Quantitative Investigation of High-Temperature Degradation in Organic Light-Emitting Diodes with Charge and Exciton Dynamics

Bum June Park and Taekyung Kim*, ***

***Dept. of Information Display, Hongik University, Seoul, 04066, Republic of Korea**
****Dept. of Materials Science and Engineering, Hongik University, Sejong, 30016, Republic of Korea**

Abstract

We analyzed the causes of device efficiency and lifetime degradation with temperature increases in exciplex host-based phosphorescent organic light-emitting diodes (PhOLEDs). To investigate charge dynamics, capacitance-voltage (C-V) measurements and the fabrication of hole-only devices (HOD) and electron-only devices (EOD) were performed. As a result, it was found that as the temperature increased, the hole mobility increased more significantly compared to the electron mobility. Additionally, through ordinary differential equation (ODE) simulations of transient photoluminescence (TrPL) and transient electroluminescence (TrEL), we were able to quantify the exciton dynamics. As a result, the triplet-triplet annihilation (TTA) rate constant of the host increased sharply with temperature increased to other rate constants, which was identified as the primary factor of the temperature-induced reliability degradation.

Author Keywords

transient photoluminescence; transient electroluminescence; ordinary differential equations; triplet-triplet annihilation

1. Introduction

Organic light-emitting diodes (OLEDs) are continuously advancing as next-generation displays, extending beyond TVs and smartphones to include automotive displays, biotechnology-integrated displays, and more.(1-3) For OLEDs to expand into various fields, high efficiency and long lifetime of the devices are essential, and reliability that ensures stable operation in diverse environments is equally important. However, OLEDs generally tend to experience a decline in efficiency and lifetime when operated at high temperatures.(4) This characteristic presents a significant challenge to the development of OLED display technologies. Therefore, analyzing the causes of reliability degradation at high temperatures is a key factor in advancing next-generation display technologies.

One of the main causes of device degradation is identified as bimolecular interactions, such as triplet-triplet annihilation (TTA) or singlet-triplet annihilation (STA). These bimolecular interactions act as quenching mechanisms, reducing the exciton lifetime. Conventionally, exciton lifetime has been indirectly estimated by exponential fitting of transient photoluminescence (TrPL) or transient electroluminescence (TrEL) data. However, this approach has limitations in fully reproducing the quenching profile caused by bimolecular interactions. To address this, a modeling technique utilizing ordinary differential equations (ODEs) for TrPL has been introduced. (5-7) This method not only considers the excited state transition but also accounts for bimolecular interactions, allowing for more accurate exciton dynamics analysis. This enables a quantitative analysis of the changes occurring in each process under high-temperature conditions and helps identify and prove the primary causes of device degradation.

In this study, several approaches were used to analyze the causes of reliability degradation under high-temperature conditions. First, the current injection characteristics were examined, revealing an increase in capacitance with rising temperature. Based on this result, the characteristics of hole-only devices (HOD) and electron-only devices (EOD) were compared, revealing that at high temperatures, hole mobility increased by 8.04 times, while electron mobility increased by 6.53 times, with a more significant increase in hole mobility. As a result, charge accumulation and recombination zone formation were observed at the emissive layer (EML)/hole blocking layer (HBL) interface. Additionally, to compare exciton dynamics, a time-dependent exciton quenching model based on transient photoluminescence (TrPL) profiles was employed. The analysis revealed that the TTA rate constant increased sharply with rising temperature. Furthermore, by fitting transient electroluminescence (TrEL) data with a similar method considering the polaron state, it was found that TTA increased more rapidly than triplet-polaron quenching (TPQ), confirming that TTA has a significant impact as the main cause of high-temperature reliability degradation.

2. Results and Discussion

In this paper, 9-(3-(triphenylsilyl)phenyl)-9H-3,9′-bicarbazole (SiCzCz) and 9,9′-(6-(3-(triphenylsilyl)phenyl)-1,3,5-triazine-2,4-diyl)bis(9H-carbazole) (SiTrzCz2) were used as exciplex hosts, and Platinum(II) [2-[3-[3-[3,5-bis(1,1-dimethylethyl)phenyl]-1H-benzimidazol-1-yl-κC2]phenoxy-κC2]-9-[4-(1,1-dimethylethyl)-2-pyridinyl-κN]-9H-carbazolato(4-)-κC1] (PtON-TBBI) was used as a blue phosphorescent dopant. The fabricated devices were evaluated by gradually increasing the temperature from room temperature (RT) to 313K, 333K, and 353K, with the device structure and performance summarized in **Figure 1**. As the temperature increased, the current injection characteristics at the same voltage improved, while the external quantum efficiency (EQE) and lifetime decreased. To identify the cause of this performance degradation, the devices were compared and analyzed from the perspectives of charge dynamics and exciton dynamics.

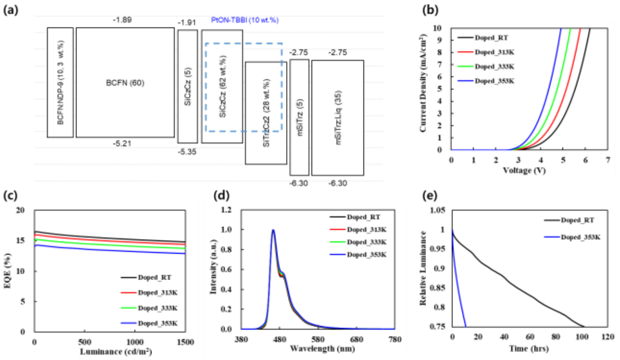

Figure 1. (a) Device structures, (b) current density (J)–voltage (V) curves, (c) EQE-luminance curves, (d) electroluminescence (EL) spectra, (e) lifetime curve measured at J=10 mA/cm². The

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data were measured at temperatures ranging from RT to 353 K.

To analyze the charge dynamics of devices under varying temperatures, capacitance-voltage (C-V) measurements were performed, and HOD-EOD were fabricated to compare current injection characteristics. The results are presented in **Figure 2**. The C-V measurements showed that capacitance increased at the high-temperature. This result indicates that as the temperature increases, the mobility of one type of charge carrier rises more significantly than the other, leading to charge accumulation between the emissive layer (EML) and the blocking layer. The zero-field mobility of HOD-EOD under difference temperatures was calculated and summarized in **Table 1**. At 353K, hole mobility increased by 8.04 times, while electron mobility increased by 6.53 times. These results indicate that holes are more effectively injected at high temperatures, resulting in charge accumulation and the formation of a recombination zone at the interface between the EML and the hole-blocking layer (HBL).

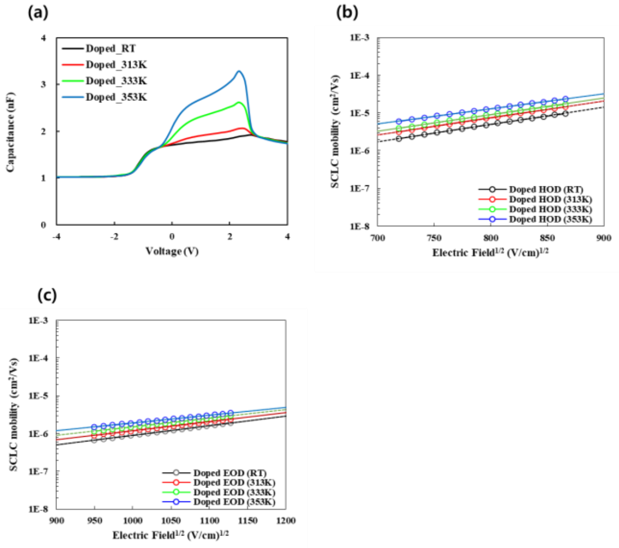

Figure 2. (a) The doped device capacitance-voltage (C-V) curve, (b) mobility characteristics of the hole-only device (HOD), (c) mobility characteristics of the electron-only device (EOD) as a function of electric field using the SCLC model

Figure 3 shows the TrPL fitting results used to analyze the exciton dynamics of the devices. The traditional TrPL fitting approach calculates the exciton lifetime using exponential fitting and measures the transition rate of the excited state based on this. The conventional TrPL fitting method calculates the exciton lifetime using exponential fitting and measures the transition rate of the excited state. However, this method does not account for bimolecular interactions, such as TTA and STA, which limits its ability to accurately explain device degradation. To more precisely analyze the device characteristics, we applied an ODE that incorporates not only the transition of the excited state but also the bimolecular interactions in the host and dopant, as shown in **Figure 3.a** The singlet and triplet densities, considering all energy transfer mechanisms, are described by **Equations (1)–(4)**;

which is given by Equation (1)-(4).

$$\frac{dS_{1.H}}{dt} = -(k_{r.H} + k_{nr.H} + k_{ISC.H} + k_{FRET})S_{1.H} + k_{RISC.H}T_{1.H} - k_{SS.H}{S_{1.H}}^2 - k_{ST.H}S_{1.H}T_{1.H} + \frac{1}{8}k_{TT.H}{T_{1.H}}^2 + S_0 \tag{1}$$

$$\frac{dT_{1.H}}{dt} = k_{ISC.H}S_{1.H} - (k_{RISC.H} + k_{nrT.H} + k_{DET})T_{1.H} - \frac{5}{8}k_{TT.H}{T_{1.H}}^2 \tag{2}$$

$$\frac{dS_{1.D}}{dt} = k_{FRET}S_{1.H} - k_{ISC.D}S_{1.D} \tag{3}$$

$$\frac{dT_{1.D}}{dt} = k_{DET}T_{1.H} + k_{ISC.D}S_{1.D} - k_{r.D}T_{1.D} - \frac{1}{2}k_{TT.D}{T_{1.D}}^2 \tag{4}$$

The subscripts H and D represent the host and dopant. S_1, and T_1 are the time-dependent singlet exciton and triplet exciton density. k_r, k_{nr}, $k_{ISC,}$ $k_{RISC,}$ and k_{nrT} are the radiative, non-radiative, intersystem crossing, reverse intersystem crossing and triplet non-radiative rate constant. k_{FRET} and k_{DET} refer to Förster resonance energy transfer and Dexter energy transfer rate constant from the host to the dopant. $k_{SS,}$ k_{ST} and k_{TT} are singlet–singlet annihilation (SSA), STA and TTA rate constant, respectively. As a simulation result, both the non-doped and doped devices showed fitting values that matched the measured data, with the rate constant for each process summarized in **Figure 3.e**. The rate constant that increased at high-temperature was the TTA rate for the Fhost, which increased by 7.59 times at 353K. This suggests that the TTA process in the host is the most critical factor in device degradation.

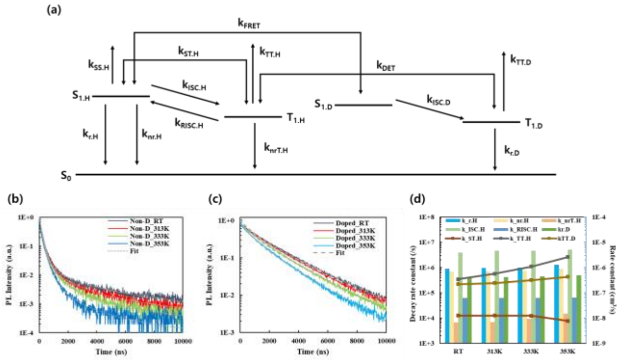

Figure 3. (a) Scheme of the kinetic processes in photoluminescence measurements for the doped film, (b) fitted results of the TrPL decay for the non-doped film (c) fitted results of the TrPL decay for the doped film using ordinary differential equations (ODE) (d) summarized parameters of TrPL ODE simulation

Table 1. Temperature-dependent zero-field mobility in hole-only devices (HODs) and electron-only devices (EODs)

	HOD				EOD			
Temp	RT	313K	333K	353K	RT	313K	333K	353K
zero-field mobility ($\times10^{-9}$ cm^2/Vs)	1.06	1.85	2.75	8.52	2.66	4.78	8.25	17.37

Additionally, to compare the degradation rates considering the polaron state, TrEL fitting was calculated using the same ODE method. The exciton dynamics diagram for TrEL is shown in **Figure 4.a**, and the ODE is provided in **Equations (5)–(7)**. (8-10)

$$\frac{dn}{dt} = \frac{j}{ed} - \gamma n^2 \tag{5}$$

$$\frac{dS_1}{dt} = -(k_r + k_{nr} + k_{ISC})S_1 + k_{RISC}T_1 - k_{SS}{S_1}^2 - k_{ST}S_1T_1 + \frac{1}{4}k_{TT}{T_1}^2 + \frac{1}{4}\gamma n^2 \tag{6}$$

$$\frac{dT_1}{dt} = k_{ISC}S_1 - (k_{RISC} + k_{nrT} +)T_1 - \frac{5}{4}k_{TT}{T_1}^2 - k_{TP}T_1 n + \frac{3}{4}\gamma n^2 \tag{7}$$

where J, e, d, γ and n are the current density of the device, elementary charge, thickness of EML, Langevin recombination coefficient and time-dependent polaron density, respectively. k_{TP} is the triplet-polaron quenching rate constant. The simulation results showed a high correlation between the measured TrEL data and the fitting data. The rate constants for bimolecular interactions obtained from the ODE fitting results are summarized in **Table 2**. The analysis revealed that as the temperature increased, TPQ increased by 2.89 times due to charge accumulation, but TTA increased by 5.74 times, showing a much larger rise. These results suggest that as the temperature increases, TTA process becomes more activated, which is the main cause of the decreased high-temperature reliability of the device.

Table 2. Bimolecular interaction rates constant by TrEL ODE simulation

Temperature	RT	313K	333K	353K
k_{TT} ($\times 10^{-12}$cm^{3}s^{-1})	0.99	4.46	4.80	5.68
k_{TP} ($\times 10^{-11}$ cm^{3}s^{-1})	3.07	3.63	6.95	8.90

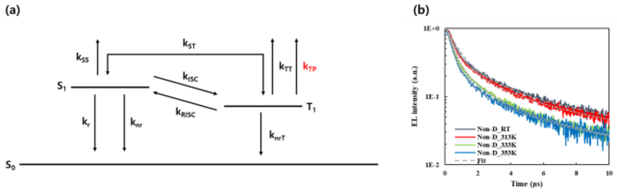

Figure 4. (a) Scheme of the kinetic processes in electroluminescence measurements for the non-doped device, (b) fitted results of the TrEL decay for the non-doped device using ODE simulation

3. Impact of Research

In this study, to analyze the causes of the degradation in high-temperature reliability of OLEDs, we conducted an in-depth investigation of device physics from the perspectives of charge and excitons. Specifically, in the analysis of exciton dynamics, we introduced an ODE-based method that considers bimolecular interactions, instead of the conventional exponential fitting method. This approach provides a more accurate understanding of exciton dynamics and enables a quantitative analysis of degradation factors. Through this analysis, we carefully examined the changes in device characteristics at high-temperature and found that the significant increase in hole mobility led to charge accumulation and changes in the position of the recombination zone. As a result, the TTA process increased dramatically, leading to a decrease in device stability. These results are expected to provide important guidance for future device design and the development of new material concepts aimed at improving high-temperature reliability.

4. Acknowledgements

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