Transient Space-Charge-Limited Current Measurements of Mobility in a Luminescent Polymer

J. C. Scott,* S. Ramos and G. G. Malliaras

IBM Research Division, Almaden Research Center, San Jose California, and Center on Polymer Interfaces and Macromolecular Assemblies (CPIMA)

Transient time-of-flight methods with voltage pulse injection have been adapted to determine the field dependent mobility of holes in the electroluminescent polymer, MEH-PPV. The time-resolved current response confirms that gold forms an Ohmic contact to MEH-PPV and that there are very few traps in the polymer. These conclusions are in agreement with earlier interpretation of steady-state current-voltage measurements.

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Introduction

Charge carrier mobility plays a pivotal role in the operation of organic light emitting diodes (OLEDs).[1] When charge carrier injection at the electrodes is Ohmic, the mobilities of electrons and holes dictate the operating voltage of the device, and hence its power efficiency. The dynamic response of an OLED is controlled by the rate at which electron and hole densities accumulate to the levels which ensure efficient recombination.[2] The relative mobilities of electrons and holes also play a role, albeit less important than their relative injection rates, in determining the quantum efficiency.[3] Because of various experimental difficulties, there are relatively few *direct* measurements of electron and hole mobilities in materials of interest for OLEDs.[4,5] It is the purpose of this article to present results on one such material, the luminescent polymer poly(2-methoxy-5-(2'-ethyl)hexoxy-phenylene vinylene) (MEH-PPV). The data were obtained from time-of-flight transients in the space-charge-limited regime using a novel extension of a standard experimental technique that we hope may be useful for other materials.

We[6,7,8] and others[9,10] have inferred charge carrier mobilities from steady state current measurements in single carrier devices. The assumptions behind this method of determination are that

(i) the current is space-charge-limited, i.e., that the injecting contact is Ohmic,
(ii) the transport is trap-free, or at least that the trapped charge density makes a negligible contribution to the space-charge field,
(iii) the mobility has a particular field dependence, usually taken to be the "Poole-Frenkel like" form $\mu \sim \exp\sqrt{E}$, and
(iv) the influence of the minority carrier may be safely neglected.

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* Corresponding author, e-mail address: jcscott@almaden.ibm.com

In view of the central role of mobility in OLEDs it is important to provide independent measurement as well as to test the validity of these assumptions. Several other methods have been suggested for the determination of mobility, including transient electroluminescence.[11,12] This approach has the difficulty of distinguishing the relative roles of electrons and holes, because by definition both signs of carrier must be injected into the device. Moreover, if the contacts limit the current it has been shown[2] that the delay in emission is not related to the transit time(s) of the carrier(s) but rather to the time required to accumulate sufficient charge in the recombination zone. The most direct method to obtain mobilities in organic semiconductors is well recognized to be transient time-of-flight (TOF) measurement.[13] This is typically performed in the "space-charge-free" limit using photogeneration of carriers. However, the photoinduced TOF technique has been successfully applied to conjugated polymers[5,14,15,16] and other luminescent OLED materials[4,17] in only a few cases. The difficulty here appears to be the necessity of preparing relatively thick (several microns), trap-free samples in order to observe non-dispersive transients with a well defined transit time.

In this article, we report TOF data in which the charges are injected by applying a voltage step to an Ohmic contact, the so-called transient space-charge limited current (SCLC) technique.[18] This method has been applied to organic semiconductors in the past,[19,20] typically using thick samples and therefore relatively high voltages. Here, we describe an experimental technique which permits the use of samples of order 100 nm in thickness, and voltages to below 1 V. Thus the same sample preparation techniques can be used as for OLEDs, and one does not need to worry that different materials processing may introduce, for example, different trapping behavior. Our new method is used to measure the mobility of holes in MEH-PPV. At the same time the data confirm that gold forms an Ohmic contact, and may permit a quantitative evaluation of charge trapping.

This article is arranged as follows. In the next section, we give the details of the experimental method.

Then we present the results and discuss their implications for the behavior of OLEDs. Finally we summarize our conclusions and present some ideas for the further extension of the transient SCLC approach.

Experimental

The transient SCLC technique is well established and is conceptually extremely simple. The sample, thickness L, is prepared in a sandwich geometry between two electrodes, at least one of which is Ohmic for the carrier of interest, i.e., it is capable of injecting and maintaining a space-charge-limited current. One applies a step change in voltage (V) and measures the time dependence of the resulting current response. For sufficiently low trap density and long trapping times, the current initially rises from a non-zero initial (post step) level to a value above its steady state value.[18] In the case of a field independent mobility, the maximum in the current occurs at a time $t_0 = 0.79t_T$, where $t_T = L^2/\mu V$ is the transit time for carriers in a field $E = V/L$. The analysis is more difficult when the mobility is field dependent, but a similar maximum is observed at the time when the first carriers reach the far electrode.

To date, the technique has been used mostly for relatively thick samples, such that the capacitance is low and the transit time, even at relatively high voltages, is long compared to the RC time constant of the circuit. (The relevant resistance is that in series with the sample, usually the input impedance of the detector electronics.) Thus the capacitive charging current has decayed long before the current maximum associated with the transit of the first carriers. The circuit that is used in this case is extremely simple: merely a voltage source, the sample and the current detector in series.[19] As the transit time becomes shorter at higher voltages and in thinner samples, it is necessary to "cancel out" the capacitive part of the response. Helfrich and Mark[21] described a bridge circuit which accomplishes this. It employed a floating voltage source and a single-ended amplifier as detector. In this work we used a different configuration of bridge that takes advantage of modern electronic equipment and offers several advantages over the earlier designs.

The circuit, still very simple, is shown in the inset to Fig. 1. Here the voltage source is referenced to ground, and can therefore be any commercial pulse generator with an appropriate rise time, pulse length, repetition rate, and voltage and current capability. The sample is placed in one arm of the bridge and the variable capacitor (C) adjusted to equal that of the sample. We find that a separate auxiliary low-level sinusoidal source is very helpful for balancing the bridge. A small variable resistor (R) is included in the tuning arm in order to compensate for any resistance in the leads to the sample. The matched resistors (R_1) in the other two arms of the bridge are selected so that the high frequency impedance of the entire bridge circuit is 50 Ohms and therefore matched to the cable from the pulse generator. Care is taken to equalize the lengths of all cables in the arms of the bridge. The short-time detection limit of this circuit is due to residual imbalances of the bridge which we believe are caused by the frequency dependent dielectric constant of the sample. We have been able to reduce this instrumental "dead-time" to <2 μs. The transient charge carrier current is detected using a commercial differential amplifier. Instruments with bandwidths up to 1 MHz and with gains of over 10^3 are readily available. Signal averaging techniques may also be used by repetitively pulsing the sample with a well-defined duty cycle. In this way, one may first investigate the behavior of a "well-rested" sample, separating the pulses by many minutes, and then explore the effects due to accumulation of trapped charge as the repetition period becomes short compared to the detrapping time.

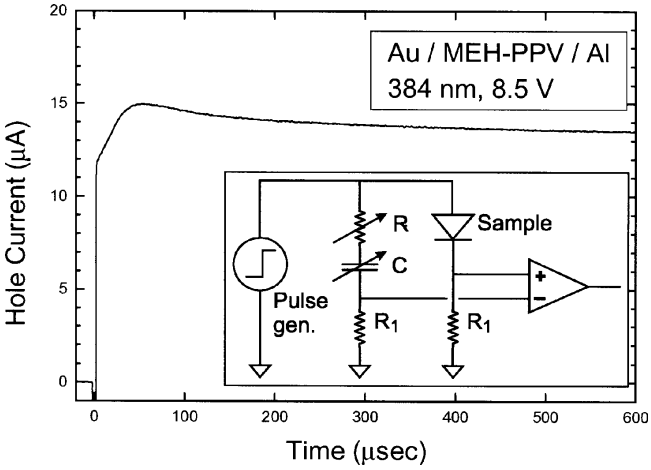

Figure 1. Typical transient current response to a step change in applied voltage. Some experimental details are given in the legend. The inset shows the bridge circuit used to minimize the influence of capacitive charging current, and to match the circuit to the transmission cable from the pulse generator.

In this article we present only data obtained with long times between pulses such that we are observing the transient behavior in a sample initially free of trapped charge. A typical response is shown in Fig. 1. The sample used here was 384 nm thick, with a gold anode and aluminum cathode. The sample was prepared in the same manner that we use for MEH-PPV light emitting diodes, as previously described.[22] For the data of Fig. 1, a voltage step from 0 to 8.5 V was applied, with a rise time of 10 ns. The current has the form expected for trap-free space-charge limited behavior. It starts (after the deadtime) at a non-zero value and rises to a clear maximum at 54 μs. It then settles to a virtually time independent steady-state value. The presence of the current maximum immediately establishes[18] that the trapping time is long compared to the transit time. The constancy of the current for times later than about $2t_T$ reveals that the trap density is low.

In Fig. 2, we plot the time of the current maximum as a function of the initial applied voltage, corrected for the built-in voltage which arises because of the difference in work-functions of the electrodes.[6] As expected, the transit time decreases as the voltage increases, until finally we can no longer detect it due to the instrumental dead-time.

Discussion

Extraction of the mobility from the time of the current maximum is complicated by the fact that the mobility depends on electric field. As discussed by Many and Rakavy[18] for the case of field independent mobility, the current maximum occurs when the first holes reach the cathode. As the carriers cross the sample, the field at the leading edge increases until at t_0 it is $2V/L$ at the cathode. It finally settles to $E_C = 1.5V/L$ in the steady state, at which time the position dependence of the field has the familiar $E \sim x^{1/2}$. When the mobility is an increasing function of electric field (as for the Poole-Frenkel form) the charge density in the low field region

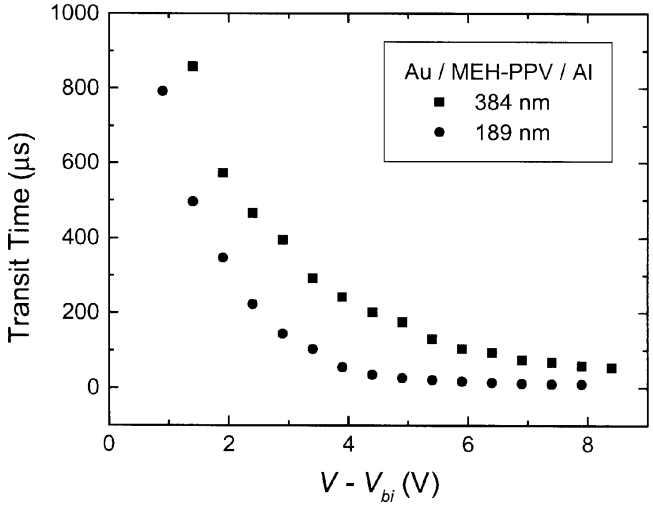

Figure 2. Transit time as a function of applied voltage for two sample of different thickness, as indicated.

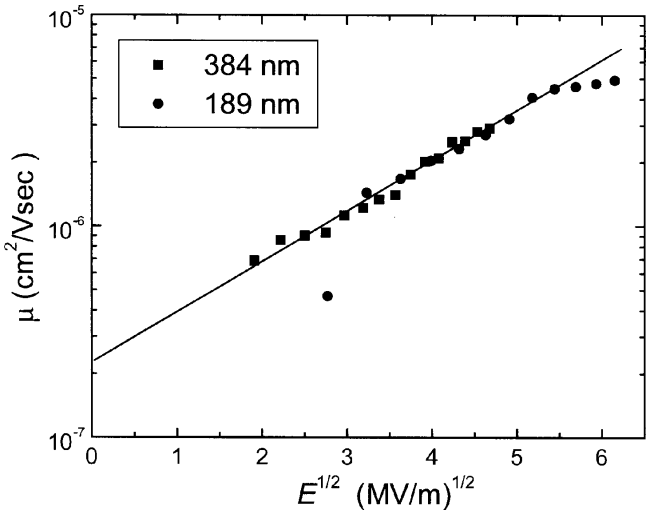

Figure 3. Mean mobility (see text for explanation of "mean") as a function of electric field, plotted according to the form of Eq. 2. The samples are the same as in Fig. 3.

near the anode is higher than the field independent case. Thus near the anode the field varies more steeply than square-root of distance, and less steeply near the cathode. We may therefore state the limits of the steady state cathode field, and correspondingly of the maximum field at the transient leading edge, as $V/L < E_C < 1.5\ V/L$. Thus when we derive a field dependent mobility from the fastest transit time, the reader should remember that we are giving a mobility *averaged over a range of fields* somewhat larger than the average field in the sample. (A more accurate treatment requires numerical analysis[23,24] and is the subject of ongoing study. Details will be published at a later date.)

With these caveats, we now present the averaged mobility values obtained from the current maxima according to the expression

$$\bar{\mu}(V/L) = 0.79L^2/t_0V. \qquad (1)$$

The results are plotted in Fig. 3, as ln(μ) versus $E^{1/2}$, where $E = (V - V_{bi})/L$ is the average field across the sample. The values of the hole mobility obtained from the time-of-flight compare well with those obtained previously from analysis of the steady state SCLC by ourselves[3,8] in MEH-PPV and others[9] in similar polymers. Writing the mobility in the form

$$\mu = \mu_0 \exp\sqrt{E/E_0}, \qquad (2)$$

we can extract the zero-field mobility $\mu_0 = 2 \times 10^{-7}$ cm²/Vs, and characteristic field $E_0 = 3.1$ MV/m.

In Fig. 4, we compare explicitly the experimental steady-state SCLC, determined as the limiting behavior of the current transient, with that expected from the measured mobility, namely[23]

$$J = (9/8)\varepsilon\varepsilon_0\mu_0 \exp(0.89\sqrt{V/E_0L})V^2/L^3. \qquad (3)$$

The values differ by about a factor of two, which may be partly accounted for by the effects of field dependent mobility but which may also reflect a small degree of trapping. The overall field dependence obtained from transient and from steady-state measurements is similar. The general agreement once again confirms that gold forms an Ohmic contact to MEH-PPV and that hole transport is close to the trap-free space-charge-limited regime.

In this first report describing the experimental method, we have presented detailed data on only a few samples, each with Au/Al electrodes. We have additional data on samples of different thickness and with other electrode materials. The results, which are in agreement with those presented here, will be given in a future publication.

The transient SCLC technique permits, in principle, the determination of the trapping time for the charge carriers crossing the sample. Indeed, by careful signal averaging techniques we are able to detect a drop in the hole current of typically <20 % which occurs with a characteristic time on the order of milliseconds. However, before we interpret this behavior as unequivocally due to trapping, it is necessary to evaluate another potential mechanism, namely ionic motion. If there is a (small) concentration of mobile anions or cations in the sample[25,26] they will drift under the influence of the applied electric field towards the electrode, setting up a dipole layer(s) and screening the field in the bulk of the material. Thus although the ion current itself may not be detectable, its effect, through changes in the electric field profile, may be observed in the electronic (here hole) current.

Conclusions

We have described an experimental technique which extends the well-established methodology of transient space-charge limited currents into a regime of sample thickness and voltage that is particularly appropriate for the study of materials used in organic light-emitting diodes. Experimental data obtained on MEH-PPV confirm clearly that gold forms an Ohmic anode for this luminescent polymer and that the transport of holes is in the trap-free space-charge-limited regime. The mobility, obtained from the time-of-flight, is found to depend on electric field, with a behavior that is well approximated by the Poole-Frenkel form. The steady-state space-charge-limited current predicted from the mobility agrees well with that measured directly.

It will be interesting to extend this method to electron transport in MEH-PPV, to bipolar devices and to other materials of interest. Such work is under way. It is worth commenting that we do not yet have useful electron data because of the difficulty of preparing reliable

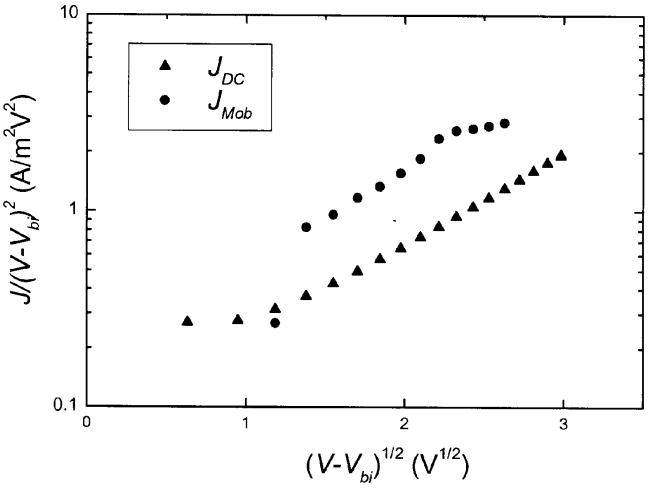

Figure 4. Comparison of the measured steady state space-charge-limited current (J_{DC}) with that predicted from the time-of-flight mobility (J_{MOB}), plotted according to Eq. 3. Sample, 189 nm in thickness, is one of those from Figs. 2 and 3.

and reproducible electrodes for the injection of electrons and the blockage of holes.

Transient SCLC measurement, using bridge circuits similar to the one discussed above, have the potential for determining additional important parameters of the materials used in OLEDs and other organic electronic devices. For example, trapping has a clear signature in the current decay following the voltage step; detrapping can be explored through variations of the pulse length and duty cycle; the field dependence of detrapping can be probed by applying a reverse bias during the "resting" time; and the effect of non-Ohmic electrode injection will be seen in early time behavior of the current and the suppression of the space-charge induced maximum. ▲

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