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Degradation Mechanisms in OLEDs

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Organic light emitting diodes (OLEDs) are widely used in modern display technologies due to their high image quality and flexibility. However, degradation processes limit their efficiency and reduce lifetime, particularly in blue-emitting pixels. This thesis examines the mechanisms causing degradation and the impact on device's lifetime.

Degradation mechanisms can be classified as external and internal. External factors, such as oxygen, water, temperature and impurities, can lead to early failure of a device due to effects like dark spot formation and growth. Abrupt failures can be mitigated by well-controlled fabrication and OLED encapsulation. Internal degradation originates from processes within the device, including phenomena such as diffusion, charge accumulation and exciton-induced reactions, resulting in luminance decay and lower efficiency.

OLED degradation is not based on a single mechanism, but rather on the interaction of multiple mechanisms. While external processes can be controlled, internal processes prove to be the main limiting factor on device lifetime. Stability and lifetime improvements require material research and effective OLED design to address the challenges of blue emission.

Keywords: OLED degradation, abrupt failure, dark spot growth, encapsulation

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Orgaanisia valoa emittoivia diodeja (OLED) käytetään laajasti moderneissa näyttöteknologioissa niiden tarjoaman korkean kuvanlaadun ja taipuvuuden vuoksi. Kuitenkin erilaiset kulumisprosessit rajoittavat niiden tehokkuutta ja elinikää erityisesti johtuen sinistä valoa emittoivan pikselin epävakaudesta. Tämä tutkielma tarkastelee kulumista aiheuttavia mekanismeja ja niiden vaikutusta laitteen elinikään.

Kulumismekanismit voidaan erotella ulkoisiin tai sisäisiin. Ulkoiset tekijät, kuten happi, vesi, lämpötila ja epäpuhtaudet, voivat johtaa laitteen ennenaikaiseen vikaantumiseen johtuen ilmiöistä, kuten tummien pisteiden muodostumisesta ja kasvusta. Äkillinen vikaantuminen voidaan estää hyvin kontrolloidun valmistuksen ja OLEDien kapseloinnin avulla. Sisäinen kuluminen ilmenee laitteen sisällä tapahtuvista prosesseista, kuten diffuusiosta, varausten kertymisestä sekä eksitonireaktioista, aiheuttaen luminanssin laskua ja alempaa tehokkuutta.

OLEDien kuluminen ei perustu yksittäiseen mekanismiin vaan monien mekanismien vuorovaikutukseen. Ulkoisten prosessien ollessa kontrolloitavissa sisäiset prosessit osoittautuvat elinikää rajoittavaksi tekijäksi. Vakauden ja eliniän parantaminen vaatii uutta materiaalitutkimusta sekä rakenteen tehokasta suunnittelua vastaamaan sinisen valon emittoinnin haasteisiin.

Avainsanat: OLEDien kuluminen, äkillinen vikaantuminen, tummien pisteiden kasvu, kapselointi

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1 Introduction

Organic light emitting diodes (OLEDs) are widely used in the display industry, particularly in televisions, smartphones and wearable electronics. Due to OLEDs' mechanical durability and self-emissive nature, they are a great choice for applications that require flexibility and high-quality images. OLEDs provide a wide range of colour temperatures in the range of 1500 to 20000 K[1], which can be used to generate visually natural images.

Display market of OLEDs has risen rapidly due to its wide applicability, and it challenges other existing technologies in many screen applications. Global OLED Display Market has reported that in 2020 global OLED Display market is valued at 42 490 million US$ and is expected to reach 185 830 million US$ by the end of 2026, showing a compound annual growth rate of 23.2%[1].

Despite the many advantages, the main issue in OLED devices is the susceptibility to degradation. Particularly device performance, energy efficiency and lifetime are limited by blue pixels due to its instability. High photon energy needed to achieve deep-blue emission raises photochemical instability, which can lead to rapid degradation of devices[2]. The aim of this thesis is to examine the different degradation mechanisms and their effect on device lifetime.

1.1 Device Lifetime Definition

Lifetime of OLEDs is evaluated based on the behaviour of luminance over time in a fixed physical environment (e.g., temperature, humidity and voltage). Internal degradation processes such as chemical reactions, morphological and other physical changes shows most notably in OLED's colour-luminance-current-voltage characteristics which manifest as a continuous loss of the device efficiency[3]. Applying higher current to the OLED device increases the brightness, and the increase in applied current lowers the device's lifetime. This means that OLEDs' lifetime is inversely proportional to its brightness[1].

Lifetime can be defined with different values depending on the luminance drop observed. Most often the lifetime is used where luminance drops to half of the initial device brightness when current density is constant, and it is denoted as $T_{1/2}$ (or T_{50})[3]. The well-known empirical scaling law (eq 1) defines a relationship with initial luminance L_0 and the device lifetime $T_{1/2}$ quantified with the constant C. The scaling law additionally has an acceleration factor n, which is material and device specified[1,3].

$$L^n{}_0 \cdot T_{1/2} = C \quad (1)$$

Additionally, different lifetime metrics can be preferred. For example, T_{70} and T_{97} refer to the lifetime in which luminance decay is 70 % and 97 % of the initial luminance, respectively[3]. The latter metric can be especially used in display manufacturing because it corresponds to our perception of brightness difference for adjacent display elements[3]. It is also worth noting that lifetime extrapolation can give under- or overestimation of the actual lifetime due to multiple independent degradation mechanisms influencing the OLED. To plot such behaviour, it is possible to use different functions with empirical fitting parameters[3].

1.2 Classification of Degradation Mechanisms

This subsection is primarily based on the review by Scholz et al. [3]. Degradation mechanisms can be mainly divided to extrinsic and intrinsic factors. There are five main visible effects of degradation: “dark spot” degradation, “catastrophic failure”, short term luminance decay, long term luminance decay and efficiency-enhancement effect.

Dark spot degradation shows as an accumulation of non-emissive point defects. Exact causes for catastrophic failure are hard to classify, but it is expected to be caused by external factors as dark spot growth. Phenomenon of very high current density bright spots create a local area of high brightness that can lead to both prior failures. Luminance decay and efficiency-enhancement effect (device efficiency rises and is followed by luminance decay) is caused by internal degradation mechanisms[1,3].

Additionally, changes in current-voltage characteristics due to device aging can occur with shifts in emission colour. The shift can appear either homogeneously over the

emissive area or as a gradient across the area. This is considered to fall under the category of intrinsic degradation mechanisms, which consist of charge accumulation, charge carrier reactions, exciton reactions, migration of ionic species and effects on electric field profile caused by molecular reorientation[3]. External causes for OLED degradation are commonly mentioned to be oxygen[1,3,4], water[1,3,4], temperature[1–3,5] and light[1,3].

1.3 OLED Structure and Working Principle

OLEDs consist of two electrodes and a thin film organic semiconductors placed between them. State-of-the-art devices that are small molecule based have many different layers that each have a certain functionality. In typical multilayer OLED there are: hole injection layer (HIL), electron injection layer (EIL), hole transport layer (HTL), electron transport layer (ETL), hole blocking layer (HBL), electron blocking layer (EBL) and emission layer (EML)[6,7]. Layers and materials used in OLED device can vary. The cathode or anode is transparent depending on the device being top or bottom emitting OLED, respectively[6,7]. Figure 1 presents the typical small molecule OLED structure.

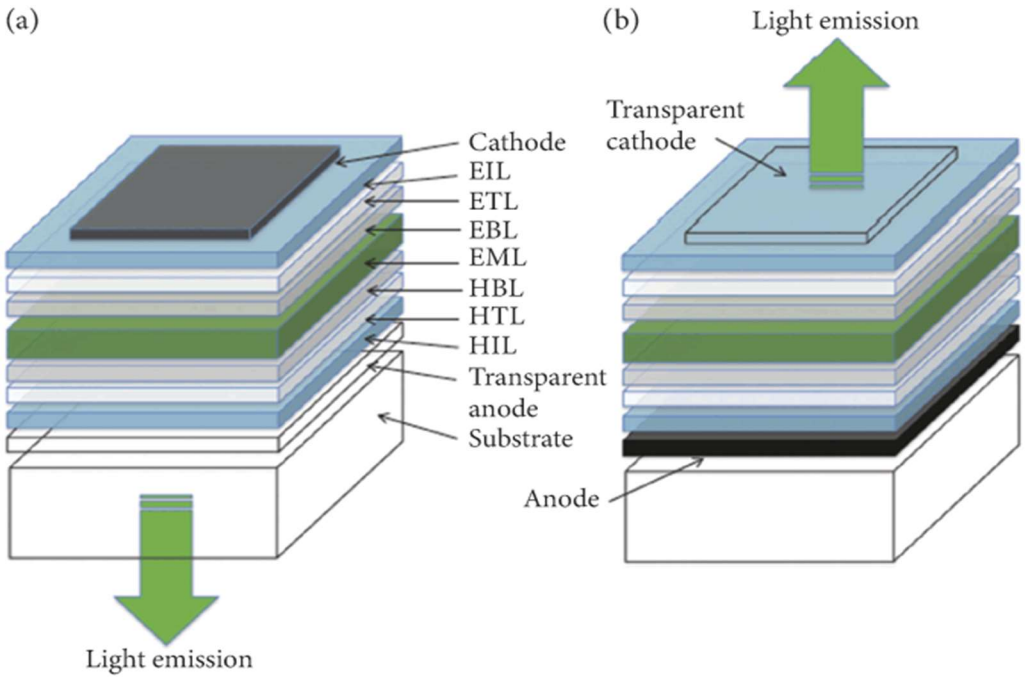

Figure 1. Typical small molecule OLED structure for a) bottom emitting and b) top emitting OLED. Reproduced from Forrest [7]. Copyright 2025 Stephen R. Forrest

These layers are separated to reach higher device efficiency. In the emission layer located in the centre of the OLED, the positive and the negative charges meet and form excited molecular states, which are referred to as excitons[6]. For electrons and holes, the process of reaching EML is similar, so we can use holes as an example. First, holes are injected from a high work function metal such as indium tin oxide (ITO) to the HTL. One can also use a low resistance and high hole conductive HIL to improve the injection[6,7]. Before reaching the EML, holes have to pass EBL, which is used to prevent leakage of opposite charge carrier type from the EML[6,7].

OLED's efficiency depends on the type of emission. To maximize the efficiency, it requires the use of triplet-dominated exciton state emission that uses either heavy-metal phosphorescent dopants or thermally activated delayed fluorescence (TADF)[7]. High efficiency also requires high transfer rate of electron and holes to the EML[7]. Fluorescent emitters such as the green fluorophore Alq_3 emits light using singlet state excitons that provide only 25 % efficiency[6,7]. For phosphorescent emitters singlet state excitons are transferred to the triplet energy state[1], allowing theoretical maximum efficiency of 100 %[6]. TADF emitters also utilize both states by converting triplet excitons to singlet excitons [1,7].

1.4 Analytical Techniques for Examination

Analytical techniques are needed to analyze the degradation of OLEDs and to research factors leading to device failure. One way to categorize the techniques is to divide them based on the optical, chemical, electrical and mechanical response[3]. Additionally, the analysis methods can be divided by the part being analyzed: interfaces, the bulk and the surface[3]. For understanding the causes for deterioration, one needs to consider physical and chemical properties that include accumulation of charge, diffusion and morphological changes[8].

The *I-V* characteristics of OLEDs are used to obtain information about transport, injection and recombination processes[3]. Using various layer thicknesses, it is possible to distinguish layer specific contributions when analyzing shifts in current and voltage

due to device aging[3]. Analytical methods for obtaining information about trapping, transport and injection behavior are charge modulation spectroscopy, Stark effect, impedance spectroscopy, voltammetric measuring and thermally accelerated current spectroscopy[3,8].

Optical methods such as Raman and infrared spectroscopy can detect specific changes in the molecular structure[3]. Additionally, in a similar way a method called ellipsometry can be used to determine optical characteristics of organic layers. These methods can determine layer thicknesses and doping concentrations of a given stack[3]. However, the complexity of modeling is what makes these methods not widely adapted for complete devices[3].

Surface analysis aims to provide information about degradation regarding for example crystallization, morphology and material's roughness[8]. One method to investigate these characteristics is to use atomic force microscopy (AFM)[3,8]. For detailed analysis of the surface looking for chemical changes, techniques like X-ray (XPS) or ultraviolet (UPS) photoelectron spectroscopy can be used[3]. Dark spots and cathode delamination are investigated using these techniques in spatially resolved manner with scanning photoelectron microscopy (SPEM)[3,8].

Depth profiling has been proven to be useful when inspecting OLED degradation. Using dynamic XPS depth profiling, single elements can individually be detected. The detection happens due to the chemical shift of corresponding element's binding energy[3]. This allows for examination of chemical changes such as bonding and also the identification of diffusion and migration mechanisms[3]. Similarly to using dynamic XPS, the secondary ion mass spectrometry (SIMS) can be used. It is not as effective as a quantitative technique, but it can also be used as a tool to analyze surfaces[3]. Techniques such as Fourier transform infrared spectroscopy (FTIR) and Auger electron spectroscopy (AES) are also used in depth profiling analysis[8].

Chemical composition of OLEDs can be difficult to investigate, but it is essential for acquiring information about internal degradation mechanisms[8]. In the past matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) has been used especially in bio- and macrochemistry[3,8]. High performance liquid

chromatography (HPLC) is also commonly used, and is coupled with various detectors such as UV absorption[3]. This method's limited sensitivity provides a challenge for OLED analysis. Other methods for chemical analysis include gel permeation chromatography (GPC), differential electrochemical mass spectrometry (DEMS), nuclear magnetic resonance (NMR) and electron paramagnetic resonance (EPR)[3,8]. These methods are often used for a specific type of investigation such as measuring the amount of unpaired electrons[3].

2 Abrupt failure of OLEDs and their appearance

This chapter assesses failure modes of OLED devices that appear suddenly and are caused mainly by extrinsic factors. Other visible degradation effects such as short term and long term luminance decay will be discussed in chapter 4 as an manifestation of internal degradation.

2.1 Catastrophic Failure

Catastrophic failure can be considered as the most undesirable failure mode. In most cases, it is caused by formation of short circuits. The electrical short circuits are caused by imperfections in the substrate surface, e.g., rough surfaces, particles and local heating effects[3]. Heating effects can cause cathode material delamination, layer stack system destruction by interdiffusion and contact formation between electrodes. These changes in OLED morphology may disable the device entirely[3].

Material decomposition may directly cause formation of bubbles or domelike structures due to gas evolution. Observations on electrode materials delamination are typically done in combination with dark spot degradation[3]. Additionally, OLED's voltage and luminance measurements have shown fluctuations before device failure, and these can be considered a result of bubble formation and corresponding dark spot growth[3]. The fluctuations will result in further breakdown of the device.

The defect-driven nature of the catastrophic failure described by Scholz et al.[3] is also supported by early polymer light-emitting diodes research done by Kasim et al. [9]. The research shows that metal atoms diffuse to the polymer, which reduces the luminance and current as well as causes layer destruction and short circuits. The results also suggested that electrical breakdown of polymer films precedes the chemical degradation[9]. Because processing conditions of OLED's have been improved, catastrophic failure can often be prevented, which is also why there is little work on the details of this failure type[3].

2.2 Dark Spot Degradation

Dark spots can be defined as a small non-emissive regions in an OLED device[3,4,8,10]. Due to electrical stress, dark spots may form in the boundaries between the organic and conducting layers[3,8,10]. The growth of the dark spots can happen during storage of the device and the region formation may already happen in device production[3,10]. Device operation still accelerates the growth[10]. Main cause for the growth has been demonstrated to be delamination of the cathode material by concluding that luminescent material shows the same photoluminescence measurements after replacing the cathode[3,10].

Main method for preventing dark spot formation is by encapsulating the device[3,8]. Device exposure to water and oxygen in the atmosphere is the limiting factor that leads to device failure[4], which is why encapsulation is used to prevent the exposure. OLED's can be improved in terms of having higher efficiency, brightness and lifetime by reducing the amount of dark spots[8]. Cathode delamination can also be countered with a technique proposed by Liew et al. using Scotch tape to remove the cathode and installing a new one in vacuum conditions[10].

Higher current densities and brightness have been reported to appear on the edges of cathode defects. This results in increased temperature which can lead to faster degradation and further delaminate the cathode[3]. Additionally, this can lead to cathode material degradation, which can result in catastrophic failure via short circuit. The reasons for delamination and dark spot growth are identified as pinhole defects in the capping material allowing water and oxygen penetration as well as moisture on the substrate surface[3].

Lim et al. researched the correlation between dark spot growth and pinhole size in OLEDs[11]. They used silica micron particles to create pinholes with controllable size on multilayer OLED device. The conclusion was that the dark spot growth rate had a linear relation to the silica particle diameter. Additionally, they observed that the dark spot growth rate was linear for all dark spots regardless of whether they were formed by silica particles. This result shows that larger dark spots demonstrate faster growth[11].

3 External degradation processes

In this thesis degradation processes are divided into two categories depending on if the effect is caused from external factors or happening inside the device. External degradation processes include effects caused by water and oxygen, impurities, temperature, voltage increase and driving scheme and crystallization or phase transition[3]. Even though light is an external factor it will be covered in the internal degradation processes, because light causes chemical reactions inside the device.

3.1 Oxygen and water

Oxygen and water are well-known external degradation factors. According to Scholz et al. both contaminants can initiate various processes in OLED devices: reactions with electropositive metal cathode (oxidation), chelate molecule hydrolysis followed by reactions of hydrolytic products, changes in morphology, organic material oxidation including electro- and photochemical reactions, and charge-transfer doping, which can result in forming filled traps and free charge carriers[3].

As mentioned in chapter 2.2, the effect of oxygen and water can be considered main factors leading to premature device failure[4]. Pinholes in the device's metal layer enhance the penetration of oxygen and moisture, which causes dark spot formation within the device[1,11]. Minimizing defects on the device's structure is essential, because oxygen and water vapour enter typically through these defects at the cathode's edges[3]. Encapsulation of devices is crucial to counter the oxidation initiated by oxygen and water and improve OLED's performance[1].

Moisture can affect the electroluminescence intensity of the device. It has been studied that the ETL and HTL are affected by moisture causing instability and formation of dark spots[1]. Yamamoto et al. used water vapour to investigate water's effects on different interfaces of a multilayer OLED. The results concluded that the interface between HTL and the EML is the most susceptible region for degradation in $Ir(ppy)_3$ PHOLED devices when exposed to moisture during fabrication. By fabricating the device in ultra-high

vacuum conditions, LT_{90} and LT_{70} were increased 56% and 32%, respectively compared to the best high vacuum fabricated device[12].

Schaer et al. proposed that water vapour leads OLEDs to have faster dark spot growth by three orders of magnitude compared to dark spot growth in pure oxygen atmosphere. In oxygen atmosphere they noticed that grey rings were formed around the dark spots on emitting surface, and it was investigated to be partial oxidation of the organic light emitting layer[13]. Additionally, they noticed that the hydrogen evolution in the cathode/organic interface creates bubbles under the cathode that lifts it from the interface. The hydrogen evolution happens due to the electrochemical reduction of water[13]. The formed bubbles eventually will burst causing additional entry ports for water to enter. Because of the delamination of the cathode and inability to inject current, dark spots appear on the light-emitting surface[13].

Scholz et al. discussed this phenomenon in the review and dictated that significant pressure buildup cannot be expected due to hydrogen being much more diffusive than water molecules[3]. They suggested that the bubble/domelike feature has a different origin. Additionally, Scholz et al. mentions that the research done by Schaer et al. is obtained with atypical devices as they reported dark spot growth stopping after current is switched off. They came to this conclusion because it is well-known that dark spot growth does not stop when device is not driven as water vapor and oxygen still penetrates the device[3].

Oxygen has additional effects on the device performance. By “doping” device with oxygen it results in higher conductivity[3]. In some cases, the process is reversible, for example by purging the OLED with nitrogen. Quenching process of the device and increased conductivity could be a result of the formation of a charge transfer state between the organic compound and the oxygen[3]. This can also cause changes in OLEDs that have been exposed to ambient conditions. The change in the *I-V* curve may not be as dramatic as by doping, but it has a vast effect on the luminescence output of the device. Compared to devices stored under nitrogen, the light output was quenched by 2 orders of magnitude for devices under ambient conditions[3].

3.2 Impurities

Fujimoto et al. has researched that OLED lifetime decreases with increased fabrication time that refers to the time of depositions of the organic and metal[14]. This suggests that vacuum chamber cleanliness influences the device lifetime. They did measurements that investigated the chamber cleanliness and correlation to device lifetime by doing angle measurements on the chamber each time device was fabricated. The results show that lifetime decreases linearly with the contact angle increase and this indicates that the impurities in the chamber is a dominant factor on the OLED lifetime[14]. The suggested method to reducing the impurities in the chamber was to use ozone gas cleaning to reduce the contact angle. The contact angle of a water drop was measured because most organic materials are hydrophobic and thus increasing the contact angle when ITO substrate surface is contaminated[14].

OLED devices' lifetime and efficiency are greatly influenced by the surface roughness and the presence of impurities[1,3]. It has been reported that high material purity enhances the carrier injection and luminous efficacy by reducing the formation of internal electric field and ionic diffusion. Halogenated impurities in OLEDs can trigger formation of radicals which can cause damage to ETL, EIL and EML layers by reactions such as reduction[1]. Additionally, cathode pinhole formation is influenced by the presence of dust particles, which can lead to water and oxygen infiltration in the device[1] as mentioned earlier.

Origin of impurities can be also located on the substrate[3]. It has been observed that during annealing of glass|ITO-substrate at 200 °C, the desorption of moisture and impurities is strong. Impurities have been widely assumed to act as nonradiative recombination centres or to act as dissociation processes of metal organic emitters catalysing agents[3]. The importance of using highly pure materials has been proved based on a HPLC-analysis by showing that the lifetime of a device triples as the dopant (emitter) purity is changed from 99.8 % to 100%[3].

3.3 Temperature

Temperature is one of the major external factors affecting OLED's lifetime. Temperature increase will shorten device's lifetime and also affect the IVL characteristics of the device. High temperatures accelerates the device degradation and device failure is imminent when a critical temperature is reached[3]. Organic electronics should be able to withstand a wide range of temperatures and environmental conditions, e.g., solar cells on a roof and a device in a parked car in the sun (temperatures above 50 °C). Therefore, organic devices demonstration of stability in temperature should be at least in the range of 70-90 °C [3]. Higher temperature can be expected to increase activation energies of chemical processes so that reaction rate doubles for every 10 K increase in temperature, according to an empirical rule[3]. Interestingly, Ishii et al. found that multiple degradation mechanisms' relative contribution to decay depends very little on temperature[5].

The reasons why temperature rise occurs in a device can be caused by internal Joule heating or by an external heat source. Local temperature increase can cause defects in the structure leading to phenomena such as dark spot formation and bubbles, or in the worst-case device failure[3,8]. Joule heating can be defined as heat production when electronic devices are used due to the circuit's resistance[8] and it scales linearly with the applied electrical power[3]. It is also researched that the electrical power input scales linearly with measured OLED temperature, which shows the effect of Joule heating. However, the slope of the relation changes in different devices, caused by the geometry, environment and the device size. The research that implies the linear relation is done with unusually high power densities. Typical power that OLEDs are run under show minor increase in internal temperature relative to ambient[3].

For large area devices Joule heating is particularly problematic as the device edges contribute less to cooling, which can lead to faster degradation[3]. Usage of doped transport layers are effective in reducing Joule heating, because it lowers the voltage and the overall resistance of the device[3]. Voltage drops in ITO:metal electric bus lines and TFT circuits besides Joule heating, can cause significant temperature increase in

devices such as screens[3,8]. Using external heating techniques in research can be advantageous, so one can control the reaction rate of observed degradation[3].

3.3.1 High temperature effects on morphology

In high temperatures Joule heat can damage the device by thermal expansion, diffusion of materials and by melting or crystallization of organic materials[1]. This damage can be negligible at lower or moderate driving currents because the Joule heat produced is not high enough[3,8]. The critical temperature of the device is linked linearly to the glass temperature (T_G) of the HTL, which suggests that the phase transition of HTL is the failure mechanism at critical temperature[3].

The device durability can be increased by using materials that have high T_G if the driving conditions used are very high. It would apparent that the critical temperature correlates with the lowest T_G of material used in a device[3]. However, this theory isn't supported by all research. Devices that use low T_G materials can reach high temperatures without breaking down[3].

3.4 Effects of driving scheme

There have been different studies about influence of driving schemes (alternating/pulsed current (AC) or direct current (DC)) on OLEDs during the last two decades[3]. Even though detailed studies exist about the reversibility of aging process, there is a lack of systematic studies considering variety of devices. This results in contradicting statements about the use of different driving schemes. For small molecule OLEDs it is known that AC driving scheme has a positive influence, but polymer OLEDs do not exhibit lifetime improvement when using AC instead of DC[3]. Lifetime improvement due to using AC mode is the effect of reversibility of device degradation. It is either induced by reverse bias or spontaneous[3].

Small molecule OLEDs show accumulation of charges at internal organic/organic interfaces and that believed to be a major contributor to the degradation[3]. The usage of AC scheme may release the accumulated charges by the reverse-bias component. Electric-field induced migration of ions could also participate in the degradation[3]. It has been found that OLEDs at the same luminance show the longest lifetime when driven with AC. Second longest lifetime is acquired by using pulsed mode, and the worst lifetime with DC scheme. OLED's reversibility has also been studied which show a "healing process", where voltage increase appears to be completely reversible after reverse bias is used on an aged device. The study varied the forward/backward rate of the current and assumed electric field-dependent mobile ion migration model[3].

However, it was monitored that the luminance exhibited only a small improvement in the "reversible direction" right after switching, so that the healing effect is not visible. This suggests that the investigated devices have been susceptible to more mechanisms in the degradation. The ion mobility model itself cannot explain the incomplete performance recovery, particularly the luminance behaviour[3]. For multilayer p-i-n structured OLEDs little has been reported for AC and DC scheme comparison on lifetime, and the behaviour is hard to link to known mechanisms such as chemical reactions or charge accumulation[3].

Cusumano et al. studied the effect of driving method on the degradation of OLEDs in 2003. They tested the lifetime by measuring decrease in luminance and the increase in voltage[15]. Using the DC scheme, they noticed a substantial luminance decay during the first hour and after that 50% of the initial luminance rate was reached at 20 h. In the case of pulsed operation, the decay at the beginning was absent and the luminance decay to 50% was slower taking 70 h[15]. The initial fast decay of luminance could be caused by Joule heating in combination with migration of mobile ionic impurities and orientation of permanent dipoles[15]. This older study supports the claims that AC has a positive influence on OLED lifetime.

3.5 Voltage increase

To addition with luminance drop at constant current, OLED degradation behaviour exhibits voltage increase caused by electrical resistance[3,8]. It is attributed to an increased injection barrier in some interfaces or a decrease in conductivity of transport layers. The reason for this is for example the accumulation of traps and multiple transport layers and interfaces can contribute to this effect[3,8]. By improving the device's charge injection and using doped transport layers, the driving voltage can be decreased[3].

It has been suggested that cause for voltage increase on an aging device can occur due to oxidation of cathode/organic interface[8]. A way to stop this increase from happening is to use a sacrificial anode made from calcium acting as a protective layer[3]. The use of this protective layer has proven to be less effective in slowing down dark spot growth, which has led to a discussion about the use of bilayer cathode. It is possible that using a cathode that is better fit to suppress dark spot growth can also lead to a smaller voltage increase and therefore a longer lifetime of the device[3]. Due to lifetime benefits not being measured from the bilayer cathode, it is difficult to land on a simple answer about which cathode should use for overall best lifetime.

4 Internal Degradation Processes

Internal degradation mechanisms are more difficult to evaluate when compared to external mechanisms because one cannot modify internal parameters. Changing the conditions where the device is driven in makes it simple to observe changes that the device faces from external causes. Observation of internal degradation mechanisms is done by applying different analytical techniques in order to pinpoint the internal change that has caused degradation such as luminance loss[3]. In this thesis, these internal degradation mechanisms are divided into diffusion and drift, charge accumulation, nonradiative recombination centres, recombination zone position and charge balance, dipole reorientation, photochemical reactions and electrochemical reactions.

4.1 Diffusion and drift

Stability and efficiency of OLEDs are dependent on transport processes which means that diffusion and drift of polarons needs to be optimized[2]. Electrically neutral molecules, atoms and gases can diffuse through the device and act as nonradiative recombination layers as well as exciton quenchers[3]. Different electrical fields acting in the device can also cause ions to drift. Additionally, it has been shown that metal diffusion into the organic is enhanced by heating[3].

Lee et al. studied metal diffusion from electrodes to organic layers in OLEDs while devices were operated[16]. They reported that the use of an ITO anode showed Indium diffusion into the organics which caused voltage increase as well as reduced luminescence. However, when MgAg cathode was used, the Mg diffusion had no substantial effects on device's performance as the diffusion depth was low[16]. As Scholz et al. also pointed out, the concentration rise of metals were noticeable in aged devices compared to unaged[3]. The degradation especially occurs from luminescence quench caused by Indium[16].

OLED processing includes an evaporation sequence that affects metal penetration and the diffusion into the devices layers[3]. This was proven to be true for devices that are bottom and top emitting. In thin LiF films metal evaporation causes Al to react with the film causing Lithium release and diffusion into the organic[3]. Because Li atoms can be assumed to instantly oxidize when reacting with electron transport material, the migration must occur with Li cations. The migration of these cations are most likely a diffusion process that is driven by concentration gradient[3]. The drift of ions likely also play some role to this as internal electric field favors positive ions to migrate to anode[3].

4.2 Charges and recombination

4.2.1 Charge accumulation and nonradiative recombination centers

OLEDs may experience excessive charge accumulation under operation at different interfaces which includes the formation of deep traps (fixed charges)[2,3,8]. The trap formation will result in nonradiative recombination centers and luminescence quenching that reduces luminance efficiency[1–3,8]. Migrating ions or chemical reaction products may be the cause for charge accumulation[3]. Voltammetric measurements have shown that the main cause for accumulation is the deep traps and the layer it occurs in is the charge recombination interface[3].

There are suggested methods for reducing the accumulation and consequently nonradiative recombination centres. Broad and centred recombination zone maximizes OLED's performance considering lifetime and efficiency[1]. Additionally, mixing charge transport layer materials to the emission zone can reduce the accumulation effects from the recombination zone widening[3,8]. Size increase of the zone will also reduce the charge density[8], which makes it less probable for chemical degradation pathways to be accessed[2]. Different approaches for reduction of the accumulation include using innovative materials to improve stability and enhancing the interface quality[8].

4.2.2 Charge balance and recombination zone position

The balance of charge carriers is determined largely by the injection efficiencies in to the layers[17]. Intuitively thinking, to get the best efficiency possible, there would have to be the same amount of electron and holes injected. That way formation of excitons would be optimized, and energy wouldn't go to waste. For example. the use of the HATCN/TAPC generation layer exhibits lower efficiencies compared to PEDOT:PSS, as it is a better hole injector and therefore exhibits charge imbalance[17]. However, it is worth noting that devices which have fully optimized charge balance might not even be emissive or ideal at all. This can be done for example by using effective luminescence quencher in the emissive layer[3].

This presented intuitive view might not be taken as the full truth even though the example showed lower efficiencies. If one device has largely exceeding amount of one type charge carrier compared to the other, there is still no fundamental reason for it being less advantageous over a device that has very similar charge densities[3]. It is even possible that modifications done on the device negatively affects the charge balance but at the same time results in the improvement of device's performance[3].

As excitons have a role in OLED's degradation, it is important to consider the effects of excitons in recombination zones and the use of mixed emission layers. Controlling the charge injection does not counter the issues of high exciton densities in the thin recombination zone[3]. Chwang et al. studied the performance of OLEDs that use graded mixed-layer emission layer, where HTL and ETL do not have a discrete boundary[18]. The use of mixed-layers instead of heterojunction (HL) emission layer exhibits a longer lifetime[18] and it is explained by factors such as: minimized accumulation at the interface, minimized exciton density and broadened emission zone[3]. For mixed-layers, the use of uniform mixing compromises efficiency for improved lifetime. As for graded mixed-layer, the efficiency is better than in uniform and optimized lifetime over HJ OLED, which makes it a great recombination zone technique[18].

4.3 Dipole reorientation

Dipoles can be reoriented by an external electric field with the magnitude around of 1 MV/cm[19], which interestingly is also comparable to electric fields produced by OLED under normal operation[3]. Caused by molecule reorientation the electric field profile of entire device can be altered[3]. Impact of this can be seen in outcoupling efficiency, recombination and quenching of excited states by charge carriers[8]. Because of the impact on those properties, OLED faces luminance decay, which is why dipole reorientation can be considered a degradation mechanism.

Additionally, the process can be reversible if the dipoles are oriented to the initial state. The experiment done by Zou et al. showed that luminance can be recovered after dipole reorientation[19], which indicates that reorientation is to be considered as a cause for degradation. However, studies now have not shown clear indications of molecular reorientation after measuring internal electric fields and such properties[3]. This suggests that considering OLED degradation, effect of dipole reorientation is not significant or only weakly contribute to device decay.

4.4 Electrochemical reactions

With addition to physical phenomena in OLEDs, there are multiple chemical reactions inside OLED devices. Electrochemical reactions are caused by charges. These reactions can appear in different regions of the device such as the organic, the cathode and the anode[3]. Corrosion and microstructural abnormalities are caused by electrochemical reaction between the electrodes[1,8]. For long lasting devices it is important to develop EMLs with electrochemical stability. It has also been suggested that the use of more electrochemically stable metals (for example Ag as a cathode) improves the lifetime[1,8]. The reactions especially with the cathode are caused by external factors such as water and oxygen[3].

ITO anodes also react with water, which produces hydroxide ions[8]. This impacts the performance, but can be countered using a thicker anode layer and that way increasing the electrochemical stability[8]. For the organic, main issue is the Alq_3 cations' instability[3,8]. The bubble formation mentioned in chapter 2.1 originates from electrochemical corrosion in the interface between cathode and the organic and causes dark spot growth[1,3,8]. Lithium salt additive is suggested to significantly increase the stability in the form of reducing the formation of radical species[8].

4.5 Photochemical reactions

As polymers and organic materials are susceptible to various photochemical reactions, those reactions are considered one of the main degradation types[1]. These reactions can be indicated by oxygen release of ITO anode, where excitons have migrated to after absorption in the polymer layer[1,3,8]. This mechanism was proposed after it was found that the polymer does not show degradation in different absorption wavelengths and assumed that these reactions happen in ITO-organic interface[3]. In addition to influence of light in this interface, reactions can occur inside the organic intra- or intermolecularly and with reaction partners such as neighboring molecules[3].

UV-irradiation is also causing photochemical degradation[1,3]. Exposure to UV can lead to phenomena such as chemical bond breakage, dark spots and decreased light intensity[8]. It also causes the formation of singlet excitons within the device and this accelerates device degradation[1]. Additionally, morphology changes are associated with exposure to UV-light[1]. Frequent UV exposure should be avoided to increase device lifetime. White OLED devices have also shown efficiency decrease caused by the damage to emitting layer by UV light[8]. UV filter materials can be used to lower the effects of UV-induced degradation[8].

Exciton induced degradation is also significant contributor to device lifetime. Exciton diffusion from HTL to EML has a crucial role regarding device lifetime[1]. Various light-induced reactions with other molecules can also occur[3]. Photochemical reactions in

OLEDs are a broad concept because it covers light induced reactions as well as excited state chemical mechanisms[3]. This thesis does not include inspection of material specific reactions within the OLED.

5 Conclusions

Degradation in OLEDs results on multiple mechanisms acting simultaneously rather than single mechanisms controlling the lifetime. External mechanisms such as the effect of water, oxygen and impurities are the main cause of early device failure but can be controlled by encapsulation and clean fabrication. When OLED device is protected from the environmental conditions, the degradation is based more on internal mechanisms such as exciton induced reactions, charge accumulation and diffusion.

When external degradation pathways are minimised, the inefficiencies and luminance decay are strongly dependent on emitter material stability and the layer structure of the device. The main limitation of lifetime is the instability of the deep-blue emission requiring high photon energy. Temperature and driving scheme also have a notable effect on lifetime as it accelerates chemical reactions and causes charge accumulation, respectively.

Future improvements in OLED stability rely on material research and even deeper investigation of internal degradation processes using various analytical techniques. Particularly finding a way to control exciton reactions to stabilize the blue pixel remains a current challenge. As lifetime is lowered with higher brightness, OLED manufacturing needs to make a compromise between better visuals and a longer lifetime. Even though the mechanisms are often inspected individually, the combined effect and interaction is the one setting the limitations and qualities of an OLED device.

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