Simultaneous measurement of electron and hole mobilities in polymer light-emitting diodes

H. C. F. Martens[a)]
Kamerlingh Onnes Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

J. N. Huiberts
Philips Research Laboratories, Professor Holstlaan 4, 5656 AA Eindhoven, The Netherlands

P. W. M. Blom
Materials Science Centre, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

The transport properties of electrons and holes in a poly(p-phenylene vinylene)-based polymer light-emitting diode (PLED) have been investigated. Using admittance spectroscopy, we are able to simultaneously obtain the electron and hole mobility, $\mu = \mu_0 \exp(\gamma \sqrt{E})$, in a single PLED. The dynamics of the electron and hole transport are separated in the frequency domain as a result of the different transit times. At room temperature, we find $\mu_0 = 5.6 \times 10^{-11}$ m^2/V s and $\gamma = 5.0 \times 10^{-4}$ (m/V)$^{1/2}$ for holes. For electrons $\mu_0 = 1.0 \times 10^{-12}$ m^2/V s and $\gamma = 8.0 \times 10^{-4}$ (m/V)$^{1/2}$ are obtained. © *2000 American Institute of Physics.* [S0003-6951(00)03538-5]

Conjugated polymers have attracted widespread attention as promising materials for large-area applications based on polymer light-emitting diodes (PLEDs).[1] Attention has especially been focused on poly (p-phenylene vinylene) (PPV) and its derivatives. Understanding charge-transport in PPV-based LEDs has been one of the major goals in the effort to optimize device performance.

To study the charge-carrier mobility μ, usually time-of-flight (TOF) or current–density–voltage [$J(V)$], experiments are performed. In TOF the transit-time τ_t of a sheet of photo-injected carriers is monitored. In the absence of dispersive transport, τ_t is directly related to μ:

$$\tau_t = \frac{L^2}{\mu V}, \tag{1}$$

with L thickness and V applied potential. Transient studies of hole transport in conjugated polymers[2–5] have established that the hole mobility is well described by

$$\mu = \mu_0 \exp(\gamma \sqrt{E})$$
$$= \mu_\infty \exp\left[-\frac{\Delta}{k_B T} + B\left(\frac{1}{k_B T} - \frac{1}{k_B T_0} \right) \sqrt{E} \right]. \tag{2}$$

Unfortunately, TOF suffers from certain restrictions. Experiments on PPV require $L \sim 1-10\ \mu$m, since the absorption depth of the optical excitation must be small compared to the film thickness. However, as the preparation procedure may influence the material structure,[6] the mobility in such thick (dropcast) films may differ from that in thin (~ 100 nm) spin-coated PLEDs. Moreover, dispersive transients due to trapping and/or strong disorder complicate the determination of τ_t. Especially for electron transport this proves to be problematic. Photocurrent transients of electrons in conju-

gated polymers reveal a featureless decay without a discernible transit time,[2,4] and electron mobilities derived from TOF have not yet been reported for PPV.

In the case of space-charge-limited (SCL) transport, μ can also be derived from $J(V)$ experiments. In the absence of traps, the single-carrier SCL current is

$$J = \frac{9}{8} \varepsilon \mu \frac{V^2}{L^3}, \tag{3}$$

with ε the dielectric constant. Hole transport in PPV is space-charge limited, and from the $J(V)$ characteristics a hole mobility of 5×10^{-11} m^2/V s for our PPV derivative has been obtained.[7] From $J(V)$ measurements on electron-only devices it has been obtained that in our material the electron current is more than three orders of magnitude lower than the hole current.[7] Furthermore, the electron current exhibited a stronger and markedly different field dependence as compared to the hole current. The low electron current and strong field dependence have been explained by assuming the presence of electron traps.[7] Recent $J(V)$ experiments by Bozano *et al.* have revealed a larger electron current,[8] which has been interpreted as a trap-free SCL current. The electron mobility following from their $J(V)$ characteristics amounts to 10^{-12} m^2/V s at room temperature, which is still a factor 30–50 lower than the reported hole mobilities for PPV. However, whether this reported electron mobility is indeed intrinsic and whether material preparation and device processing play a role in the reduced electron transport[7,8] is not clear.

Summarizing, the current state of affairs is that (1) transport properties of holes in conjugated polymers have been widely studied by TOF and $J(V)$ experiments, (2) extensive investigation of electron transport has not yet been possible, and (3) established techniques require purpose-made single-carrier devices in order to derive the mobility. Thus, to improve the present knowledge of carrier transport in PLEDs requires a technique capable of deriving both the electron-

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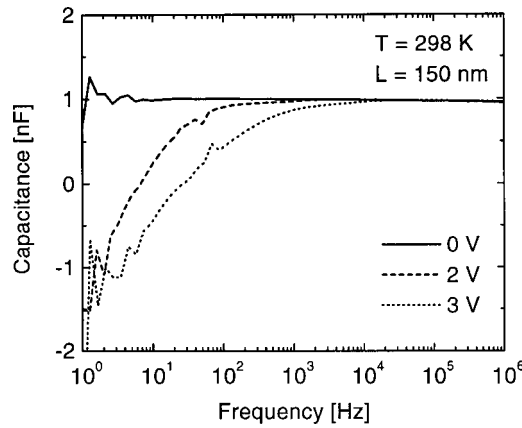[a)]Electronic address: martens@phys.leidenuniv.nl

FIG. 1. Frequency-dependent capacitance of a polymer LED as a function of bias voltage. At zero bias the capacitance is nearly frequency independent. At finite bias voltage a negative contribution to C sets in. Upon increasing the bias the negative contribution shifts to higher frequency.
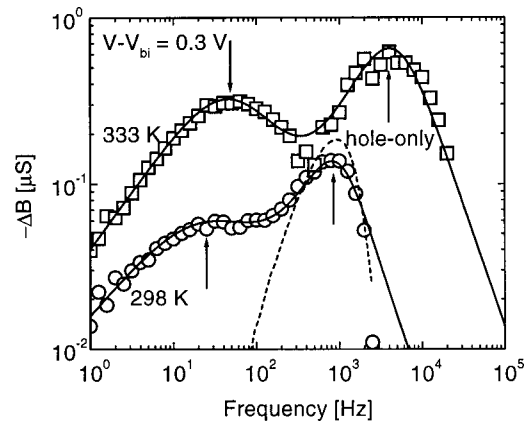

FIG. 2. Double-logarithmic plot of the negative differential susceptance $-\Delta B = -\omega(C-C_0)$ of a PLED ($L=150$ nm) at $V-V_{bi}=0.3$ V for two temperatures. Two relaxation peaks are clearly distinguished. For comparison, $-\Delta B$ of a hole-only device ($L=150$ nm, $V-V_{bi}=0.3$ V) is shown, revealing only a single relaxation peak; its position coincides with the high-frequency peak of the PLED. Solid lines are fits to determine the relaxation times; the arrows indicate the corresponding τ^{-1}.

and hole-transport properties, and which can be applied to actual PLEDs in order to eliminate possible effects of different fabrication procedures on the charge transport.

Here, we present a technique which meets the above requirements. The electron and hole mobilities are simultaneously obtained by means of admittance spectroscopy on PLEDs. Charge transport at time-scale τ is reflected in the frequency domain around $\omega \approx \tau^{-1}$, which allows us to unravel different dynamical processes. In a recent study[9] it has been demonstrated that the finite transit time τ_t of holes in PPV-based hole-only devices is reflected in the admittance. From the specific frequency-dependent response the hole mobility could be derived.[9] In the PLED the transit of both electrons and holes can be clearly separated in the frequency domain, yielding the respective carrier mobilities. In contrast to $J(V)$ and TOF, admittance spectroscopy does not suffer from the presence of deep traps, since release rates from deep traps are $\ll 1$ s^{-1} and, hence, fall out of the frequency window studied here (Hz–MHz).

The material studied is OC_1C_{10}–PPV.[10] The polymer is spin coated on an indium–tin–oxide (ITO) anode on top of a glass substrate. The cathode is formed by evaporating Ca. The different work functions of ITO and Ca give rise to a built-in voltage $V_{bi}=1.7$ V. The fabrication and admittance experiments are performed under a nitrogen atmosphere. In an admittance experiment the relaxation of charge density under the influence of an (ac) electrical disturbance is probed. In general, the corresponding ac current is not in phase with the ac voltage and the admittance Y is complex:

$$Y = i_{ac}/v_{ac} = G + iB = G + i\omega C, \qquad (4)$$

with G conductance, B susceptance, C capacitance, $i = \sqrt{-1}$, and $\omega = 2\pi f$ the angular frequency.

In Fig. 1 the frequency-dependent capacitance of a PLED ($L=150$ nm) is shown as a function of bias. At $V=0$ V the capacitance is essentially frequency independent, and equals the geometrical capacitance $C_0 = \varepsilon A/L$. At finite bias a negative contribution to C appears, shifting to higher frequencies when increasing V. This inductive contribution is more clearly resolved by plotting the differential susceptance $-\Delta B(\omega) = -\omega(C-C_0)$. Figure 2 displays $-\Delta B$ at $V-V_{bi}=0.3$ V for two temperatures. For comparison, we in-

clude the room temperature $-\Delta B$ for a hole-only device ($L=150$ nm and $V-V_{bi}=0.3$ V). While in the hole-only device only a single peak is present, for the PLED two relaxation peaks can be distinguished. The relaxation frequencies increase when heating the sample.

The inductive contribution in hole-only devices stems from redistribution of space charge when the electrical field is varied.[9] Changing the applied voltage leads to injection of additional space charge. Under the influence of the bias field, the injected charge moves into the device to relax to the new equilibrium space-charge distribution. Due to the finite τ_t the corresponding current lags behind the ac voltage, and this gives an inductive contribution to the capacitance, see Eq. (4). For times short compared to τ_t, or frequencies $\omega > \tau_t^{-1}$, the injected carrier density cannot relax and the inductive contribution disappears. For single-carrier SCLC, the admittance Y_{SC} can be analytically calculated, see Eq. (4) of Ref. 9. The relaxation time τ is obtained by maximizing $-\Delta B_{SC} = \omega C_0 - \mathrm{Im}(Y_{SC})$ with respect to ω, giving $\tau \approx 0.29 \times \tau_t$. The factor 0.29 stems from the nonhomogeneous electrical field in the device; it would be absent for a homogeneous field.

In a PLED, both electrons and holes are present and charge redistribution will be governed by two transit times. Indeed, Fig. 2 clearly reveals two inductive processes, reflecting the transit of electrons and holes. At room temperature, the position of the high-frequency peak coincides with that of a hole-only device with similar thickness and bias field, and we assign it to the transit of holes. Then the low-frequency peak reflects the electron transit, and shows that μ_n is at least one order of magnitude less than μ_p. Anticipating that $\mu_p \gg \mu_n$, the charge density in the bulk of the device is dominated by hole space charge, and the electrical field will be close to that of a hole-only device.[11] In this case, the relaxation times in the PLED are $\tau_n \approx 0.29 \times \tau_{tn}$ and $\tau_p \approx 0.29 \times \tau_{tp}$. Indeed, in the PLED and hole-only device the "hole-transit peaks" are located around the same frequency. The peak positions are obtained using a peak-fitting procedure, see the solid lines in Fig. 2, from which we derive the carrier mobilities.
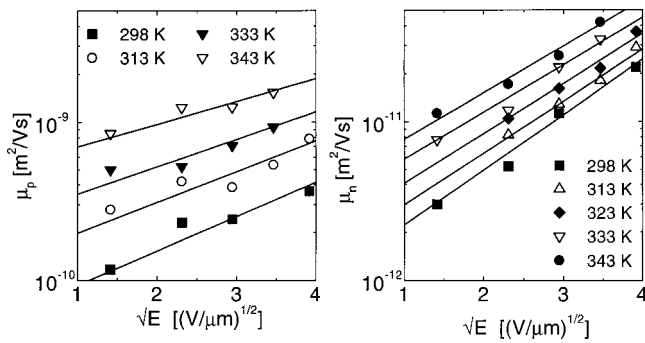
FIG. 3. Hole mobility (left) and electron mobility (right) in $OC_1C_{10}-PPV$ as a function of $\sqrt{E}$ and T. Solid lines are fits to the $\ln(\mu) \propto \sqrt{E}$ equation for hopping transport in a spatially correlated potential.

Figure 3 displays the temperature and field dependence of the derived electron and hole mobilities. The data are fitted to the $\sqrt{E}$ law. At room temperature we obtain for holes $\mu_0 = 5.6 \pm 0.9 \times 10^{-11}$ m^2/V s and $\gamma = 5.0 \pm 0.5 \times 10^{-4}$ (m/V)$^{1/2}$. For the electron mobility we find $\mu_0 = 1.0 \pm 0.2 \times 10^{-12}$ m^2/V s and $\gamma = 8.0 \pm 0.5 \times 10^{-4}$ (m/V)$^{1/2}$. In Fig. 4 the temperature dependence of γ and μ_0 are shown; solid lines are fits to Eq. (2). This gives for holes $\Delta = 0.42$ eV, $\mu_0 = 3.3 \times 10^{-4}$ m^2/V s, $B = 3.1 \times 10^{-5}$ eV (m/V)$^{1/2}$, and $T_0 = 520$ K, in good agreement with previously reported values.[9,12] The electron parameters are $\Delta = 0.29$ eV, $\mu_0 = 6.5 \times 10^{-8}$ m^2/V s, $B = 3.1 \times 10^{-5}$ eV (m/V)$^{1/2}$, and $T_0 = 900$ K. Interestingly, despite the much lower electron-only current in our material[7] compared to the measurements of Bozano and co-workers,[8] the electron mobility derived here from admittance spectroscopy and that from Bozano's $J(V)$ experiments are in excellent mutual agreement. Likely, the deep traps that limit the electron current in our material have release rates $\ll 1$ s^{-1}. Such slow dynamics are not visible in the present frequency range and only the ''mobile'' electrons are observed.

The $\sqrt{E}$ mobility, Eq. (2), stems from hopping transport in a spatially correlated random potential.[13] Simulations of transport in a correlated disorder model (CDM) give an expression for the mobility, parametric in disorder bandwidth σ, and site separation a.[13] In a recent study of hole transport in PPV derivatives,[14] it was shown that the CDM adequately describes $\mu_p(T,E)$ in PPV. For $OC_1C_{10}-PPV$, hole transport is characterized by $\sigma = 112$ meV and $a = 1.2$ nm.[14] Applying

the same analysis to μ_n gives $\sigma = 95 \pm 10$ meV and $a = 4 \pm 0.5$ nm. The apparent reduction of the energetic disorder for electrons, which is expected to enhance the transport,[14] is in contrast with the fact that the electron mobility is still about a factor 30–50 lower than the hole mobility. Furthermore, for highly ordered organic semiconductors it has been found that the electron and hole mobility are nearly equal.[15,16] This suggests that the derived electron mobility does not reflect the intrinsic electron transport in PPV. Additionally, the strong field dependence of the observed electron mobility translates into a four times larger site separation for electron transport. Since a is merely related to the topology of the polymer, such a large difference in site separation for electrons and holes is highly unlikely. Presumably, an additional mechanism increases the field dependence of μ_n. It has been shown recently that the presence of uncorrelated traps in the CDM leads to an additional field dependence of the mobility.[17] Therefore, the relatively low electron mobility and its strong field dependence are strong indications for the presence of electron traps. As a result, the reported electron mobility in the present study and Ref. 8 most likely represents an effective mobility. Disentanglement of the various contributions to electron transport in PPV is a subject of further investigation.

In summary, we have presented a method, based on admittance spectroscopy, to simultaneously determine the electron and hole mobility in PLEDs. In the temperature range studied, the hole mobility exceeds the electron mobility by more than an order of magnitude. For increasing field the difference decreases due to the stronger field dependence of the electron mobility. The different transport properties of holes and electrons, could indicate that the latter are governed by extrinsic effects.

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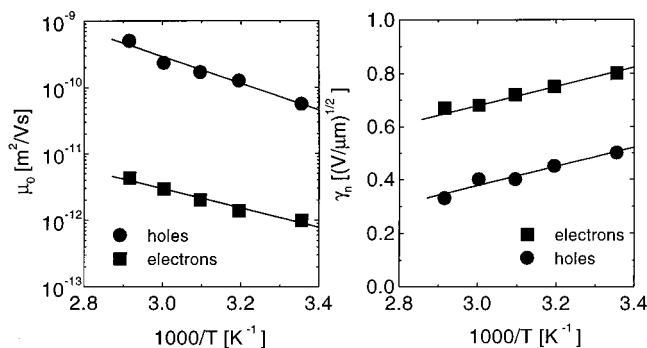
FIG. 4. Temperature dependence of zero-field mobility μ_0 and ''field activation'' factor γ derived from the measured $\mu_n(E,T)$ and $\mu_p(E,T)$. The data are fitted to Eq. (2).