ₃–TPT, which allows only electron transport through the device. In both cases, the devices were driven at a current density of 50 mA/cm². The insert gives the structure of TPT electron transport molecule.

interface. Under these conditions, the density of electrons in the AlQ₃ layer adjacent to the HTL–AlQ₃ interface is increased, thus leading to rapid recombination and therefore a shorter lifetime of the cationic AlQ₃ species. This, in turn, leads to significant decrease of AlQ₃ degradation and consequently increases device stability. High electron density at the HTL–AlQ₃ interface may also lead to direct production of excited states, without the formation of cationic AlQ₃ intermediates, by direct injection of holes from the HTL into anionic AlQ₃ [45]. This process could greatly reduce formation of cationic AlQ₃ species and is probably the dominant mechanism for improved stability of OLEDs with a mixed emitter layer. In addition to improved carrier balance, holes in the mixed layer will preferentially reside on NPB sites because of the lower ionization potential of the NPB relative to that of AlQ₃ (~5.2–5.4 eV and ~5.6–5.7 eV, respectively), whereas electrons will reside on AlQ₃ sites. As in the mixed layer NPB and AlQ₃ molecules are in close contact, recombination of holes and AlQ₃ anions to produce excited states of AlQ₃ directly will be a dominant recombination process. Later, the same argument was also used by Choong *et al.* to explain stability of their bipolar transport and emitter layer (BTLE) devices [46]. In fact, the argument was used to explain other phenomena pertaining to OLEDs stability [20]. For example, the correlation between a lower ionization potential of the hole transport material and a higher device stability [19] was explained in terms of the same processes. In this case, a lower ionization potential of the HTL leads to a more difficult injection of holes into the AlQ₃ as a result of the higher hole injection barrier at the HTL–AlQ₃ interface. The reduced injection of holes into the AlQ₃ layer leads to a higher density of electrons in the AlQ₃ layer adjacent to the HTL–AlQ₃ interface, which in turn, leads to a shorter lifetime of cationic AlQ₃ species. The increase in device stability on using metals with lower work function for the cathodes [31]–[33] was explained in terms of an easier injection of electrons from the cathode into the AlQ₃ layer, which leads to a higher density of electrons in the AlQ₃ layer adjacent to the HTL–AlQ₃ interface, and hence, a higher device stability.

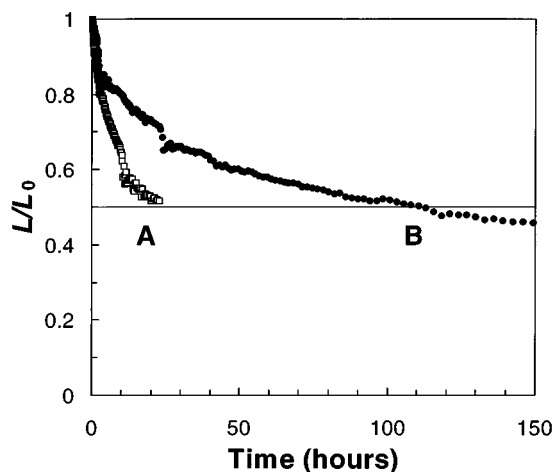


Fig. 5. Luminance decay as a function of time for two devices in which the hole transport zone consists of two layers, made of NPB and TPD hole transport molecules, in different orders. The structures corresponding to curves A and B are given in the text. In both cases devices were dc driven at 31.25 mA/cm^2 .

Recent additional experimental results, which give further support to the proposed OLED degradation model, are presented in the remaining part of this section.

A. OLEDs With Dual Hole Transport Layers

OLEDs with dual layer HTL consisting of separate layers of pure NPB and pure TPD were constructed in the following arrangements where the hole transport layer structures are denoted in bold [41], [47]

- A. ITO-**NPB-TPD**-AlQ₃-Mg:Ag
- B. ITO-**TPD-NPB**-AlQ₃-Mg:Ag

Because of the higher ionization potential of TPD relative to that of NPB (5.5–5.6 eV and 5.2–5.4 eV, respectively) structure A is expected to enhance the injection of holes into the AlQ₃ layer by means of hole cascading. On the other hand, due to the relatively high hole injection barriers at the ITO-TPD and NPB-AlQ₃ interfaces in structure B, injection of holes into the AlQ₃ layer is made more difficult. According to the conventional approach [19], [23], the improvement of hole injection should lead to increased device life, and therefore, device A should show better performance than device B. But according to the proposed degradation mechanism the opposite should hold, OLEDs of structures B should be more stable than OLEDs of structure A, as the presence of additional barriers will impede hole transport. Lifetime measurements reveal that this indeed is the case. OLEDs of structure B have ~ 5 times longer half life compared to OLEDs of structure A (Fig. 5).

B. Doping the HTL

According to the model, doping the hole transport material with a dopant leads to the increased device stability as a result of the role of dopant in slowing down the hole transport by acting as a hole trap. Widely used dopants, such as rubrene, almost always have an ionization potential that is smaller than the ionization potential of the host molecule. However, in the opposite scenario, when ionization potential of the dopant is larger, no significant influence on hole transport, and therefore, no change

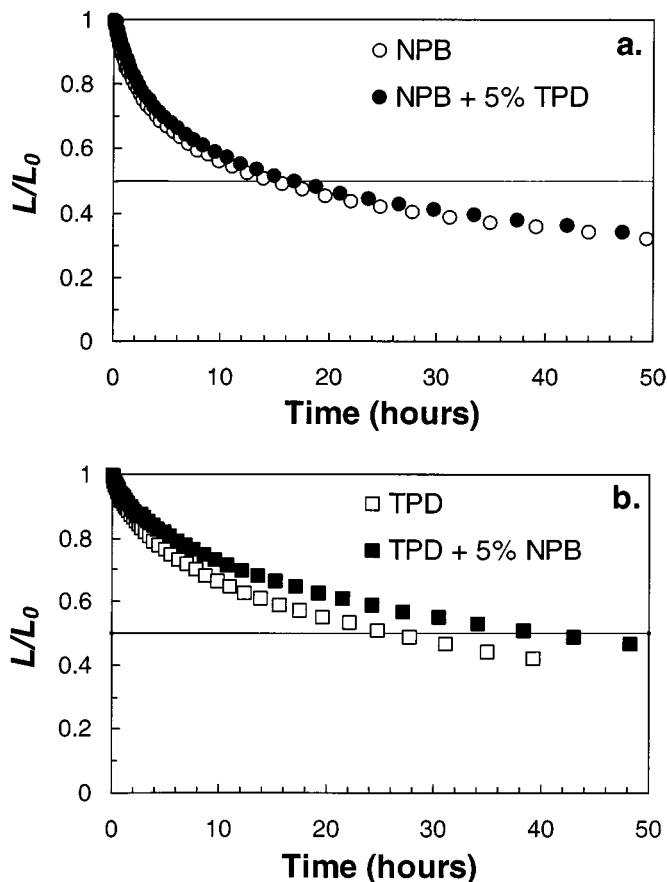


Fig. 6. Comparison of luminance decay of devices without and with dopant in the hole transport layer. (a) NPB hole transport layer, doped with TPD. (b) TPD hole transport layer, doped with NPB.

in device lifetime, should be expected according to the model. We have, therefore, performed experiments where we doped 5% of NPB into TPD and vice versa, and compared the device lifetimes with devices without the dopant [47]. According to the proposed model, we expect that doping TPD into NPB will not affect device stability, while doping NPB into TPD should lead to a half life increase. That this is indeed the case is demonstrated by results shown in Figs. 6(a) and (b). 5% of TPD in NPB does not change the stability at all [Fig. 6(a)], while 5% of NPB in TPD leads to small, but clearly measurable increase in device half life of about 50% [Fig. 6(b)]. This indicates that ionization potential of TPD is somewhat larger than that of NPB, but the difference is probably not as large as reported in the literature and quoted in the preceding paragraph. The concept of hole transport layer doping to increase the device life was explored in some detail in [48]. In agreement with the proposed degradation model, it was found that a variety of dopants lead to device stability improvement.

C. Time-Resolved Fluorescence Measurements

The nature of AlQ₃ degradation is further elucidated by time-resolved fluorescence measurements [49]. It is shown that device aging leads to an increase of fluorescence decay rate with the initial amplitude of multiexponential fluorescence decay remaining essentially constant. This is consistent with the idea that the products of cationic AlQ₃ degradation are fluorescence

quenchers. Further insights into the nature of electroluminescence aging were obtained by measuring simultaneously photoluminescence and electroluminescence aging in devices containing 5-nm-thick AlQ₃ layer sandwiched between NPB hole transport and tetraphenyltriazine (TPT, insert Fig. 4) electron transport layer [50]. These studies showed that cationic AlQ₃ degradation products act not only as fluorescence quenchers, but also as charge traps and electron-hole recombination centers.

Clearly, in view of the above discussion, the model of OLED degradation based on the instability of cationic AlQ₃ species seems to be capable of explaining a large number of experimental observations. However, an observation that does not appear to support this model has been reported recently by Hung *et al.* [51]. Using simple OLED structures containing only NPB and AlQ₃, Hung *et al.* modified ITO anodes with CHF₃ plasma polymerized thin film. When compared to devices without the CHF₃ film, these modified anodes lead to both a decrease in device operating voltage, indicating increased hole injection, and an increase in device half life. At the first glance, improved hole injection should lead to increased hole supply to AlQ₃ and decrease in device life, and thus contradicts the model. One possible explanation is that very efficient anodes will lead to significantly reduced electric field in the hole transport layer and at the HTL–AlQ₃ interface which will decrease (rather than increase) hole injection into AlQ₃, despite of the overall reduction in the device operating voltage. Detailed understanding and realistic modeling of bipolar space charge limited transport in these structures could perhaps provide answers to these questions [52].

IV. OTHER PROPOSED OLED DEGRADATION MODELS

In addition to the model discussed above, according to which degradation is attributed to the instability of AlQ₃ cationic species, two other models for explaining device degradation were proposed. The first model associates degradation with diffusion of indium species from the anode into the organic layers, while the second attributes it to changes in the internal electric field in the organic layers caused by mobile ions which are present as contaminants in the organic material or released from the electrodes. Because the amount of experimental data supporting these two models is relatively small, only a brief discussion will be provided for each.

A. Indium Migration Model

According to the model, which was proposed by Lee *et al.* in 1999, OLED intrinsic degradation is attributed to penetration of indium species released from the ITO anode into the organic layers, which results in luminescence quenching [21]. Using secondary ion mass spectrometry (SIMS) and mass spectrometry, Lee and coworkers were able to detect In in the organic layers of devices that had been aged, where its concentration was ten times higher than in as-prepared devices. To investigate whether the presence of trace amounts of indium in the organic layers can be causing OLED electroluminescence degradation, they tested OLEDs that deliberately contained indium as a dopant in the different layers of experimental devices at a concentration of 0.25%. The results showed a sub-

stantially lower electroluminescence efficiency only in devices where the indium was doped in the emission zone of the AlQ₃ layer, while doping the hole transport layer or the CuPc hole injection buffer layer had no effect. Based on these observations, it was concluded that substantive indium diffusion from ITO anode occurred upon device operation, where its deep penetration, possibly assisted with electrical migration of charged In atoms, could be a major cause of luminescence quenching and hence OLED degradation. It is worth mentioning, however, that an In concentration of 0.25%, as was used in the experimental devices, could be unrealistically too high to assume that trace levels of indium in real OLEDs may have similar effects. It is also important to note that the devices investigated in that study had long lifetimes, exceeding 2000 h at an average forward current of 20 mA/cm².

It must be pointed out that, with some additional assumptions, this model can, indeed, explain a variety of observations pertaining to device degradation, such as, the dependence of device stability on 1) ITO surface treatment; 2) the use of buffer layers at the anode contact; and 3) doping the hole transport layer. For instance, the effectiveness of UV ozone cleaning and oxygen plasma treatment of the ITO surface in improving device stability can be associated with their ability to reduce oxygen deficiency of as-grown ITO films, and therefore, reduce the amount of unbound indium atoms available for diffusion into the organic layers [21]. The increase in device stability on using different buffer layers at the ITO contact, such as CuPc [25], plasma polymerized CHF₃ [51], or amorphous carbon [53], can be explained in terms of the role of these buffer layers in acting as barriers for In diffusion. This explanation can be valid when the buffer layer leads to either an increase or a decrease in the operating voltage of the device, an observation that is not readily understood by the model that assumes the instability of cationic AlQ₃ species. The increased stability of devices with a doped hole transport layer may be attributed to the role of the dopant molecules in scavenging and immobilizing the In atoms, and hence, reducing their penetration to the AlQ₃ emitting layer.

However, the model cannot explain a number of other observations that are difficult to overlook. For instance, the notion that In diffusion is assisted with electrical migration of charged In atoms is not consistent with the fact that long-term degradation behavior of OLEDs, in general, is essentially similar under both dc and ac driving conditions [54]. The use of ac driving, especially when the magnitude of the reverse voltage is greater than that of the forward voltage [25], as it is often the case, should prevent or at least substantially reduce the migration of the charged In atoms, and hence, increase device stability. Another observation was reported by Shen *et al.* [55] who detected no change in device lifetime on coating the ITO with a Pt layer, suggesting that In diffusion may not be an important factor in electroluminescence degradation. Furthermore, Hung *et al.* [56] found that OLEDs containing sputter deposited cathodes had an increased half life over conventional devices containing thermally evaporated Mg:Ag cathode. Other groups reported similar observations [31]–[33]. The ability to change device stability by only modifying the electron-injecting contact, without altering the ITO contact or the hole transport layer can not, so far, be explained in terms of the migration of indium originating from the ITO anode.

B. Mobile Ions Model

The degradation model based on mobile ions was introduced to explain a common observation that has almost always been associated with the decrease in device luminance during OLED operation, which is the tendency of the driving voltage to increase [57], [58]. The increase in voltage is however often reversible, at least partially, on either resting the device at zero applied bias or reversing its polarity [59]. Shen and coworkers [57] presented a systematic study of this phenomenon on blue-green emitting devices of (unfortunately) an unspecified structure. The device degradation reflected in operating voltage increase and electroluminescence decrease was modeled assuming the existence of mobile ions in the organic layers of the OLED. According to this model, the redistribution of mobile ions, such as, In, Sn, Mg, etc. from the electrodes or other contaminants incorporated during the fabrication process, under the externally applied electric field, induces an internal field, which partially cancels the external one. Luminance decay is attributed to increased ion concentration, which could act as charge recombination or fluorescence quenching centers. However, it must be pointed out that the model is essentially based on a mathematical analysis that correlates solutions for time-dependent transient equations for mobile ions distributions with experimental changes in voltages, without direct experimental proof.

Models based on redistribution of space charge, of whatever origin, either ionic or due to charge traps, may be relevant for understanding the fast initial (short-term), often reversible, decay in OLED electroluminescence. This is in many cases particularly pronounced under dc driving conditions [59], and also reflected in variations in initial (short-term) OLED electroluminescence decay behavior for ac versus dc driving conditions [54]. However, the fact that changes in both luminance and driving voltage after long-term operation (>100 h) are mostly irreversible, as well as the fact that long-term degradation rate is essentially the same for both dc and ac driving [54] suggests that this degradation mechanism, if indeed operative, can only have a limited effect on long-term device degradation.

V. DISCUSSION AND CONCLUSION

From the above discussion it is obvious that, at the present time, no single model explains all experimental observations. It appears that the model based on unstable cationic AlQ₃ species is able to explain the widest variety of the observed OLED aging phenomena. Perhaps the only observation that is not consistent with this model is the observation that the increased device stability is, in some cases, associated with what appears to be an increased hole injection. As discussed before, the reason for increased stability in that case may lie in the reduction of hole injection into AlQ₃ as a result of reduced internal electric field.

The assumption that ITO contact buffer layers (CuPc, plasma polymerized CHF₃, amorphous carbon) or dopants in the hole transport layer act as indium scavengers could explain increased device life based on the indium migration degradation model. However, many experiments contradict this hypothesis. For example, it is difficult to understand why changing the order of two hole transport layers (NPB and TPD), as described in Section III, should affect indium migration. Also, the introduction

of a Pt-coated ITO as anode does not seem to influence device life [55], which according to the indium migration model, is unexpected. It could be argued that thin Pt films are not continuous, and therefore, In migration from ITO to the organic phases is not blocked. However, even with incomplete Pt coverage of ITO, the effective area available for In migration should be substantially reduced and at least some influence on device life should be observable. The ability to change device stability by only modifying the electron-injecting contact, without altering the ITO contact or the hole transport layer, is yet another phenomenon not supported by the indium migration model.

This contradiction between indium migration and unstable cationic AlQ₃ models could be reconciled by simply assuming that these two mechanisms operate in different time scales. It is important to note that the measurements of indium concentration in different OLED layers [21] have been performed on very stable devices showing half lives in excess of 2000 h at a high current density of 20 mA/cm². The measurements were done only at the beginning and at the end of device aging. It is entirely possible that indium migration is responsible for aging at very long times and becomes a dominant aging mechanism only after the cationic AlQ₃ degradation has been sufficiently reduced. It would be very interesting to study the time evolution of indium concentration as the experiment is progressing by performing indium analysis measurements on devices that were aged for different times. In this case, the quantitative correlation between the detected amount of indium and decrease in device luminance should be observed.

The experimental evidence for the existence of both reversible and irreversible part of device degradation is very strong [57]–[60]. Redistribution of mobile ions or space charge by deep trap population [57], [58], and perhaps reorientation of internal dipoles [61] are all plausible candidates for explaining the reversible part of changes in device operation. It is, therefore, highly likely that device degradation is governed by different phenomena at different time scales. At short times (on the order of tens of hours), OLED performance degradation may be governed by space charge redistribution phenomena due to various slowly migrating charged or dipolar species. At longer times (hundreds to thousands of hours), degradation due to instability of AlQ₃ cationic species may dominate, and at very long times (several thousands of hours) indium migration induced degradation may be significant. The given times scales would correspond to typical accelerated OLED aging testing conditions at currents on the order of few times 10 mA/cm².

Although significant progress in understanding OLED degradation phenomena has been accomplished in the last couple of years, the complete, fully consistent picture of the degradation processes is still lacking. Most studies specifically addressing the intrinsic degradation problem concentrated on devices containing AlQ₃. As these materials are generally used in devices emitting light from the green to the red part of the spectrum, the study of AlQ₃-related aging processes is highly relevant for practical devices. However, blue-emitting OLEDs, and often OLEDs based on triplet emitters [62] use different materials as emitter hosts. It may be that the mechanisms involved in degradation on AlQ₃-based devices are quite universal. On the other hand, other materials, like blue emitters (oxiadiazoles,

antracenes, triazines, etc.), may show fundamentally different degradation mechanisms. Therefore, the field of research on OLED stability and degradation retains its significance. It will play an important role in further developments of OLED technology.

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