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Degradation of organic light emitting diode: Heat related issues and solutions

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ABSTRACT

Degradation of organic light emitting diodes (OLEDs) is the most serious obstacle towards their commercialization. OLED degrades due to various internal and external mechanisms. External degradation is mainly caused due to the instability of low work function cathode, pin-hole formation during fabrication which provides a path for oxygen and moisture infiltration. Operation of OLED also leads to degradation with major causes being morphological instability of organic layers, trap formation, indium or oxygen diffusion from anode, interface deterioration etc. Heat generation in the OLED also acts as a source of degradation. Most of the heat is generated instantaneously upon biasing of OLED due to resistive or Joule heating as a consequence of high resistance of organic layers and non-radiative recombination. Generated heat can be reduced by reducing the effects of the generation sources such as improving conductivity of organic layers by doping, using additional layers to improve charge injection, employing emissive layers with low recombination losses etc. However, these ways can only reduce the heat up to a certain amount. To further improve the lifetime of OLED, the generated heat can be dissipated by employing heat sinks using either thermally conducting substrate or encapsulation etc. We present a review on OLED degradation with a particular focus on heat generation, its consequences and ways of reduction.

1. Introduction

Organic light emitting diodes (OLEDs) are currently commercialized as information displays for smartphones and large-screen TVs and promise large market opportunities for flat panel, flexible displays and solid-state lighting sources [1–5]. OLEDs have striking features as high color purity, ease of fabrication, low power consumption, color purity and low cost [6–11]. Organic semiconductors (OSCs), building blocks of OLEDs, are cheap and abundant [12–16]. Current state-of-the-art OLEDs are performing at over 100 lm/W efficiency at lab scale and 30 lm/W at industrial applications due to significant improvement from the first observation of electroluminescence in OSCs [17–24]. The main challenge ahead is the lifetime of OLEDs due to several internal and external degradation sources. Light emitting diodes based on both inorganic and organic semiconducting materials suffer from internal energy losses and these losses convert into heat [25,26]. The generated heat can then act itself as a source of degradation and decrease the lifetime of device [27–30]. Therefore, reduction of heat and dissipation is required in order to increase lifetime of OLEDs. To date this issue has been more widely discussed in inorganic LEDs in comparison to their organic counterparts [31–34].

Degradation of OLEDs is a widely reviewed topic and several mechanisms responsible are described. A typical OLED is a multilayer device with a stack of organic layers sandwiched between two electrodes. Most efficient structure use separate organic layer for injection and transport for electrons and holes. An emission layer with a host-guest system having a phosphorescent guest and compatible host is used and to block un-recombined charge carrier, typically, electron and hole blocking layer is employed. Charge carriers are injected into the transport layers upon application of a forward bias by electrodes with the aid of injection layers. Transport layers are generally opted for high mobilities for respective carriers and then the operation of emission layer is efficient exciton formation and decay. Un-recombined carriers are then stopped by blocking layers. Blocking

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layers are sometimes also selected to stop the exciton from diffusing into the transport layer. Generated photon upon exciton decay then out-couples from the device. Degradation of OLEDs is caused by several different mechanisms both due to internal and external sources.

2. Degradation in OLEDs

2.1. External degradation

In the early days of research, the future of OLEDs was doubtful due to instability of OSCs under ambient conditions. Other than the instability of OSCs, the other issue has been the requirement of low work function electrodes as cathode which requires control on the deposition environment as an exposure of oxygen and moisture could cause degradation [35]. Exposure of device to ambient conditions would cause the cathode degradation and generation of non-emissive areas-often termed as dark-spots in the OLED community.

Fig. 1a presents the optical photographs of operating OLEDs showing such dark-spots. A number of studies [35–40] were thus performed for finding the origins of dark-spot growth during the initial days of OLED research. Dark-spot are originated from pre-existing particle defects on the substrate and subsequent deposition of cathode leading to pin-hole formation in the metal thin film and provide an opportunity to moisture and oxygen to diffuse through it causing localized delamination of cathode and formation of dark-spot. Study of degrading OLED by Schaer et al. [29] showed that these dark-spots form like a bubble (Fig. 1b). An electrical bias applied to device accelerates the growth in the size of dark-spots and stopping the current stops the process. It was also reported that gases evolve by the electrochemical processes at cathode/organic interface which cause the formation of these bubbles [41–43]. Indeed, the formation of dark-spot is related to delamination of cathode and not related to underlying organic layer. Therefore, redeposition of the cathode after peeling of the degraded one restores the performance. It is observed that formation of new dark-spots during operation is less probable than the widening of the dark-spot already present. As an example,

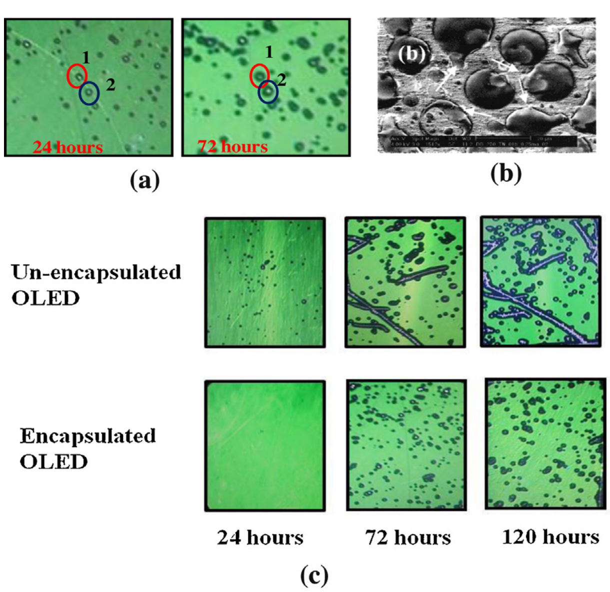

Fig. 1. (a) Optical image of operating OLED (under a current density of 10 mA/cm^2) showing the dark-spots and their broadening upon degradation. (b) SEM image of the bubbles formed in cathode at dark-spot areas. [printed with permission, Adv. Funct. Mater. 2001, 11, 116] (c) Optical images of un-encapsulated and encapsulated OLED at different times.

dark-spots '1' and '2' broadened in size upon degradation of OLED. It is also observed that the absolute number of dark-spots does not change during the operation [29].

When the device is fabricated, presence of oxygen and moisture inside the vacuum system degrades the organic layers [44–46]. Additionally, presence of small particles inside the device may also cause the degradation of device, if they puncture through the organic layers and come in contact with aluminum [47]. Further, the widely used electron injection layer (LiF) has a hydrophilic nature, as a result, absorbs moisture and degrade the device [48]. Appearance of dark-spots is dependent on the device growth conditions; however, broadening of dark-spots can be controlled by a proper encapsulation. Fig. 1c presents the optical images of an un-encapsulated and encapsulated OLED under operation at different time. A proper encapsulation slows down the appeared dark-spots during the operation and thus is effective in slowing down the degradation. Proper encapsulation of OLED prevents the corrosion of low work function cathode which was the initial concern of researchers. However, OLEDs have several other sources of degradation and such degradation is often referred as operational degradation.

2.2. Operational degradation

Operational degradation refers to the losses of luminance efficiency with time due to application of field. Here, we aim to briefly describe the possible operational degradation mechanisms and detailed knowledge of operational degradation can be found in previously published review [35]. The main causes of operational degradation are (i) thermal stability of organic layers, (ii) traps and luminescence quencher formation, (iii), anode instability and (iv) interface degradation [35]. Here, we will discuss briefly about these sources and their effects on the device performance. Thermal stability is determined by the glass transition temperature (T_g) of organic layers. *N*,*N*′-Bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine (TPD) was used as the hole transport layer (HTL) in early OLEDs, and it has a low T_g (≈60 °C) [49]. Similarly, 4, 7-diphenyl-1, 10-phenanthroline (BPhen); often used as electron transport material (ETM), has a low T_g value of 65 °C. Device temperature often increases over T_g value of such compounds during operation, which leads to its crystallization and degrades the device [50]. Therefore, to avoid the crystallization of organic layers, molecules with high T_g values are required. This transpired the synthesis of novel transport materials and at later stages hole transport materials (HTMs) and ETMs with high T_g found successful. Such degradation only occurs for a device under operation.

Second, bulk trap states are formed during the operation of device in the form of non-luminescent centers inside the emissive layer. These trap states decrease the conductivity of organic layers which also lead to an increase in operating voltage [51]. Indeed, the formation of traps upon operation of OLEDs is often observed in case of electrons than the holes. Study by different groups [51,52] on poly(phenylene vinylene) (PPV) inferred that the trap formation in OLED is more often caused by electron. Third, prominent mechanism of operation degradation is interface deterioration. Polymer based LEDs (PLEDs) have only two interface, one for electron injection and other for hole injection. Any deterioration of these interfaces will lead to interface degradation. Contrary to PLEDs, small molecule OLEDs (SMOLEDs) have many interfaces depending upon the device structure, and the interface degradation is a severe problem in these devices. The first report on SMOLEDs with a simple HTL/ETL interface for light emission was found to have very short life time of nearly 50 h due to existence of barrier for holes at the interface of Alq_3/diamine used in the device. Presence of such barrier at the organic interfaces originates traps and degrades the device under operation [53].