The accumulation of diffusive charges in organic light-emitting diodes

Dong Zhao [a], Hans-Peter Loebl [b],*

[a] Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany
[b] Philips Technologie GmbH, Innovative Technologies, Research Laboratories, Philipsstrasse 8, D-52068 Aachen, Germany

ARTICLE INFO

ABSTRACT

We investigated the accumulation of diffusive charges within the emitting layer of organic light-emitting diodes (OLEDs). The presence of accumulated charges can be probed by both transient electroluminescence (transient EL) and impedance measurements (IM). As an example we studied OLED devices using a red phosphorescent emitter iridium(III)bis(2-methyldibenzo[f,h]quinoxaline) (acetylacetonate) [Ir(MDQ)2(acac)] and green emitter Ir(ppy)3 co-doped into a mixed host matrix. The results deduced from both transient EL and IM measurements are in good consistency, enabling us to compare the accumulation of diffusive charges in different devices quantitatively. Experimental results indicate that the lifetime of OLED devices is reduced by the diffusive charges. We ascribe this to the exciton–polaron annihilation where the diffusive charges play an important role. The quantification of the accumulation of diffusive charges in the emitting layer may help to improve the lifetime of OLEDs.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Excessive charges in the emitting layer of organic light-emitting diodes (OLEDs) can lead to effects such as exciton–polaron annihilation [1–3] and field-induced quenching [4]. Yet the in-depth characterization of the excessive charges is absent and the properties of those charges have rarely been discussed. Recently, Weichsel et al. reported an inspiring study on the accumulation of excessive charges. The time response of the OLED's luminescence after turning-off (in the following called off-state luminescence) can reveal an overshoot which indicates the storage of the excessive charges at the interface of the emitting layer [5]. The fact that such excessive charges can move towards the other end of the emitting layer in the off-state implies that such charges are mobile, unlike trapped charges which are localized at isolated energetic trap sites.

The existence of excessive mobile charges within the emitting layer has been verified by investigating the transient electroluminescence in the off-state [6]. The bi-exponential long tail of the off-state luminescence results from the trap-assisted recombination between the trapped charges and the excessive mobile charges [6]. The off-state luminescence typically decays on a time-scale in the order of 10 µs in phosphorescent OLEDs with the red emitter iridium(III)bis(2-methyldibenzo[f,h] quinoxaline)

(acetylacetonate) [Ir(MDQ)2(acac)], whereas the typical time required for space charges transiting from the boundary of the emitting layer to the center of the recombination zone is rather in the order of hundred nanoseconds. This implies that the excessive mobile charges do not drift directly to the center of the recombination zone as ordinary space charges do. Instead, they take a detour within the emitting layer, and stay there for much longer time before they are neutralized. It has been reported also that the J–V curve of an OLED cannot be well fitted over the whole range without taking the diffusion current [7,8] into account. Based on these experimental facts we assume that the excessive mobile charges is a portion of charges which do not drift but show diffusive behavior Their trajectories are random, differentiating them from the ordinary drifting space charges which contribute to the direct component of the current, the conduction current. The response of these diffusive charges to small alternating driving voltages corresponds to the displacement current.

In this work, these diffusive charges are studied in detail using impedance spectroscopy and transient electroluminescence. We find a correlation between the amount of diffusive charges and the lifetime of the OLED device, which can be attributed to their involvement in exciton–polaron annihilation processes.

This paper is organized as follows. In Section 2, we theoretically predict the influence of diffusive charges on impedance and transient electroluminescence measurements. The experimental description is in Section 3. Section 4 presents the results of our measurements and compares them with theoretical expectation.

* Corresponding author.
E-mail address: hans-peter.loebl@philips.com (H.-P. Loebl).

Section 5 is the summary. The detailed derivations are in the appendix section, Appendix A.

2. Theory

In the on-state, the space charges, Q_c, drift towards the recombination zone, which corresponds to the conduction current:

$$J_c = \mu E q Q_c \tag{1}$$

where μ is the charge mobility, E is the strength of the electric field, and q is the elementary charge. When a small alternating voltage is applied in addition to the direct voltage, the electric field becomes time dependent, and the total current density reads:

$$J = J_c + \varepsilon \frac{\partial E}{\partial t} \tag{2}$$

which is the sum of conduction current and the displacement current. The electric field is determined by the total charge density according to Poisson's equation:

$$\frac{\varepsilon}{q} \frac{\partial E}{\partial x} = Q_s \tag{3}$$

where Q_s is the density of the space charges. $Q_s = Q_c$ holds, if all the space charges drift in the electric field and contribute to the conduction current. The capacitance and conductance has been derived by Shao et al. [9] and Kassing [10], respectively. In reality however, not all the space charges drift towards the recombination center nor recombine there with no delay. Complex local environment can scatter the charges, turning a portion of space charges into diffusive charges. The diffusive charges have unpredictable trajectories because of the stochastic collisions and scatterings. As a consequence of their random trajectories, the diffusive charges do not contribute to the conduction current. Thus the total number of charges, Q_s, in real devices is the sum of conducting charges, Q_c, and diffusive charges, Q, i.e. $Q_s = Q_c + Q$. We therefore rewrite Eq. (3) as:

$$\frac{\varepsilon}{q} \frac{\partial E}{\partial x} = Q_c + Q \tag{4}$$

With Eqs. (2)–(4) and the small signal approximation [11], we deduce the capacitance which reads:

$$C = \frac{\varepsilon^2 A \theta^2 (\cos\theta - 1 + \theta^2/2)}{\mu J_0 T_L^2 \left[(\cos\theta - 1 + \theta^2/2)^2 + (\theta - \sin\theta)^2 \right]} + \frac{\varepsilon A \theta q Q (\theta - \sin\theta)}{J_0 T_L \left[(\cos\theta - 1 + \theta^2/2)^2 + (\theta - \sin\theta)^2 \right]} \tag{5}$$

where $\theta = \omega T_L$, A is the area of the device, J_0 is the direct current, and T_L is the charge transit time, during which the charges drift from the electrode to the recombination zone. When the diffusive charges, $Q = 0$, Eq. (5) is identical with the capacitance derived by Shao and Kassing for space-charge-limited diodes, which is roughly the geometric capacitance, C_{geo}. The second term in Eq. (5) is an extra capacitance related to the density of diffusive charges. The extra capacitance leads to a pronounced bump in the low frequency region (Fig. 1).

We have shown in our earlier work [6] that the diffusive charges can be quantitatively evaluated with transient electroluminescence measurements when the off-state luminescence is dominated by trap-assisted recombination between the diffusive charges and the trapped charges. Here, we eliminate the Q in Eq. (5) with parameters obtained by transient EL measurement. In Eq. (5), $J_0 T_L$ is the amount of charges arriving at the recombination zone after the charge transit time. We assume strong recombination [12], i.e. all drifting charges recombine immediately at the
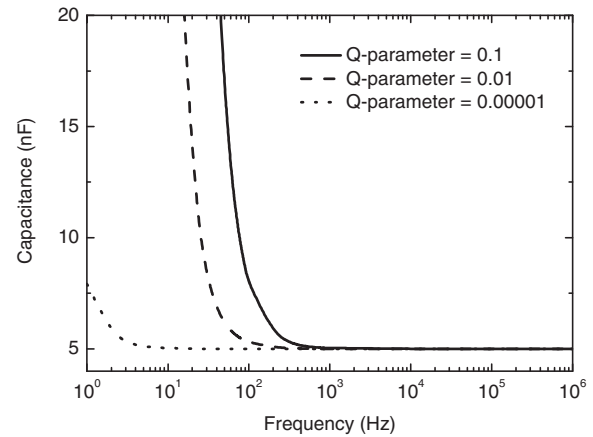

Fig. 1. The capacitance versus the frequency calculated from Eq. (7). $C_{geo} = 5$ nF, $T_L = 500$ ns, $\varepsilon = 3$, $A = 20$ mm^2.

recombination zone, and $J_0 T_L = Q_c$ holds. Hence, $Q/(J_0 T_L + Q)$ is the ratio of the diffusive charges to the total amount of injected mobile charges, which has been defined in our previous paper [6] as the Q-parameter, $\tilde{Q}^*$, and can be obtained by fitting the turn-off luminescence [6]. Therefore we rewrite Eq. (6) with $Q/J_0 T_L$ replaced by:

$$\Theta = \frac{\tilde{Q}^*}{1 - \tilde{Q}^*} \tag{6}$$

Substituting Eq. (6) into Eq. (5) and approximating the first term on the right side of Eq. (5) by the geometric capacitance, we get:

$$C \approx C_{geo} + \frac{\Theta \varepsilon A \theta (\theta - \sin\theta)}{\left(\cos\theta - 1 + \theta^2/2 \right)^2 + (\theta - \sin\theta)^2} \tag{7}$$

Eqs. (6) and (7) suggest an explicit relation between the capacitance and the Q-parameter which characterizes the amount of diffusive charges. The 'extra' capacitance (second term in Eq. (7)) increases with the Q-parameter. At high frequency, the capacitance approaches the geometric capacitance (Fig. 1). It may be non-trivial to point out that to get Eq. (7) from Eq. (5), we have assumed that the amount of diffusive charges in the on-state and in the off-state is identical. The validity of this approach is based on the assumption that the internal system is in a quasi-steady state shortly after turning-off the OLED-device [6].

To summarize: we suggest the presence of the diffusive charges in the emitting layer. The non-drifting behavior of the diffusive charges leads to an 'extra' capacitance in low-frequency region. The amplitude of the 'extra' capacitance is proportional to the Q-parameter which can be extracted from the time dependence of the off-state luminescence (time resolved EL measurement).

3. Experimental

To verify the theory, we have fabricated a series of OLEDs on indium-tin oxide (ITO, transparent anode) coated glass substrates by thermal evaporation of organic molecules at a base pressure of typically 10^{-5} Pa. The diode area was 20 mm^2. We chose 1,1-bis((di-4-tolylamino) phenyl) cyclohexane (TAPC) as hole transport material. bis-4,6-(3,5-Di-3-pyridylphenyl)-2-methylpyrimidine (B3PyMPM) or bis-4,6-(3,5-di-4-pyridylphenyl)-2-methyl pyridine (B4PyMPM) are doped with 4,4′,4″-Tri(N-carbazolyl)triphenylamine (TCTA) and the emitter molecules. The structure of the devices was: ITO (150 nm)/TAPC (52 nm)/TCTA (10 nm)/TCTA: B3PyMPM: $y = $ Ir(ppy)$_3$: $x = $ Ir(MDQ)$_2$acac(30 nm)/B3PyMPM (45 nm)/LiF (1 nm)/Al (100 nm) for the first series of experiments (B3 series). The red emitter molecules Ir(MDQ)$_2$acac act as hole