

Degradation Analysis of Solution-Processed OLEDs by Impedance Spectroscopy and Molecular Simulation

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Keywords: solution-processed OLEDs, interface mixing, impedance spectroscopy, recombination region.

ABSTRACT

A detailed analysis of the degradation of solution-processed OLED using impedance spectroscopy yields information about trap formation at the interfacial mixing area where the charges recombine. In addition, the most degraded region in the device was also found in this region. The formation of trap at the mixing region was potentially caused by the dissociation of the molecules which have been suffered from the quenching due to an interaction of excitons and polarons. Molecular simulation was utilized to calculate the possibility of bond dissociation of the molecules. As a result, we found that the dissociation of host molecules played a major role in device degradation.

1. Introduction

The short lifetime of solution-processed organic light emitting devices (s-OLEDs) has been considered as one of the most obstacles that prevent s-OLED from being commercialized. It was believed that the interface mixing, which is formed when two layers are successively spin-coated, is the main reason for the short operational lifetime.^[1,2] Unfortunately, there have been not so many reports systematically studied on the device lifetime of s-OLEDs. Thus, we have not much information on the degradation mechanism of s-OLEDs. Therefore, we analyzed the device degradation to find a plausible mechanism by using impedance spectroscopy (IS). We found that the interfacial mixing region of the hole transport layer (HTL) and the emitting layer (EML) was most stressed. Bond dissociation energy (BDE) of the molecules was also calculated by molecular simulation. From these studies, we found that dissociation of the host and hole transport molecules from the anion excited state (AES) and the anion ground state (AGS) can cause device degradation. We tried to elucidate the phenomenon that the resistive component of the device changes from degradation process.

2. Experiment

We fabricated full s-OLED devices as follows: ITO patterned substrates were cleaned by sonication in acetone and isopropyl alcohol for 15 min. UV ozone

treatment was then applied for these substrates for 20 min. Then, hole injection layer (HIL, PEDOT:PSS) was spin-coated in the ambient condition at 8000 rpm for 23 s, and then annealed for 20 min at 160°C. A 0.4wt% of hole transport material (HTM) dissolved in toluene was loaded and spin-coated on the predeposited HIL (3000 rpm for the 30 s, annealing at 220°C for 60 min). A 1 wt% of KHU-H1 (host 1) and a 1 wt% of NH (host 2) dissolved in toluene, and a 0.5 wt% of Ir(mppy)₃ (GD) solubilized in chlorobenzene were mixed. To make EML solution with an appropriate composition, a host and a dopant solution were mixed at a ratio of 9:1 and spin-coated at the condition of 3000 rpm for 30 s. They were annealed at 100°C for 15 min. Devices were then transferred to the thermal evaporator with vacuum pressure of about 10⁻⁷ Torr to form exciton blocking layer (EBL, 5 nm), LG201:Liq (ratio 1:1, 45 nm), Liq (1nm), and Al (100 nm), respectively.

3. Results

Full devices were fabricated with the following structures:

Device A: ITO/PEDOT:PSS (40nm)/x-HTM (17nm)/KHU-H1:GD (10 %, 30nm)/EBL (5nm)/ LG201:Liq (1:1, 45nm)/Liq (1 nm) / Al (100nm).

Device B: ITO/PEDOT:PSS (40nm)/x-HTM (17nm)/NH:GD (10%, 30nm)/EBL (5nm)/ LG201:Liq (1:1, 45nm)/Liq (1nm)/Al (100nm).

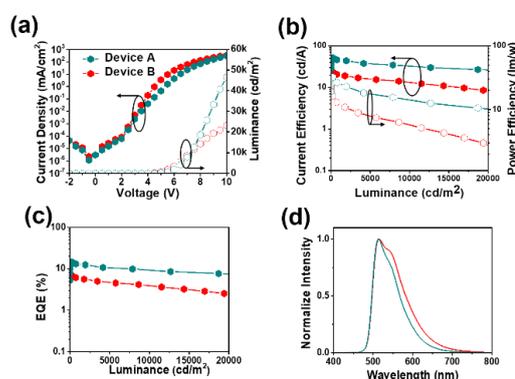


Fig. 1 Device characteristics: (a) Current Density (J) -Voltage (V) -Luminance (L), (b) Current Efficiency-L and Power Efficiency-L, (c) External Quantum Efficiency (EQE)-L characteristics and (d) Electroluminescence (EL) spectra of resultant devices.

Fig. 1 shows device characteristics of **Device A** and **Device B**. The operating voltage (V_{op}) was 5.5 V and 5.2 V, and the turn-on voltage (V_{on}) was 3.1 V and 3.0 V for **Device A** and **Device B**, respectively (**Fig. 1(a)**). The maximum power efficiency, current efficiency and external quantum efficiency were 32.3 lm/W, 51.5 cd/A, 14.6 % for **Device A**, and 26.2 lm/W, 22.8 cd/A, 7.6 % for **Device B**, respectively (**Fig. 1(b)** and **1(c)**). Meanwhile, the half-lifetime (LT50) of **Device A** (42 hours) was almost triple that of **Device B** (12 hours) (**Fig. 2**). All the data are summarized in table 1.

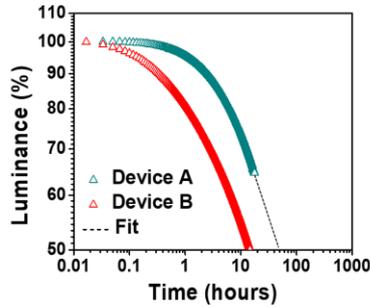


Fig. 2 The operational lifetime of devices with an initial brightness of 1000 cd/m².

Table 1. Summary of device performances.

| Device | ^a V_{on} / ^b V_{op} [V] | ^c P.E./ ^d C.E./ ^e E.Q.E | | | ^f LT ₅₀ [h] |
|----------|--|--|----------------|--------------------------|--------------------------------------|
| | | [lmW ⁻¹ / cdA ⁻¹ / %] | | | |
| | | Maximum | | at 1000cdm ⁻² | |
| A | 3.1/5.5 | 32.3/51.5/14.6 | 25.6/45.7/13.0 | 42 | |
| B | 3.0/5.2 | 26.2/22.8/7.6 | 12.2/20.3/6.0 | 14 | |

^a V_{on} : turn on voltage (at 1cd/m²) ^b V_{op} : operating voltage (at 1,000cd/m²)
^cP.E.: Power efficiency ^dC.E.: Current efficiency ^eE.Q.E: external quantum efficiency ^fLT50: half-lifetime.

To understand the reason for the difference in efficiency and lifetime of the two devices. We investigated the charge transport behavior in EML by fabricating electron only device (EOD) and hole only device (HOD) with the following structures.

- EOD A:** ITO/ZnO(40nm)/PEI(10nm)/KHU-H1:GD (50nm) / Al(100nm).
- HOD A:** ITO/PEDOT:PSS(40nm)/KHU-H1:GD (50nm)/ MoO₃(10nm)/ Al(100nm).
- EOD B:** ITO/ZnO(40nm)/PEI(10nm)/NH:GD (50nm)/ Al(100nm).
- HOD B:** ITO/PEDOT:PSS(40nm)/NH:GD(50nm)/ MoO₃(10nm)/ Al(100nm).

In **Fig. 3(a)**, the hole mobility of KHU-H1:GD layer is double the electron mobility while the electron mobility of

NH:GD is about three orders higher than the hole mobility of this layer. Therefore, it would be expected that the recombination region is slightly shifted toward the EBL (or ETL) side in **Device A** and completely pulled back to the HTL/EML interface in **Device B** (**Fig. 3(b)**). Since the broad recombination region in **Device A** was shifted away from the interfacial mixing region, the lifetime and efficiency could be enhanced a lot. However, in **Device B**, the recombination dominantly occurred in the interfacial mixing zone which could facilitate the exciton-polaron quenching (EPQ) so that the device lifetime and efficiency decreased seriously.

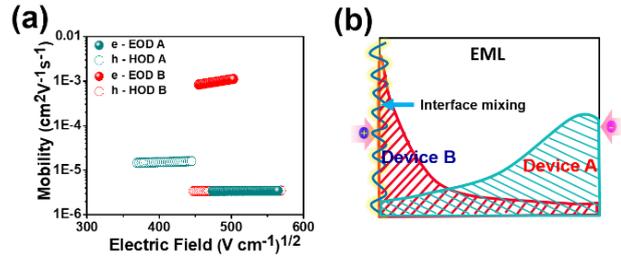


Fig. 3 (a) Charge mobilities estimated by the space-charge limit current regime and (b) predicted recombination region of **Device A** and **Device B**.

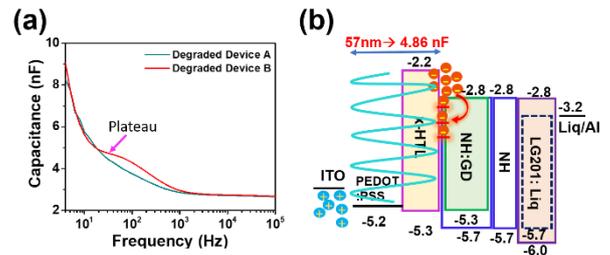


Fig. 4 (a) Capacitance-frequency of degraded devices at 4 V and (b) the scheme illustrate the trapping and plateau formation in degraded **Device B**.

To investigate the change of chemical properties of the materials used in these devices, IS technique was utilized to analyze the degradation of pristine and degraded devices which correspond to the devices obtained before and after a continuous operation of those devices to reach half lifetime (LT50). In **Fig. 4(a)**, a plateau at 4.8 nF was detected between ITO and x-HTL/EML interface which was 57 nm apart. This plateau is plausibly caused by the traps at the interface.^[3] The observation of this plateau only in degraded **Device B** suggested that this device has lower operational stability. In other words, we can conclude that the device degradation can be accelerated by serious trap formation at the mixing interface.

From the fitting of Nyquist plots, we could see where the deterioration was concentrated (**Fig. 5**). In other words, after the half-lifetime measurement, in **Device A**,

R_0 and R_1 slightly decrease by 1.27 and 2 times, respectively, while R_2 and R_3 increase by 1.5 and 2 times, respectively (**Fig. 5(a)** and **6(a)**). Meanwhile, in **Device B**, R_1 increases greatly by a factor of 13 while R_0 , R_2 and R_3 increased by 1.3, 7.6, and 2.5 times as show in in **Fig. 5(b)** and **Fig. 6(b)**. The most increase in resistance (R_1) indicating that the x-HTL and mixing region were the most stressed. Detailed data are also summarized in **Table 2**.

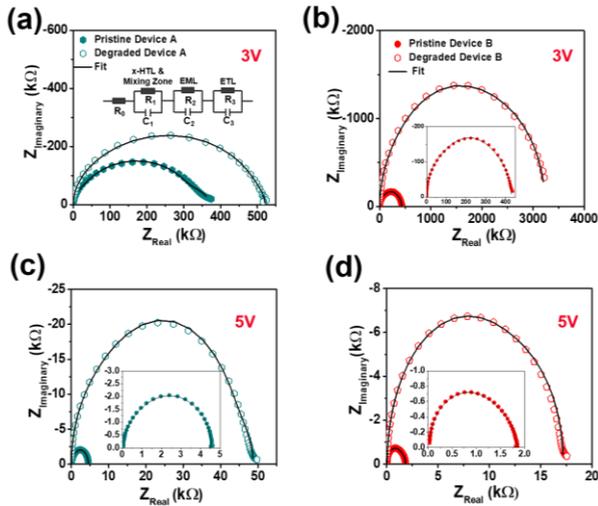


Fig. 5 Nyquist plots and fits of (a) **Device A** at 3 V, (b) **Device B** at 3 V, (c) **Device A** at 5 V, and (d) **Device B** at 5 V. The equivalent circuit for fitting was shown in the inset of (a), the plots of pristine devices were also enlarged as illustrated in the insets of (b)-(c).

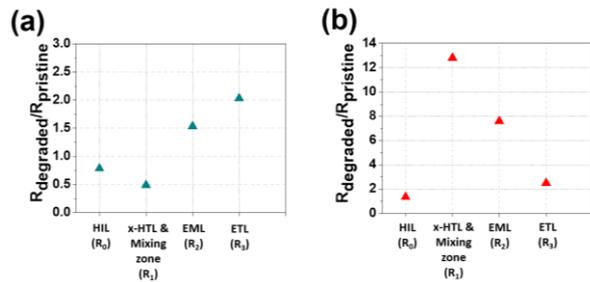


Fig. 6 The resistance change as $R_{\text{degraded}}/R_{\text{pristine}}$ ratio in (a) **Device A** and (b) **Device B** at 3 V.

A similar trend was also observed at 5 V. In **Device A**, the more serious increase in resistance was recorded for R_2 and R_3 which increased by 11 and 12 times, respectively. Meanwhile, in **Device B**, x-HTL and the mixing region (R_1) still show the most increase which is 14 times. Furthermore, if we consider the trap location in the above discussion (**Fig. 4**), it is clear that the interfacial mixing region would be more stressed than bulk region of x-HTL.

The dissociation of molecules from EPQ in the mixing region of degraded **Device B** was probably the main reason for trap formation. EPQ can result in an unstable charged excited state^[4]

$$\Delta E_{\text{DAE}} = \text{BDE} - E_{S_1, T_1}$$

where ΔE_{DAE} is the dissociated activation energy, BDE is the bond dissociation energy, E_{S_1, T_1} is the lowest singlet or triplet exciton energy. Negative ΔE_{DAE} implies that the bond willingly dissociates. The most probable bond dissociation of HTM and host molecules which are in AGS and AES are shown in **Fig. 7**. NH molecules with negative ΔE_{DAE} were highly susceptible to the bond dissociation from the quenching between singlet/triplet exciton and polaron. Additionally, the mixing effect at the x-HTL/EML interface could also facilitate the injection of electron from NH molecule into HTM molecule resulting in the formation of the AGS in HTM molecule which has anionic BDE in the range of 1.65 eV - 1.88 eV. The dissociations of AGS for HTM and NH (**Fig. 7(a)** and **(c)**) did not willingly happen because the anionic BDEs were still above 1.5 eV which is considered to be the minimum threshold to stabilize the bond.^[4] However, serious electron accumulation at the interfacial mixing region can also make slow degradation from the AGS possible.

Table 2. Summary of the resistance change of the s-OLEDs after continuous operation at 3 V and 5 V.

| Devices | State | R_0 | $R_1 (\Omega)$ | $R_2 (\Omega)$ | $R_3 (\Omega)$ | |
|---------|-------|----------|----------------|-------------------|-------------------|-------------------|
| 3 V | A | Pristine | 40.3 | 5.5×10^4 | 2.8×10^5 | 3.1×10^4 |
| | | Degraded | 31.6 | 2.7×10^4 | 4.3×10^5 | 6.3×10^4 |
| | B | Pristine | 29.9 | 7.8×10^4 | 2.5×10^5 | 9.6×10^4 |
| | | Degraded | 40.3 | 1.0×10^6 | 1.9×10^6 | 2.4×10^5 |
| 5 V | A | Pristine | 38.7 | 5.7×10^2 | 3.3×10^3 | 7.0×10^2 |
| | | Degraded | 30.7 | 4.0×10^3 | 3.6×10^4 | 8.6×10^3 |
| | B | Pristine | 27 | 3.3×10^2 | 7.0×10^2 | 7.8×10^2 |
| | | Degraded | 47.1 | 4.7×10^3 | 7.1×10^3 | 5.3×10^3 |

Meanwhile, even though KHU-H1 in **Device A** has negative ΔE_{EPQ} for the bond ① and ② and low anionic BDE of 1.2 eV for bond ① (**Fig. 7(b)**), the device still showed better operational stability. This is probably because of the lower EPQ level in this device. Additionally, direct charge trapping emission from the phosphorescent dopant at the mixing interface can occur due to its deep lowest unoccupied molecular orbital. As a result, the possibility of the bond dissociation in the host molecule (KHU-H1) was significantly reduced.

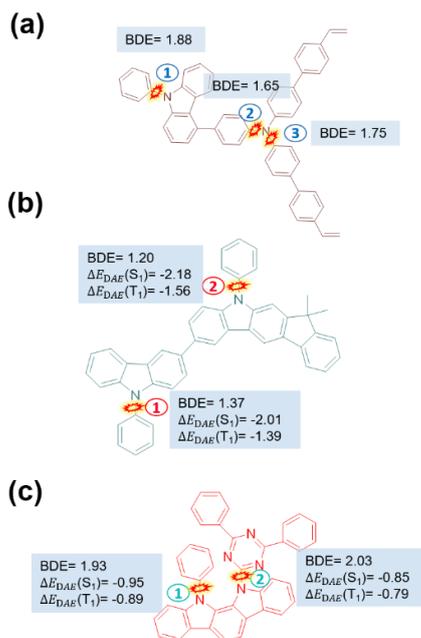


Fig. 7 The most probable dissociation bonds from AGS and AES of (a) HTM (b) KHU-H1 (c) NH. Dissociations from cationic and neutral states were excluded due to high BDE or positive ΔE_{DAE} . The BDE and ΔE_{DAE} values are shown for each bond (unit: eV).

4. Conclusion

In conclusion, we have thoroughly and carefully analyzed the device degradation by impedance spectroscopy and molecular simulation. The device degraded seriously when charges recombine at the interfacial mixing zone. In other words, the most increase in the resistance after a continuous operation was observed at the interfacial mixing region. This can be attributed to the presence of traps which are mostly formed by the dissociation of host molecules from AES. Slow degradation of host and HTM molecules could also occur from the dissociation of AGS in the case charge accumulation. These results can be a reference to improve the stability of solution-processed OLEDs.

Acknowledgment

This research was supported by the Industrial Strategic Technology Development Program (20011059, Development of inks for emitting layers with high performance and long lifetime) funded By the Ministry of Trade, Industry & Energy (MOTIE, Korea). This work was also supported by Basic Science Research Program through the National Research Foundation of Korea

(NRF) funded by the Ministry of Education (2021R1A2C1008725).

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