APPLYING CHEMICAL REACTION PRINCIPLES TO INVESTIGATE THE DYNAMICS OF ORGANIC LIGHT-EMITTING DEVICES

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Abstract

The Dow Chemical Company is placing increased focus on value-added markets, continuing a transformation from what was an inorganic chemicals company over 100 years ago, to a petrochemicals and plastics company, and now to an increasingly science-driven company operating at the intersection of sciences including materials science and physics. This transformation presents opportunities to apply trusted methods in chemical engineering to new and exciting areas of growth. Dow has partnered with the University of Minnesota to develop a more fundamental understanding of organic light-emitting devices (OLEDs), a growth area in display technologies. In this presentation, we detail the application of mean-field kinetic modeling to describe exciton and polaron dynamics in OLEDs and pair this analysis with optical measurements to develop a more complete understanding of degradation in model OLEDs. The model successfully replicates the full rise and fall of measured electroluminescent transients and is constructed from physically relevant terms that address charge formation, exciton formation and lifetime, and bimolecular exciton annihilation/quenching. The model is extended to describe the roll-off of steady state external quantum efficiency. The model and optical measurements are combined to provide insight into OLED performance and degradation mechanisms, which can be used to target improved designs.

Keywords

OLED, exciton, polaron, dynamics, kinetic model, roll-off, electroluminescence, photoluminescence

Introduction

Fully understanding the dynamic mechanisms that occur under electrical excitation of organic light-emitting devices (OLEDs) is critical for understanding device performance. External quantum efficiency (EQE) roll-off (i.e., decreased EQE with increasing current density), device degradation, and the impact of molecular structure and device architecture on performance are all influenced by dynamic processes within the device. Transient electroluminescence (EL) is an important technique for analyzing dynamic processes. The EQE roll-off behavior of Ir-based phosphorescent OLEDs has been well characterized and previously attributed to bimolecular exciton quenching and a loss of charge balance (Reineke, et al., 2007; Erickson and Holmes, 2014). While the associated rates of quenching have been previously extracted using transient photo-luminescence (PL) measurements, the derived models have to date been unable to fully replicate the transient EL decays. Previous attempts to model transient EL have used a biexponential decay that is not grounded in a treatment of exciton and polaron dynamics (Baldo, et al., 2000; Erickson and Holmes, 2014). Here, we model the transient evolution of both the exciton and polaron densities, and are able to successfully replicate the full transient EL behavior. Central to this approach is the use of a spatially independent exciton formation rate that results from a dynamic polaron population, allowing the model to fit both the rise in EL as well as the subsequent decay. We pair this photophysical model with optical measurements to better understand the dynamic processes responsible for device performance.

Methods

Transient electroluminescence is an application of a short, constant current-voltage pulse, usually on the order of hundreds of nanoseconds to several microseconds, while recording the resulting luminance behavior. The system of differential equations used to replicate the transient behavior, including both the rise and fall of luminance, are as follows:

$$\frac{dN(t)}{dt} = -\frac{1}{2}k_{tt}N(t)^2 - \frac{N(t)}{\tau} - k_{tp}N(t)P(t) + \frac{1}{2}k_{ppx}P(t)^2 \quad (1)$$

$$\frac{dP(t)}{dt} = -k_{ppx}P(t)^2 + \frac{2J(t)}{ew} \quad (2)$$

where N and P are the exciton and polaron population densities, respectively. The natural exciton lifetime, τ is an exponential decay. The triplet-triplet annihilation, k_{tt}, and triplet-polaron quenching, k_{tp}, are bimolecular decay terms. Excitons are populated from the polaron population via the exciton formation rate, k_{ppx}. Polarons are generated from the injected current density (captured by the last term in Eq. 2). This model is spatially independent, modeling exciton and polaron densities under a mean-field approximation. Experimentally, only the exciton population is observed, being strictly proportional to the observed luminance, which is fit using the model above. The model is also solved for the steady-state solution to allow for modeling of EQE roll-off. The model and optical measurements are combined to provide insight into OLED performance and degradation mechanisms, which can be used to target improved designs

Results and Discussion

Transient EL was performed on a model OLED device based on the phosphorescent guest fac-tris(2-phenylpyridine) iridium(III) ($Ir(ppy)_3$). The dynamic model (Eqs. 1 and 2) was successfully employed to describe the full rise and fall of the EL transient over a wide range of current densities and device areas, as shown in Figure 1. Note that the measured EL is FFT filtered to allow for a more straightforward comparison of fit vs. measured data as the EL noise floor is approached at values of normalized EL less than 0.01. The fit parameters are listed in Table 1 and compared to values extracted from PL measurements (where possible) on the same device. Good agreement is seen between the fit and measured values, providing increased confidence in the model.

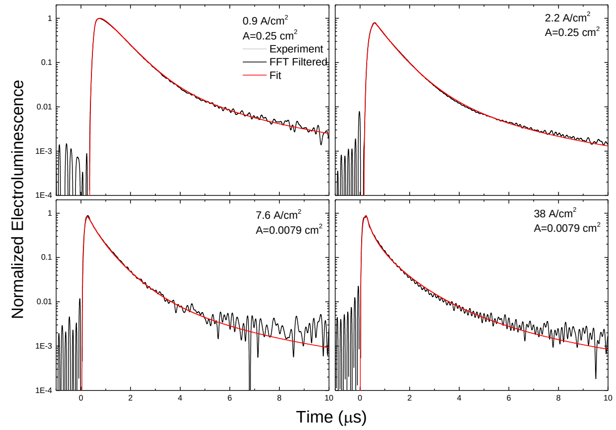

Figure 1. Transient EL Modeling Results

Table 1: Model Parameters vs. Measurements

Parameter	Transient EL	PL Measurement
τ (s)	$6.1 \pm 0.3 \times 10^{-7}$	$1.7 \pm 0.2 \times 10^{-6}$
k_{tt} (cm^3/s)	$2.1 \pm 0.8 \times 10^{-13}$	$4.1 \pm 2.5 \times 10^{-13}$
k_{tp} (cm^3/s)	$1.5 \pm 0.6 \times 10^{-13}$	2.8×10^{-13}
k_{ppx} (cm^3/s)	$3.9 \pm 1.1 \times 10^{-12}$	--

Conclusions

We present a model of transient EL that is grounded in physical exciton and polaron dynamics that fully replicates the rise and fall of the EL transient in a model OLED across multiple orders of magnitude in current density and device area. In further implementations, the model will allow for the comparison of the physical parameters to better understand how these fundamental mechanisms are related to device performance and degradation. When paired with PL measurements, a better understanding of electrical vs. optical losses can be obtained, facilitating a better understanding of degradation mechanisms.

References

Baldo, C., Adachi, C., Forrest, S.R. (2000). Transient analysis of organic electrophosphorescence. II. Transient analysis of triplet-triplet annihilation. *Phys. Rev. B*, *62*, 10967.

Erickson, N.C., Holmes, R.J. (2014). Engineering Efficiency Roll-Off in Organic Light-Emitting Devices. *Adv. Funct. Mater.*, *24*, 6074.

Reineke, S., Walzer, K., Leo, K. (2007). Triplet-Exciton Quenching in Organic Phosphorescent Light-Emitting Diodes with Ir-Based Emitters. *Phys. Rev. B*, *75*, 125328.