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Temperature dependence of electroluminescence degradation in organic light emitting devices without and with a copper phthalocyanine buffer layer

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Abstract

Temperature dependence of electroluminescence degradation was investigated in two types of organic light emitting devices (OLEDs) based on tris(8-hydroxyquinoline) aluminum (AlQ_3) emitter molecule, one without and another with copper phthalocyanine (CuPc) buffer layer at the hole-injecting contact interface. Electroluminescence degradation in time was measured for devices operated at 22 and 70 °C. Results unexpectedly showed that devices without the CuPc buffer layer demonstrated negligible change in half-life when operated at 22 or 70 °C, while devices with the CuPc layer showed the expected decrease in half-life when the temperature was increased. The results are explained within the framework of recently proposed OLED degradation mechanism, which identifies AlQ_3 cations as unstable, leading to device degradation. © 2002 Elsevier Science B.V. All rights reserved.

Since first organic light emitting devices (OLEDs) were successfully realized, their characteristics aroused the interest at many academic and industrial research laboratories [1,2]. In the last decade a great progress has occurred in understanding the light emission mechanism of OLEDs [2–4]. The development of new materials and device structures led to dramatic increase in device stability and light emission performance [5].

Two major sources of degradation have been identified. The first, associated primarily with degradation at the device cathode, occurs through the formation of non-emissive regions [6–8]. The second is reflected in a long-term "intrinsic" decrease in the electroluminescence efficiency of the device [7]. Although the mechanisms giving rise to the non-emissive regions have been identified [6–10], the dominant cause of the intrinsic degradation has been elucidated only recently [11]. Earlier studies showed that doping the hole transport layer (HTL) [12,13], or introducing a buffer layer at the hole-injecting contact [5] significantly reduces the intrinsic degradation. Half-life exceeding 4000 h (at an initial luminance of 500 cd/m^2) have been achieved [5], which can be further increased by doping the emitting layer [14]. Therefore, morphological instability of the HTL has been speculated to cause OLED degradation. On the other hand, other reports show no correlation between the morphological stability of the HTL and

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the OLED degradation [15]. At the present time experimental evidence strongly supports the degradation mechanism based on instability of AlQ_3 cations whose degradation products act as fluorescence quenchers [11,16].

In this letter, we report degradation studies of OLEDs based on AlQ_3 at elevated temperatures. We investigated two different OLED structures. The first is a standard double-layer device based on N,N′-di(naphthalene-1-yl) N,N′-diphenyl-benzidine (NPB) and tris(8-hydroxyquinoline)aluminum (AlQ_3) hole and emitting electron transport materials. The second is a device with a similar structure that also contains a copper phthalocyanine (CuPc) buffer layer between the ITO hole-injecting contact and the HTL.

In all our degradation studies we used the controlled experiment approach. The two samples without and with CuPc buffer layer, whose performance was compared, were always fabricated in the same pump-down cycle of the vacuum system. ITO substrates were cleaned with detergent solution, rinsed with ethanol, and subjected to UV ozone cleaning. In case of devices without a buffer layer at the hole-injecting contact, the OLEDs had a 600 Å NPB layer as HTL, and a 750 Å ALQ_3 layer as emitting and electron transport layer. In case of devices with a buffer layer at the hole-injecting contact, the devices had an additional 150 Å CuPc layer between the ITO and NPB layer. All devices had the same cathode, which consisted of a 1200 Å thick layer of a magnesium–silver alloy. Mg and Ag were co-evaporated from different sources at rates of 4 and 0.4 Å/s, respectively. NPB, ALQ_3 and CuPc were deposited at a rate of 1.5 Å/s. Depositions were carried out by thermal evaporation from resistively heated tantalum boats on substrates maintained at room temperature. The base pressure in the chamber was about 5×10^{-6} Torr. Deposition rates were individually controlled using quartz crystal monitors.

For stability tests, pairs of devices without and with the CuPc buffer layer, fabricated on the same substrate, were placed into a test box that was continuously purged with dry nitrogen. The initial luminance of the devices was measured using a Minolta CS-100 Chroma Meter. Silicon photodiodes were used to measure relative light intensity during aging experiments. The first stability test was performed at 22 °C on a pair of devices, which was never exposed to elevated temperatures prior to the test (virgin devices). The second stability test was performed at 70 °C on another pair of virgin devices, using a flexible electric heating tape wound around the box. A temperature of 70 °C was chosen in order to avoid a possible NPB phase transition, which has a glass transition temperature of about 95 °C [5]. Heating was controlled using an Omega CN9000 temperature controller and temperature of the OLED was monitored with a thermocouple in contact with the glass substrate. The third stability test was performed at 22 °C on a third pair of devices, which, without being operated, was heated to 70 °C for about 100 h, prior to the test (preheated devices). Finally, the fourth stability test was performed at 70 °C on a fourth pair of preheated devices.

Stability tests were performed using AC driving conditions. The duty cycle of the AC bias was 50%, with 62.5 mA/cm^2 constant current bias in the forward direction and 15 V constant voltage bias in the device reverse direction, at a frequency of 1 kHz. As the injected current at the reverse bias cycle was negligibly small, AC driving resulted in an average device current of 31.25 mA/cm^2. The electroluminescence and peak forward bias voltage of the devices under testing were simultaneously monitored and continuously recorded using a computer controlled data acquisition system.

Fig. 1 shows results for the virgin and preheated ITO/NPB/ALQ_3/Mg:Ag devices operated at room temperature and 70 °C. The initial light intensity for the virgin devices was about 910 and 790 cd/m^2 when measured at room temperature and 70 °C, respectively, whereas the initial light intensity for the preheated devices was higher, amounting to about 1150 cd/m^2 at room temperature and 950 cd/m^2 at 70 °C. Plots (a) and (b) give the forward bias voltage and relative electroluminescence intensity as a function of the device operating time. Clearly device operating voltage, for the same current density, decreases as the temperature is increased (Fig. 1(a)). This is not unexpected as carriers mobility in organic materials and carriers injection from electrodes are generally expected to increase with temperature. The dominant contribution to

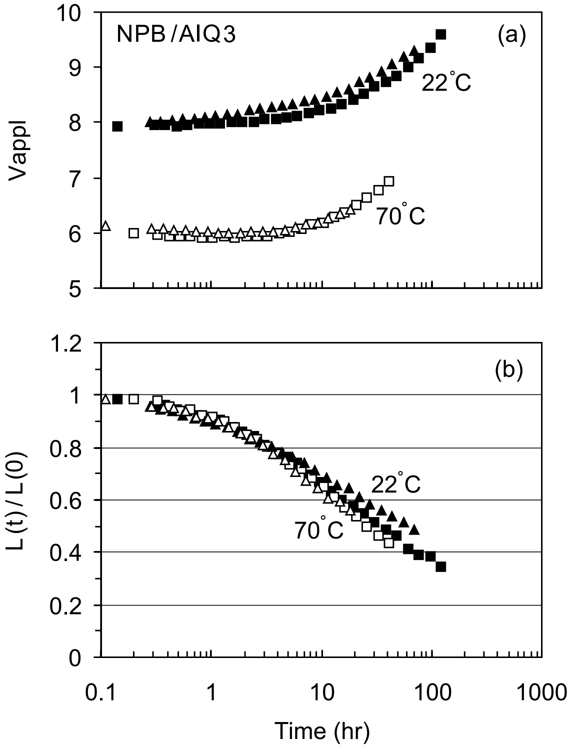

Fig. 1. Applied voltage (a) and relative EL intensity (b) as a function of time for NPB/ALQ$_3$ devices operated at 22 and 70 °C. Solid and opened symbols represent measurements at 22 and 70 °C, respectively. Squares represent measurements on virgin devices and triangles measurements on preheated devices, as explained in the text.

operating voltage reduction probably comes from AlQ$_3$ as its mobility is much lower (on the order of 10^{-5} cm^2/V s) than the mobility of holes in NPB (10^{-3} cm^2/V s), and is strongly temperature and electric field dependent [17–19]. What is however unexpected is that the device half-life changes very little as the temperature is increased (Fig. 1(b)). This observation will be discussed later offering an explanation within the framework of the recently proposed degradation mechanism of AlQ$_3$ based OLEDs [11].

Fig. 2 shows results for stability test of ITO/CuPc/NPB/ALQ$_3$/Mg:Ag devices. The initial light intensity for the virgin devices was about 1220 and 1150 cd/m^2 when measured at room temperature and 70 °C, respectively, whereas the initial light intensity for the preheated devices changed little, amounting to about 1270 cd/m^2 at room temperature and 1110 cd/m^2 at 70 °C. Again the temperature increase leads to a decrease of the device operating voltage (Fig. 2(a)), as expected. In this case the device half-life change with increasing temperature also shows the expected behavior, i.e. a significant decrease in half-life as temperature is increased (Fig. 2(b)). We would also like to comment on the magnitude of half-life, at room temperature, of devices with CuPc buffer layer presented in this work, which is much shorter than the best results presented in the literature [5]. Half-life of devices with CuPc buffer layer were found to depend on CuPc synthesis and purification, as well

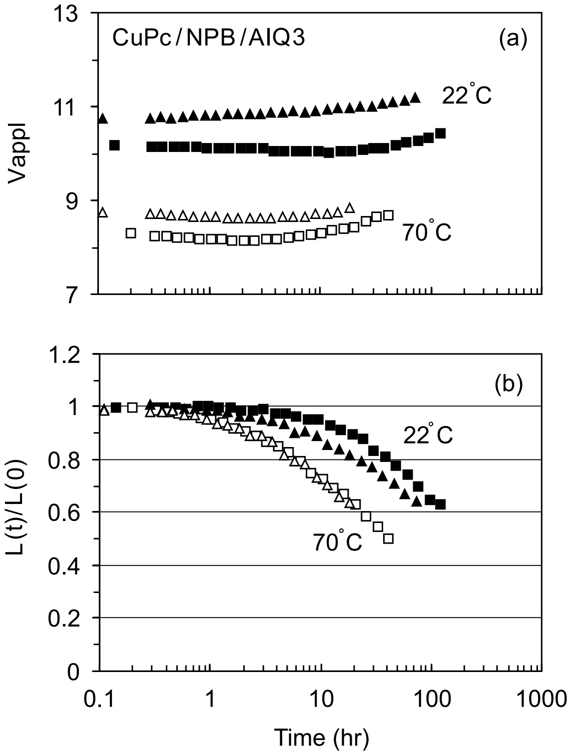

Fig. 2. Applied voltage (a) and relative EL intensity (b) as a function of time for CuPc/NPB/ALQ$_3$ devices operated at 22 and 70 °C. Solid and opened symbols represent measurements at 22 and 70 °C, respectively. Squares represent measurements on virgin devices and triangles measurements on preheated devices, as explained in the text. Variations in initial applied voltages of virgin and preheated devices are probably not meaningful, as freshly made CuPc devices showed about 0.5 V scatter in initial applied voltage.

as ITO cleaning procedure. In this work, we used UV ozone cleaning for the ITO substrates, rather than oxygen plasma cleaning, which is frequently used. This might be the reason for the shorter half-life of our devices. However, the qualitative effect of CuPc buffer layer on device stability still shows the same trend, i.e. leads to an increase in device life. Therefore our comparisons between devices with and without a CuPc buffer layer are meaningful.

Obviously it is of fundamental interest to understand why devices without and with the CuPc buffer layer show different behavior in half-life change when the temperature of the devices is increased. Recently, Aziz et al. have shown that the dominant contribution to device degradation at room temperature comes from instability of AlQ_3 cations which are generated when holes are injected into AlQ_3 and whose degradation products act as fluorescence quenchers [11]. Different strategies for life extension, such as introduction of the CuPc buffer layer [5], and doping of the hole transport [12,13], are essentially effective as they lead to slowing down of hole transport and/or injection and therefore produce higher electron concentration at the HTL/AlQ_3 interface. This, in turn, leads to increased recombination rate of holes injected into AlQ_3, shorter lifetime of unstable AlQ_3+ species, and consequently increased device stability. We will now argue that essentially the same mechanism plays important role in temperature behavior of OLEDs based on AlQ_3.

In case of devices without the buffer layer (Fig. 1) increased temperature leads to a significant increase in the injection of electrons from the cathode into the AlQ_3, as well as an increase in the electron mobility in the AlQ_3 layer which is reflected in the decrease in device operating voltage. Our experiments on OLEDs with the same thickness of AlQ_3 layer and various thicknesses of NPB layer show that operating voltage is only slightly affected by changes in NPB layer thickness, indicating that the transport of holes across the HTL requires a very small part of the operating voltage, even at room temperature, in agreement with other reports [17]. The fact that the half-life is not significantly affected by increased temperature shows that the balance of electron and hole injection into AlQ_3 remains essentially unchanged as the temperature is increased, resulting in similar concentration of unstable AlQ_3+ cationic species, reflected in an insignificant change in device half-life at 70 °C compared to room temperature.

In case of devices with the buffer layer (Fig. 2), its presence leads to slowing down of hole transport, and hence an increased device lifetime at room temperature. However, when the temperature is increased, the hole-slowing effect of the CuPc buffer layer decreases, apparently to a larger extent than the high temperature-induced increase in electron injection and mobility in AlQ_3. This leads to increased relative concentration of injected holes with respect to electrons at the interfacial region of AlQ_3 in contact with the HTL, and, as a result, an increased lifetime of the unstable AlQ_3+ species and, hence, increased degradation rate of the device at the higher temperature.

It is also interesting to note that voltage change during aging of the devices is much smaller in devices containing a CuPc layer, in agreement with previous observations [5]. Although it is difficult to pinpoint exactly the mechanism of this phenomenon, we speculate that the increased voltage stability of CuPc containing devices is perhaps caused by the more balanced electron and hole injection, which results in reduced accumulation of space charge.

In conclusion, we studied the operational stability of ITO/NPB/ALQ_3/Mg:Ag and ITO/CuPc/NPB/ALQ_3/Mg:Ag devices at two temperatures (22 and 70 °C). The influence of temperature on the operational stability strongly depended of the type of device. Devices containing the CuPc buffer layer showed expected decrease in device half-life on increasing temperature. Devices without the buffer layer, on the other hand, showed insignificant change in stability at higher temperatures. These results are explained within the framework of the degradation mechanism based on unstable AlQ_3 cations. This degradation mechanism, therefore, does not only govern OLEDs intrinsic degradation at a constant temperature, but also appears to play a dominant role in the temperature dependence of device degradation rate.

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