Degradation Phenomena in Small-Molecule Organic Light-Emitting Devices

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Studies of electroluminescence degradation mechanisms in small-molecule-based organic light-emitting devices (OLEDs) are reviewed. Luminescence degradation due to the growth of visible nonemissive defects, widely referred to as “dark spots”, as well as device catastrophic failure phenomena are addressed briefly. A special emphasis is given to intrinsic degradation phenomena that cause the decrease in the electroluminescence efficiency of the OLEDs during operation. In the discussion of intrinsic degradation, some widely accepted models that have been proposed to explain the degradation behavior are introduced and reviewed in view of experimental observations. These models are (i) the morphological instability model, (ii) the unstable cationic AlQ_3 model, (iii) the indium migration model, (iv) the mobile ionic impurities model, and (v) the immobile positive charge accumulation model.

I. Introduction

The discovery of electroluminescence in organic materials dates back to the middle of the 20th century. However, the interest in this phenomenon as a technology emerged only in the past decade. In the 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 it clear they were not suitable for practical applications, such as displays. 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 poly(vinylcarbazole) (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 (AlQ_3), an emitter and electron-transport material, and a tertiary diamine hole-transport material.[4] The devices were produced by thermal evaporation of organic small-molecule materials and a metal cathode on a conductive substrate in a vacuum. The half-life (time of operation elapsed before emission brightness decreases to 50% of its initial level) of these devices was measured in hundreds of hours, many orders of magnitude longer than any organic thin film devices reported previously. Soon after, in 1990, another important development followed. Burroughes et al. reported observation of electroluminescence in a single-layer device made of the polymer poly(phenylenevinylene) (PPV), formed by a spin-coating process.[5] These two developments renewed the interest in organic light-emitting devices (OLEDs) as a potential technology for flat panel display applications. 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/m^2, is needed. To obtain this level of display brightness, the luminance of the individual OLEDs often needs to be higher, typically in the range of 200−600 cd/m^2, depending on several factors, such as the emission color and pixel aperture ratio. For some specialized applications where the usage duty cycle is low, such as, for example, cellular phone displays, a shorter device half-life may be acceptable. A device half-life is sometimes referred to as device lifetime or simply device life.

In general, degradation in OLEDs essentially appears in the form of a decrease in device luminance in time. The decrease in luminance can proceed through three independent and visually distinct modes. These modes are referred to as (i) dark-spot degradation, (ii) catastrophic failure, and (iii) intrinsic degradation. The first mode, associated primarily with degradation at the device electrodes, occurs through the formation of nonemissive regions, referred to as dark spots, and leads to a decrease in device luminance as a result of losses in the emissive area of a device.[6−8] The second mode, mainly associated with defects in the organic layers,

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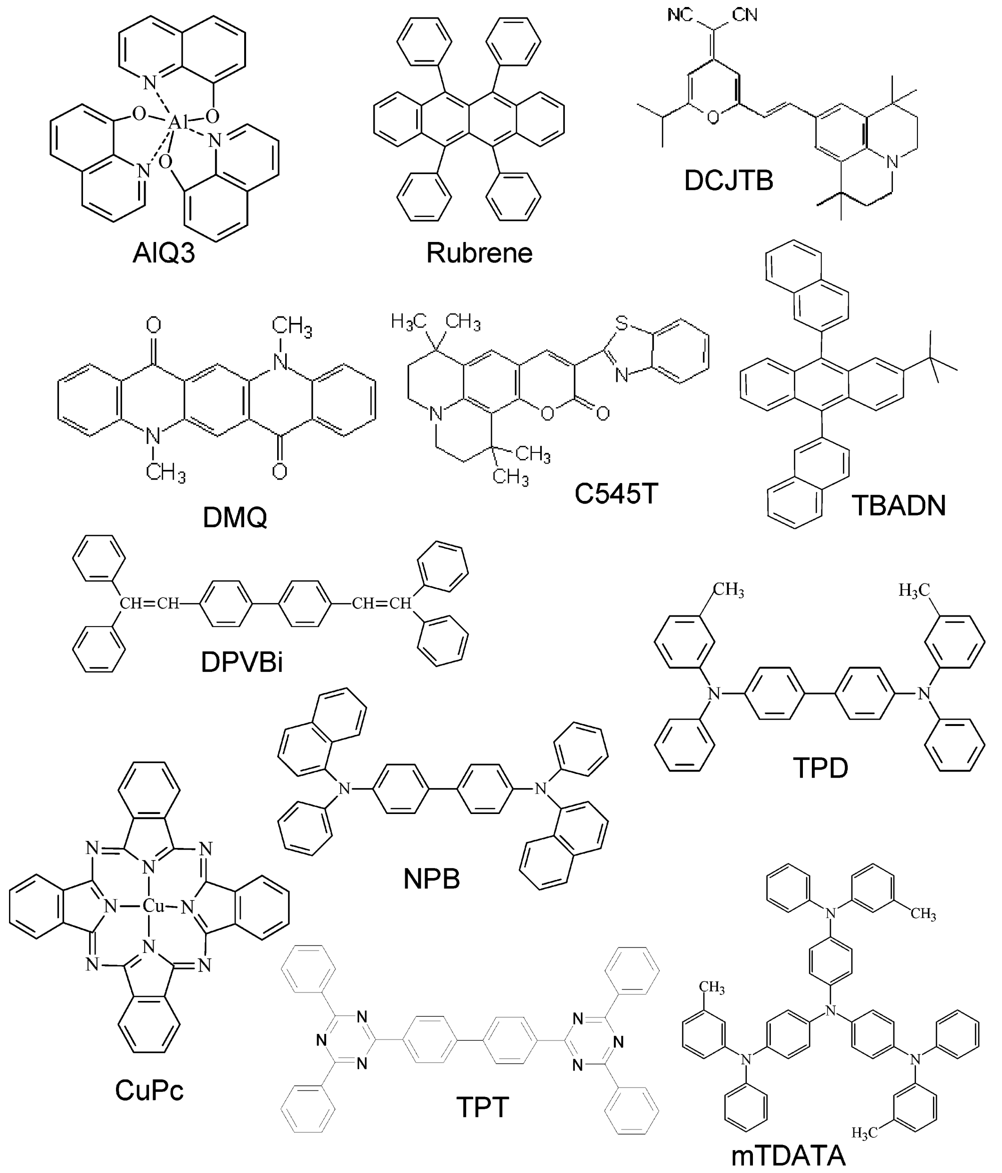

Figure 1. Chemical structures of some of the materials commonly used in small-molecule-based OLEDs. Chemical names for these molecules are given in the text.

occurs through the development of electrical shorts that result in a sudden decrease or total loss of luminance as a result of large leakage currents.[9,10] The third degradation mode is reflected in a long-term "intrinsic" decrease in the brightness of the emissive area of a device, without any obvious change in device appearance, and mainly occurs during device operation.[7] While the first two modes of degradation can be effectively controlled by means of proper device encapsulation and adequate control over device fabrication conditions, the intrinsic degradation mode has been far more challenging and continues to be an issue for OLED commercialization.

In this paper, we will review some of the work that has been done to explore the mechanisms behind degradation in small-molecule-based OLEDs and to increase the stability of these devices. Although the scope of this review is limited to small-molecule-based OLEDs, reference to work addressing dark-spot degradation and catastrophic failure modes in polymer OLEDs is sometimes made because of the commonalities of these degradation modes in both small-molecule and polymer OLEDs. On the other hand, because intrinsic degradation phenomena are believed to be essentially specific to the organic material system in question, the discussion of these phenomena will be exclusive to small-molecule-based OLEDs.

Throughout this paper, we make extensive reference to widely used small-molecule OLED materials and various device architectures. Therefore, giving a background on common small-molecule materials and general device structure, first, is perhaps useful. Figure 1 shows the molecular structure of most commonly used materials in small-molecule-based OLEDs. Since the report on the first efficient OLED by Tang and Van Slyke in 1987,[4] tris(8-hydroxyquinoline)aluminum (AlQ_3) has been and continues to be the most widely used emitter material. Being a green emitter with an energy gap of ~2.6 eV, it has been used in devices emitting from the green to red part of the visible spectrum. The different colors are accomplished by doping AlQ_3 with narrower band gap emitters to obtain the desired electroluminescence (EL) colors. Some widely used dopants are 5,6,11,12-tetraphenylnaphthacene (ru-

Table 1. Values of Highest Occupied Molecular Orbital (HOMO) Energy Levels, in eV, for Some of the Materials in Figure 1

AlQ_3	Rubrene	CuPc	MTDATA	TPD	NPB
5.6−5.8	~5.3	5.2−5.3	5.0−5.1	5.3−5.5	5.2−5.4

brene) and [2-(2-propyl)-6-[2-(2,3,6,7-tetrahydro-2,2,7,7-tetramethyl-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)ethenyl]-4*H*-pyran-4-ylidene]propanedinitrile (DCJTB), which produce yellow and red emission, respectively. In green-emitting OLEDs, AlQ_3 is usually doped with other green emitters, which leads to enhanced brightness or improved color purity. Two typical green dopants are *N*,*N*-dimethylquinacridone (DMQ) and 10-(2-benzothiazolyl)-2,3,6,7-tetrahydro-1,1,7,7-tetramethyl l-1*H*,5*H*,11*H*-[1]-benzopyrano[6,7,8-*ij*]quinolizin-11-one (C545T). For blue-emitting OLEDs, stilbenes and anthracenes are usually used as the emitters, of which, 1,4-bis(2,2-diphenylvinyl)biphenyl (DPVBI) and 9,10-bis(2-naphthyl)-2-*tert*-butylanthracene (TBADN) have been the most widely studied. In addition to the emitter, a small-molecule OLED includes several other materials. Copper phthalocyanine (CuPc) is commonly used as a buffer layer contacting the hole-injecting anode. *N*,*N′*-Diphenyl-*N*,*N′*-bis(3-methylphenyl)-1,1-biphenyl-4,4′-diamine) (TPD), *N*,*N′*-di(naphthalen-1-yl)-*N*,*N′*-diphenylbenzidine (NPB), and 4,4′,4″-tris(*N*-3-methylphenyl-*N*-phenylamino)triphenylamine (MTDATA) have been the most frequently used hole-transport materials (HTMs). AlQ_3 and triphenyltriazine (TPT) are often used as electron-transport materials (ETM). In the interest of the present discussion, Table 1 shows typical values for the highest occupied molecular orbital (HOMO) energy level of some of these materials. (The ranges in the table represent widely accepted values. More details, including references, are provided in the Supporting Information). Transparent indium thin oxide (ITO) is almost exclusively used as a hole-injecting anode. A Mg:Ag alloy (9:1 by volume) is often utilized as an electron-injecting cathode; however, other cathode materials (Ca, Al:Li alloy, Al, etc.) are also widely used. To facilitate further discussion and introduce some common acronyms, Figure 2 shows a schematic diagram of a typical OLED structure. Often ITO is first covered 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.

Dark-spot degradation and the catastrophic failure modes are addressed briefly in sections II and III, respectively, followed by a more detailed discussion of intrinsic degradation in section IV. The special attention given to intrinsic degradation in this review is motivated by the fact that, in comparison to the other two, this mode is still the least understood and continues to pose a major technological challenge.

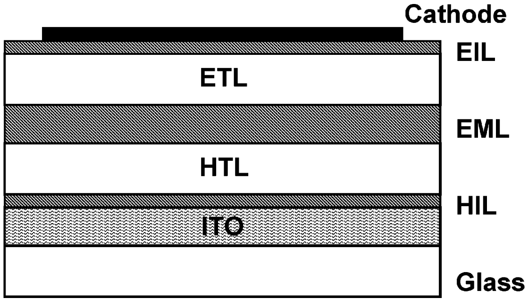

Figure 2. A typical OLED device structure. The function of different layers and the meaning of acronyms are given in the text.

II. Dark-Spot Degradation

As the name implies, dark-spot degradation refers to the decrease in OLED luminance as a result of the formation and growth of nonemissive defects, or dark spots, within the emissive area of the device. Although the growth of dark spots occurs even during OLED storage (i.e. nonoperation), the behavior is generally accelerated by operation, suggesting that the underlying dark-spot formation mechanisms are electrochemical in nature or are thermally activated by Joule heating as a result of current flow. The growth of these defects proceeds fast enough that they become visible to the unaided eye within a few hours of exposing the OLED to air, thus making it the first degradation mode to receive wide attention.[6,7,10,11] In the earlier studies, local oxidation of the metal cathode at pre-existing defect sites or delamination of the metal from the underlying organic layers were identified as important factors behind the evolution of dark spots under ambient conditions. Realizing the ambient-induced nature of the phenomenon, hermatic sealing of the OLEDs in inert atmospheres has been used as a means to control dark-spot formation.[6] With encapsulation techniques providing adequate control over dark-spot degradation, later studies on dark-spot formation and the underlying mechanisms have been essentially motivated by scientific curiosity rather than technological need.

Various mechanisms for the formation of dark spots have been proposed. A widely accepted mechanism attributes their formation to local delamination of the cathode from the organic layers, thus causing the "bubble" or "domelike" structures sometimes observed in the cathodes of OLEDs.[7,13−18] In this case, dark spots are the result of interruption in electron injection caused by loss of contact between the cathode and the organic layer at these delaminated areas. The delamination itself was found to be caused by gas evolution produced by electrochemical processes at the cathode/organic interface in the presence of ambient moisture that penetrates through cathode pinholes or other preexisting defects.[8,15,16,18,19] Gas evolution can also result from decomposition of the organic layers or other gas-releasing phenomena associated with Joule heating during device operation.[12,13,17,20] Morphological changes in the organic layers, which can sometimes be ambient-induced, can also lead to cathode delamination due to a gradual increase in roughness of the organic films resulting from the growth of grains and other protruding features.[21,22] Dark spots can also be caused by delamination at the anode/organic interface possibly by gas release from preexisting adsorbed moisture on the indium−tin oxide (ITO) anode.[14,17] In all these cases, delamination is facilitated by poor adhesion between the electrodes and the organic layers.[11]

The formation of dark spots is also often attributed to the presence of microscopic shorts between the two electrodes, again due to preexisting structural defects in the organic layers or the electrodes, which, under external bias of the OLED, turn into hot spots due to the higher local current densities. The localized heating results in the oxidation of the cathode metal into a nonconductive species and results in a nonemissive area due to loss of electron injection.[6,15] In a recent study,[23] Kosolov et al. proposed a mechanism in which dark spots originate at nonconductive regions at the cathode/organic interface which then grow by oxidation. In agreement with earlier studies,[16,26] the oxidation creates local carrier blocking interfaces at the dark-spot locations. Contradiction between conclusions that the organic layers at the sites of the dark spots become defective[16,23,26] and others that show that, despite the electrode damage, the organic layers remain essentially intact[8] can be resolved by assuming the presence of different types of dark spots.[14,16] Interdiffusion between organic layers has also been suspected to cause the dark-spot formation.[24] Later observations, however, did not support that mechanism.[7,25]

In conclusion, although a significant number of studies have focused on exploring the mechanistic processes behind dark-spot degradation, they mostly arrive at essentially similar conclusions. Despite some apparently different subtleties, the similarities are dominant. Dark-spot degradation is caused by the evolution of structural defects in the OLED layers, and more specifically at the two electrode/organic interfaces but to a larger extent at the cathode/organic interface. Although the driving processes are essentially extrinsic in nature, induced by the presence of external species from the ambient conditions, preexisting structural defects act as nucleation sites. Adequate control over substrate/ITO cleanliness and smoothness and over the device fabrication process significantly reduces the density of structural defects and hence the number of potential dark spots. In the meantime, protection from the ambient, by proper encapsulation, is effective in suppressing their growth. Exploration of other means to control the growth of dark spots has recently yielded some interesting results. Fung et al. showed that coating the cathode with a layer of a reactive metal leads to a decrease in dark spots.[27] The behavior was attributed to the role of the reactive metal in acting as a sacrificial layer for electrochemical corrosion. Chan et al. found that heating the substrate during deposition of the organic layers can also lead to a decrease in dark spots.[28] More recently, we demonstrated that cathodes utilizing a mixture of metals and organic materials are more resistive to dark-spot degradation.[29]

III. Catastrophic Failure

The catastrophic failure refers to a sudden decrease or total loss of luminance due to the development of electrical shorts across the device. The loss in luminance results from the large leakage currents through the shorts. The development of shorts is attributed to preexisting morphological defects in the organic layers or the electrodes that become hot spots during device operation,[6,9,10] thus leading to the melting or decomposition of the organic layers and hence a direct contact between the two electrodes (or a short) at these sites. Although the loss in OLED usually occurs suddenly, it is believed that the evolution of the shorts themselves occurs over a period of time, which will obviously be longer in devices with less preexisting defects. Because of the progressive nature of their development, these shorts are sometimes referred to as progressive electrical shorts (PES).[10] Being a structural-defect-related failure mechanism, the use of materials with better film-forming properties and more stable morphology is necessary to reduce its occurrence.[9] In addition, the use of ac driving in operating the devices also reduces their occurrence, since, given the rectifying nature of an OLED, current flow during the reverse bias cycle can take place almost exclusively through any existing shorts, thus burning them out before they progress into bigger ones.[30] More recently, Kim et al. described a preoxidation method for healing the shorts by means of exposing the organic films to oxidative gases prior to cathode deposition.[10]

Another catastrophic failure behavior is thermally induced and occurs upon heating the OLEDs to above a critical temperature that usually corresponds to the glass transition temperature, T_g, of the organic materials.[31−33] Fenter et al. attributed the behavior to a strain-driven mechanism that acts to alleviate mechanical stresses caused by the large thermal expansion coefficient of the organic materials at temperatures approaching their T_g.[34] Interestingly, and contrary to expectations, the study ruled out crystallization of the organic materials from having a role in this failure mode.

IV. Intrinsic Degradation

Intrinsic degradation refers to the progressive decrease in the luminance of the OLED in time that occurs during device operation. The decrease in luminance is not associated with any obvious change in device appearance. Because the decrease in luminance is observed even when the devices are operated using constant current driving, it essentially reflects an intrinsic decrease in the electroluminescence quantum efficiency of the OLED. Unlike the two previous modes of degradation, which are essentially attributed to external factors and involve mechanistic processes that are mainly independent of the specific organic material system, intrinsic degradation is primarily material-dependent. Although some of the underlying mechanisms that have been identified for a particular material system are expected to extend to other systems, experimentation has yet to prove that.

A number of models have been proposed to explain the intrinsic degradation behavior of OLEDs. In these mechanisms, the decrease in the electroluminescence quantum efficiency of the devices during operation is attributed to a number of unrelated factors. The most important of these are (i) the morphological instability model, (ii) the unstable cationic AlQ_3 model, (iii) the indium migration model, (iv) the mobile ionic impurities model, and (v) the immobile positive charge accumulation model. A brief discussion of each of these models is given in this section.

(i) Morphological Instability Model. For a long time it was believed that morphological instability of the organic layers, more specifically the hole-transport layer, was responsible for OLED degradation. The idea was based on observations that TPD films, coated on glass or ITO substrates, showed significant crystallization and subsequent increase in surface roughness within a few days of their fabrication.[11,35,36] From these results, it was concluded that similar morphological changes could be occurring in the HTL of an OLED and may, therefore, be behind OLED degradation, perhaps as a result of interlayer delamination at the TPD/AlQ_3 and the subsequent interruption of efficient charge injection or due to the creation of nonradiative recombination sites at the boundaries of the crystalline domains. In that regard, Joule heating due to current flow in the device was assumed to accelerate such crystallization and thus explains the decay in OLED luminance primarily during operation.[37] Introducing another organic material as a dopant in the HTL, thus creating a host−guest system, was found to increase the operational stability of the devices,[11] a phenomenon that was attributed to the role of the guest in preventing the host crystallization by an entropy effect. Following the same approach, Hamada et al.[38] realized an OLED with a long half-life exceeding 3500 h at 500 cd/m^2 initial luminance by means of doping TPD HTL with Rubrene. From these results, the notion that OLED degradation is predominantly due to morphological instability of the HTL gained wide acceptance. However, we must point out that to the best of our knowledge, morphological changes similar to what is often observed in uncovered TPD films were never detected in an OLED. In fact, in an unpublished study, we found that coating TPD with AlQ_3—as is the case in an OLED—suppressed TPD crystallization, possibly due to good adhesion with AlQ_3 and immobilization of TPD molecules by the absence of a free surface.

Motivated by the belief that increasing the morphological stability of the HTL would improve OLED operational stability, a significant body of research focused on the design of high-T_g hole-transport materials and resulted in the synthesis of a number of important OLED materials. The incorporation of high-T_g HTMs in OLEDs certainly realized an increased resistance to catastrophic device failure that would usually result from exposures to elevated temperatures[31−33,39−43] and contributed to improving device shelf life;[11] nevertheless, it did not impact device operational stability at room temperature.[32,37] In 1998, we showed that it is possible to achieve high OLED operational stability by means of using a mixed HTM + AlQ_3 emitting layer.[25] The study was originally conducted to verify whether interdiffusion between the HTM and AlQ_3 played a role in the decrease of OLED luminance,[35,36] and the results convincingly showed that intermixing cannot be a major cause of device degradation. More importantly, the study revealed that operational stability can be increased, despite using the same undoped HTM in the HTL, by only modifying the emitting layer. Therefore, morphological instabilities of the organic layers are no longer seen to be a dominant factor in intrinsic degradation of OLEDs, especially for room-temperature operating conditions.

(ii) Instability of Cationic AlQ_3 Model. In this model, device degradation is attributed to the idea that cationic AlQ_3 species are unstable and that their degradation byproducts lead to a decrease in device electroluminescence.[44] The idea is based on experiments showing that the photoluminescence quantum yield of AlQ_3 thin films decreased by ~55% after being subjected to "hole-only" currents of 50 mA/cm^2 for 50 h. On the other hand, the photoluminescence yield remained essentially unchanged upon the flow of "electron-only" currents under the same conditions.[44] The decrease in the photoluminescence quantum efficiency of the AlQ_3 films upon exposure to hole currents was found to be associated with a decrease in the lifetime of AlQ_3 excited state and pointed to the formation of luminescence quenchers.[45] A similar decrease in the AlQ_3 photoluminescence quantum efficiency, in the vicinity of the HTL/AlQ_3 interface, was detected in aged OLEDs.[46] The studies also showed that cationic AlQ_3 degradation products act not only as fluorescence quenchers but also as charge traps and electron−hole recombination centers.[46] Obviously, the model is limited to AlQ_3-based OLEDs; however, its importance stems from the fact that AlQ_3 continues to be the most widely used small-molecule emitter and is utilized in devices emitting in the green to red part of the visible spectrum.

According to this model, the role of doping the HTL in increasing device operational stability[38,47,48] is explained in terms of the role of the guest molecules in acting as hole traps and therefore slowing down the transport of holes to the HTL/AlQ_3 interface.[49−51] Under these conditions, the density of electrons in the AlQ_3 layer adjacent to the HTL/AlQ_3 interface is increased, thus leading to rapid recombination and therefore a shorter lifetime of the unstable cationic AlQ_3 species. It is also possible that because of the high electron density at the HTL/AlQ_3 interface, the production of cationic AlQ_3 species is greatly reduced, as holes can be injected directly from HTL into anionic AlQ_3 species to produce excited states.[52] The use of materials that have an ionization potential deeper than that of the HTM as dopants, and therefore did not act as hole traps in the HTL, was shown to have no effect on device stability,[53] thus further supporting the argument.

The high stability of OLEDs containing a ~15 nm thick CuPc buffer layer at the hole-injecting contact[30] is attributed to a similar effect. Using this CuPc buffer layer, Van Slyke et al. obtained a half-life at 20 mA/cm^2 of 4000 h from an initial luminance of 510 cd/m^2 in a device that had NPB and AlQ_3 as HTL and EML, respectively. In this case, the high stability is attributed to the role of the CuPc layer in creating a hole-injection barrier[54] that slows down the delivery of holes to the HTL/AlQ_3 interface.[44] The additional increase in the stability of these devices by doping the AlQ_3 layer with DMQ green dopant[55] can be explained in terms of the role of the dopant molecules in acting as electron−hole recombination sites,[56] which would further reduce the residence time of holes on the AlQ_3 host. The higher stability of OLEDs using double-layered MTDATA/TPD HTL relative to devices using a single-layered TPD HTL[57] can be explained in terms of the lower hole mobility of MTDATA relative to that of TPD ($\sim 3 \times 10^{-5}$ and $\sim 10^{-3}$ cm^2/V s, respectively[58]), which would slow the delivery of holes to the HTL/AlQ$_3$ interface. By using double-layered HTL utilizing different materials (TPD and NPB), we showed that device stability is increased only when the order of the TPD and NPB layers led to the formation of a larger barrier for hole injection.[59] Reversing the order of the two layers, thus reducing the hole-injection barrier, produced less stable devices.

Attributing intrinsic degradation to instability of cationic AlQ$_3$ is perhaps the only model so far that can explain the enhanced stability of OLEDs containing a mixed HTM + AlQ$_3$ layer.[25,60,61] With a half-life amounting to 4560, 1040, and 505 h for continuous operation at 22, 70, and 100 °C, respectively, from an initial device luminance of ~1750 cd/m^2, OLEDs utilizing these mixed layers demonstrate remarkable durability, especially at elevated temperatures.[62] The stability of these devices is explained in terms of the preferential residence of holes, inside these mixed layers, on the HTM sites because of the lower ionization potential relative to that of the AlQ$_3$. Electrons, on the other hand, preferentially reside on AlQ$_3$ sites, resulting in a high density of anionic AlQ$_3$. Because in the mixed layer HTM and AlQ$_3$ molecules are in close proximity, the direct recombination between holes from HTM sites and AlQ$_3$ anions to produce excited states of AlQ$_3$ directly, without necessarily forming the unstable cationic AlQ$_3$ intermediates, is believed to be a dominant recombination process.[44,61,63] The same argument is used to explain the high stability of OLEDs containing a graded mixed layer.[64,65] More recent studies showed that the activation energy for temperature dependence of device degradation in these mixed layer OLEDs closely corresponded to the difference in ionization potential of the HTM and the AlQ$_3$, thus further supporting the argument.[66]

The above argument can also explain the higher stability of OLEDs often observed when metals with lower work function are used in the cathodes.[67−69] The more efficient injection of electrons from the lower work function metal into the AlQ$_3$ layer leads to a higher density of electrons in the AlQ$_3$ layer adjacent to the HTL/AlQ$_3$ interface and hence a lower density of the unstable cationic species and thus a higher device stability.[44] A similar behavior was observed by Wakimoto et al.,[70] who used a thin electron-injection layer consisting of alkaline metal compounds and Al capping as cathodes, leading to the conclusion that efficient electron injection improved device stability.

The model can also be used to explain other phenomena pertaining to OLEDs' stability. For example, the correlation between a lower ionization potential of the hole-transport material and a higher device stability[37] can be 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 AlQ$_3$ as a result of a higher hole injection barrier at the HTL/AlQ$_3$ interface. The reduced injection of holes into the AlQ$_3$ layer leads to a higher density of electrons in the AlQ$_3$ layer adjacent to the HTL/AlQ$_3$ interface, which, in turn, leads to a shorter lifetime of cationic AlQ$_3$ species.[44]

Clearly, in view of the above discussion, the model of OLED degradation based on the instability of cationic AlQ$_3$ species seems to be capable of explaining a large number of experimental observations related to device stability. The model is also supported by results from Papadimitrakopoulos et al.[71] from cyclic voltammetry on AlQ$_3$ that showed that AlQ$_3$ oxidation was irreversible. However, there are some observations that cannot be readily explained by the model. For example, in the devices of Gyoutoku et al.,[72] the insertion of a carbon buffer layer at the hole-injecting contact led to a decrease in device turn-on voltage by 2.5 V. Nonetheless, with a half-life of 4000 h from an initial luminance of 500 cd/m^2, the stability of the device does not appear to be compromised by the presence of the layer. Hung et al.[73] reported a similar effect, where coating the ITO with CHF$_3$ plasma polymerized thin film prior to deposition of the HTL led to an increase in stability despite a ~1 V reduction in operating voltage. The report by Hu et al.[74] suggests that a similar behavior may have been observed when a CuO$_x$ buffer layer was coated on the ITO anode. At first glance, improved hole injection, as indicated by the lower turn-on voltage in all three cases, should lead to increased hole supply to AlQ$_3$ and a decrease in device life, thus contradicting the model. One possible explanation is that very efficient anodes will lead to a significantly reduced electric field in the hole-transport layer and at the HTL/AlQ$_3$ interface, which may decrease (rather than increase) hole injection into AlQ$_3$, despite 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.[75]

(iii) Indium Migration Model. According to this 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.[76] The idea that electroluminescence degradation in small-molecule OLEDs might be caused by indium or other ITO species released from the anode existed before[54] and had its origins in polymer OLEDs, where the larger body of experimental work gives it wider acceptance.[77−82] Using secondary ion mass spectrometry (SIMS) and mass spectrometry, Lee and co-workers were able to detect indium in the organic layers of devices that had been aged, where its concentration was 10 times higher than in as-prepared devices. To investigate whether the presence of trace amounts of indium in the organic layers could cause a significant decrease in OLED luminance, 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 substantially lower electroluminescence efficiency only in devices where the indium was doped in the emission zone of the AlQ$_3$ layer, while doping the hole-transport layer or the CuPc anode buffer layer had no effect. On the basis of 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 indium atoms, could be behind luminescence quenching and hence OLED degradation. It is worth mentioning, however, that an indium 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 a long half-life, exceeding 2000 h at an average forward current of 20 mA/cm^2.

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 (i) ITO surface treatment, (ii) the use of buffer layers at the anode contact, and (iii) 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 thus create a more stable surface that would reduce the release of indium.[76,83−86] The increase in device stability on using different buffer layers at the ITO contact, such as CuPc,[30] MTDATA,[57] amorphous carbon,[72] plasma-polymerized CHF_3,[73] or CuO_x[74] discussed above, can be explained in terms of the role of these buffer layers in acting as barriers for indium diffusion. That explanation would remain valid regardless of whether the introduction of these buffer layers would increase or decrease OLED operating voltage, an observation that is not readily understood by the previous model based on the instability of cationic AlQ_3 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 indium atoms and hence reducing their penetration to the AlQ_3 emitting layer.

However, the model cannot explain a number of other observations that are difficult to overlook. For instance, the notion that indium diffusion is assisted by electrical migration of charged indium is not consistent with the fact that the long term degradation behavior of OLEDs, in general, is essentially similar under both dc and ac driving conditions.[87] Shen and co-workers showed that degradation of device electroluminescence under dc driving subsequent to operating for 100 h using ac driving essentially followed the same trend.[88] The use of ac driving, especially when the magnitude of the reverse voltage is greater than that of the forward voltage,[30] as it is often the case, should prevent or at least substantially reduce the migration of the charged indium atoms and hence increase device stability. It is also difficult to understand why changing the order of two hole-transport layers (NPB and TPD),[59] as described in the section on the unstable cationic AlQ_3 model should affect indium migration. The widely observed correlation between an increased electron injection efficiency of the cathode and a higher OLED stability[67−70] is yet another phenomenon that does not support the model. The ability to change device stability by only modifying the electron-injecting contact, without altering the ITO contact or the hole-transport layer, cannot, so far, be explained in terms of the migration of species originating from the ITO anode.

(iv) Mobile Ionic Impurities Model. The degradation model based on the presence of mobile ionic impurities 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.[88−91] The increase in voltage is however often reversible, at least partially, on either resting the device at zero applied bias or reversing its polarity.[90,91] Shen and co-workers[88] presented a systematic study of this phenomenon on a standard bilayer AlQ_3-based OLED. The device degradation, reflecting an operating voltage increase and electroluminescence decrease, was modeled by 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, and Mg, 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. Following a very similar argument, reorientation of molecular dipoles, which might also be present as impurities in the device, had been suspected to play a similar role in device degradation.[91,92]

Models based on redistribution of space charge, of whatever origin, either ionic or due to charge traps, with a relatively short time frame ($<$100 h), may be relevant for understanding the fast initial (short-term), often reversible, decay in OLED electroluminescence. This is in many cases particularly pronounced under dc driving conditions[90,91] and also reflected in variations in initial (short-term) OLED electroluminescence decay behavior for ac vs dc driving conditions.[87] However, the fact that changes in both luminance and driving voltage during long-term operation ($>$100 h) are mostly irreversible, as well as the fact that the long-term degradation rate is essentially the same for both dc and ac driving,[87] suggests that this degradation mechanism, if indeed operative, can only have a limited effect on long-term device degradation.

(v) Immobile Positive Charge Accumulation Model. According to this model, which was proposed by Kondakov and co-workers in 2003,[93] the observed decrease in OLED luminance during operation is associated with an accumulation of trapped (or immobile) positive charges at the HTL/EML interface. By analyzing changes in the capacitance−voltage characteristics that occur as a device ages during long-term operation (over a period of 5000 h), the authors convincingly argued that the decrease in luminance efficiency is linearly correlated with a build-up of a trapped positive charge located at the HTL/EML interface. Although each of the two quantities changed in a nontrivial manner during device operation, they were essentially quantitatively linearly correlated, regardless of the device driving conditions (dc vs ac, 5−40 mA/cm^2, room temperature vs 70°C). The phenomenon was observed in both green devices (utilizing NPB and AlQ_3 as HTL and EML, respectively) and blue devices (utilizing NPB, TBADN, and AlQ_3 as HTL, EML, and ETL, respectively), suggesting that it may have a wider significance. From the study, it was not

possible to identify the chemical nature of the increasing trapped positive charge. The authors, however, suggested it may represent metal ions that have diffused from the electrodes during device operation or, more likely, the generation of hole traps (and trapped holes), which can act as nonradiative recombination centers and hence decrease the luminance efficiency.

The notion that positive charge may be present at the HTL/EML interface is supported by earlier reports. In a study on standard bilayer devices with TPD and AlQ_3 as HTL and EML layers, respectively, Matsumura and co-workers in 1999[94] concluded that positive charges accumulated at the HTL/EML interface. They observed that the amount of positive charge changed with changing the cathode metal, where increasing the electron injection efficiency of the cathode (by using cathodes made of Al, Mg:Ag, and Li:Al in that order) decreased the positive charge. In an earlier study, Matsumura and Jinde[67] also detected changes in EL spectra of standard bilayer devices with TPD and AlQ_3 as HTL and EML layers, respectively, during device aging. Using mathematical models for microcavity effects to analyze the EL spectra, they deduced that the changes corresponded to a decrease in the thickness of the recombination zone. The calculated change in thickness of the recombination zone was essentially equivalent to the observed change (decrease) in device luminance during aging, thus suggesting that the distance of hole penetration into the AlQ_3 bulk decreased as the devices degraded. Clearly, the decrease in the distance of hole injection at the HTL/AlQ_3 interface during aging is supportive of the argument that degradation is associated with an accumulation of a positive charge in the vicinity of that interface. Berleb et al. also found evidence for a fixed charge residing in the vicinity of the HTL/AlQ_3 interface.[95] It is also worth pointing that the study by Kondakov et al. is perhaps the first to address degradation mechanism in blue OLEDs.

Although the close correlation between the decrease in electroluminescence efficiency and the increase in accumulated positive charge at the HTL/EML shown by Kondakov et al. indeed strongly suggests that the two quantities are interrelated, it is not possible to know whether the decrease in luminance is directly caused by the increase in the accumulated charge, regardless of any other chemical degradation processes that may be associated with them, or if both the charge increase and the luminance decrease are interrelated through a chemical degradation process.

A scenario in which the decrease in luminance is directly caused by the increase in the accumulated positive charge, regardless of any associated chemical degradation processes, can be a case when quenching of singlet excited states by cationic species through Forster energy transfer is efficient. As is widely known in this case, the quenching efficiency depends on the overlap between the emission spectrum of the excited state and the absorption spectrum of the cationic species. Young et al attributed the observed decrease in EL efficiency at high currents in OLEDs with a DCJTB-doped AlQ_3 EML to this process, where the $^1DCJTB^*$ was quenched by $DCJTB^+$ or $AlQ_3{}^+$, which increased in concentration as the current increased.[96] Similarly, Ganzorig and Fujihira recently pointed out that the decrease in EL efficiency at high currents in OLEDs with an AlQ_3 EML and an Al cathode may be due to quenching of $^1AlQ_3{}^*$ by a large concentration of $AlQ_3{}^+$ in the EML.[97] Although neither study addressed the involvement of this quenching process in OLED long-term degradation, it is possible to attribute the results of Kondakov et al. to the same effect where the quenching of $^1AlQ_3{}^*$ and $^1TBADN^*$ progressively increases as the concentration of $AlQ_3{}^+$ and $TBADN^+$ is increased due to an increase in hole traps that occurs during device operation.[93] In that regard, approaches to decrease the accumulation of positive charges at the HTL/EML interface (by increasing recombination rate with electrons) would be expected to increase device stability. Interestingly, because of the parallelism between this case and the model on instability of cationic AlQ_3 discussed above, which also depends on a high concentration of holes at the HTL/EML interface, many of the experimental observations that supported the earlier model can also be used to support the present one. For example, the role of a CuPc buffer layer at the hole-injecting contact in increasing device stability[30] can still be attributed to its role in creating a hole-injection barrier[54] that slows down the delivery of holes to the HTL/AlQ_3 interface, thus increasing the density of electrons in the AlQ_3 layer adjacent to the HTL/AlQ_3 interface, which results in a more efficient neutralization (recombination) of the holes available at the interface and hence less accumulation of excess holes at the interface. A similar effect would be achieved by increasing the electron-injection efficiency of the cathodes, thus explaining the correlation between a lower cathode work function and an increased device stability.[67-70] It must be pointed out, however, that this scenario provides no insights on why the generation of these hole traps occurs.

An alternative scenario, where both the positive charge increase at the HTL/EML interface and the OLED luminance decrease are interrelated through a chemical degradation process, can be a case where the accumulation of positive charges at the interface may drive a chemical degradation process whose byproducts act as luminescence quenchers, charge traps, and nonradiative recombination sites. In that case, the model based on the instability of cationic AlQ_3 can very possibly be this chemical degradation process. In that regard the immobile positive charge accumulation model and the unstable cationic AlQ_3 model may be addressing two aspects of the same degradation mechanism. However, one must not overlook the fact that the correlation between luminance degradation and the build-up of trapped positive charge at the HTL/EML interface appears to be not limited to OLEDs with an AlQ_3-based EML. Its detection in OLEDs with TBADN-based EML certainly indicates that the immobile positive charge accumulation model is addressing an effect that may be more common to a wider variety of OLED structures and compositions.

General Discussion on Intrinsic Degradation Models. From the above discussion it is obvious that, at the present time, no single model explains all experimental observations. It appears that the unstable cationic AlQ_3 model is able to explain the widest variety of the observed OLED aging phenomena in devices utilizing

AlQ_3 in the EML. However, because of the obvious parallelism between that model and the immobile positive charge accumulation model, most of the experimental observations that support the first can also argue for the latter. The two models appear to be addressing two aspects of the same degradation mechanism where both the positive charge increase at the HTL/EML interface and the OLED luminance decrease are interrelated through a chemical degradation process based on the instability of AlQ_3 cationic species. From that viewpoint, the accumulation of positive charges at the interface may be the result of AlQ_3^+ chemical degradation whose byproducts act as luminescence quenchers, charge traps that lead to the accumulation of space charge, and nonradiative recombination sites. Results from cyclic voltammetry on AlQ_3 that showed that AlQ_3 oxidation was irreversible[71] gives further evidence that this can indeed be the chemical degradation mechanism in devices with AlQ_3-based EML. However, observations that degradation in blue-emitting devices with TBADN-based EML may also be associated with a similar effect certainly indicates that the immobile positive charge accumulation model is addressing a more universal effect that may be common to a wider variety of OLED structures and compositions. Perhaps the only observation that is not consistent with either model is the observation that the increased device stability is, in some cases, associated with modifications that also lower device turn-on voltage, thus suggesting increased hole injection. As discussed before, the reason for increased stability in that case may lie in the reduction of hole injection into AlQ_3 as a result of reduced internal electric field at the HTL/EML interface.

That device stability can be increased by means of treating the ITO surface, introducing ITO contact buffer layers (CuPc, plasma-polymerized CHF_3, amorphous carbon), or doping the hole-transport layer can also argue for the indium migration model. In that case, the success of these techniques can be explained in terms of their role in stabilizing the ITO surface or in acting as indium scavengers. However, the number of experimental observations that do not support this model cannot be overlooked. For example, it is difficult to understand why changing the order of two hole-transport layers (NPB and TPD),[59] as described in the section on the unstable cationic AlQ_3 model should affect indium migration. The ability to change device stability by only modifying the electron-injecting contact, without altering the ITO contact or the hole-transport layer, is another phenomenon not supported by the indium migration effect.

This contradiction between the indium migration model and the unstable cationic AlQ_3 model 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[76] have been performed on very stable devices showing half-lives exceeding 2000 h at a high current density of 20 mA/cm^2. 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 AlQ_3 degradation has been sufficiently reduced. Perhaps, studying the time evolution of indium concentration as the experiment is progressing—by performing indium analysis measurements on devices that were aged for different times—may offer useful insights. In this case, the quantitative correlation between the detected amount of indium and the decrease in device EL efficiency should be observed. Studies to investigate changes in the ITO surface, as would be expected to accompany such diffusion phenomenon, similar to what had been observed in polymeric OLEDs before, might also be useful.[79,80]

The experimental evidence for the existence of both reversible and irreversible components of device degradation is strong. Redistribution of mobile ions,[88−90] reorientation of internal dipoles,[91,92] or redistribution of space charge due to various trapping effects 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 in different time scales. In the short-term (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. In a longer time frame (hundreds to thousands of hours), degradation due to accumulation of positive charges and the associated instability of AlQ_3 cationic species may dominate. In the very long term (several thousands of hours), indium migration induced degradation may be significant. The given time scales would correspond to typical accelerated OLED aging testing conditions at currents on the order of few times 10 mA/cm^2.

On the other hand, in view of a growing body of experimental results, the long suspected morphological instability question is becoming less widely seen as a dominant factor in device operational stability, especially for room temperature operation conditions. However, that may not be the case if the devices are operated at temperatures approaching the T_g of the organic materials used (usually above 60 °C).

V. Summary and Conclusions

In general, the decrease of OLED luminance in time proceeds through three independent and visually distinct degradation modes: (i) dark-spot degradation, (ii) catastrophic failure, and (iii) intrinsic degradation.

Dark-spot degradation occurs through the formation of nonemissive regions (dark spots) and reduces device luminance as a result of losses in the emissive area of a device. It is essentially caused by various environment-induced electrode degradation phenomena, which lead to the growth of defective regions in the electrodes, and thus interrupts conduction. Because of the surrondings-induced nature of the underlying phenomena, dark-spot degradation can be effectively suppressed by proper device encapsulation and therefore is no longer seen as an obstacle for OLED commercialization.

Catastrophic device failure, which appears as a sudden loss of OLED luminance (which can be partial or total), occurs as a result of the development of electrical shorts across the device. Short nucleation occurs at preexisting structural defects and therefore can be reduced by proper substrate cleaning and adequate control over device fabrication process. Catastrophic failure can also occur as a result of exposing the devices to temperatures approaching the T_g of the organic materials and is caused by thermally induced morphological changes and mechanical stresses. As a result, using materials with higher thermal stability (i.e. higher T_g) has been very successful in increasing the critical temperature at which catastrophic failure of the device occurs.

Intrinsic degradation appears as a decrease in the brightness of the emissive area of a device, without any obvious change in device appearance, caused by a decrease in the EL efficiency that mainly occurs during device operation. Although significant progress in understanding OLED intrinsic phenomena has been accomplished in the last 5 years, a complete, fully consistent picture of the degradation processes is still lacking. Most studies specifically addressing the intrinsic degradation problem concentrated on devices containing AlQ_3. As this material is generally used in devices emitting light from the green to the red part of the visible spectrum, the study of AlQ_3-related aging processes is highly relevant for practical devices. However, blue-emitting OLEDs and often OLEDs based on triplet emitters use different materials as emitter hosts. It is possible that the mechanisms involved in degradation of AlQ_3-based devices are quite universal. On the other hand, other materials, like blue emitters (stilbenes, anthracenes, triazines, etc.), may show fundamentally different degradation mechanisms. As the operational stability of OLEDs is, in general, not yet satisfactory for many important applications, intrinsic degradation continues to be an issue for OLED commercialization. The field of research on OLED stability and degradation, therefore, retains its significance and will play an important role in further developments of OLED technology.

Supporting Information Available: A table listing the HOMO energy levels of some of the materials in Table 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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