Current-Voltage Characteristics of Polymer Light-Emitting Diodes

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ABSTRACT

Conduction in pristine conjugated polymers (other than polyacetylene) is by polaron hopping between sites corresponding to conjugation lengths. The strong increase of current $I$ with voltage $V$ observed for both emission-limited and ohmic contacts is due in large part to mobility increase as increasing field makes it more possible to overcome internal barriers, such as energy differences between sites. For emission-limited contacts an additional source of nonlinear increase of $I$ with increasing $V$ is greater ability to escape return to the injecting electrode due to the image force. For ohmic contacts additional nonlinearity comes from space charge effects. We are able to fit $I$ vs. $V$ for electron or hole conduction in some poly($p$-phenylene vinylene), PPV, derivatives with ohmic contacts for reasonable values of the parameters involved.

Keywords: contacts, mobility variation with field, polarons, hopping, disorder

2. INTRODUCTION

Contact injection into conducting polymers has usually been described as tunneling of electrons or holes into a broad conduction or valence band, respectively, in the polymer through interface barriers arising from the band offset between the polymer and the metal electrodes. This picture must be corrected in several respects. First, the existence of broad continuous bands requires essentially infinite conjugation length whereas, it is generally acknowledged, typical conjugation lengths of PPV, for example, are $\sim 6$ or 7 monomers. For the typical conjugation length the average spacing between levels is $\sim$ several $kT$ at room temperature. A more essential objection is that the carriers are much more likely to tunnel into polaron levels than into the discrete levels in the “conduction band” or “valence band” because the polaron levels are lower in energy. The polaron levels available for electron injection lie below the lowest unoccupied molecular orbital (LUMO), while those available for hole injection lie above the highest occupied molecular orbital (HOMO). The separation of the polaron level from the LUMO or HOMO depends on chain length. For PPV, calculations give the separation as 0.15 eV or 0.2 eV for very long segments, increasing to $\sim$ 0.7 eV for a 3-monomer long segment. Although the polaron levels do not exist unless they are occupied by an electron or hole, tunneling into them may be facilitated by preparation of the appropriate chain deformation through the large zero point fluctuations characteristic of quasi-one-dimensional materials.
Once an electron or hole tunnels into a polaron level near the contact, under the influence of the electric field it moves toward the other contact, hopping from one conjugation length to another. The variation in conjugation length and the presence of defects result in a spread in energy of the hopping sites (diagonal disorder). Additional disorder is provided by the random orientation and variations in separation of the sites (off-diagonal disorder). As has been pointed out by a number of authors, the situation for hopping transport in a conjugated polymer is quite similar to that in molecularly doped polymers. Strong evidence for the similarity comes from the fact that the field dependence of the mobility $\mu$ generally observed for molecularly doped polymers,

$$\mu = \mu_0 e^{\alpha E^{1/2}},$$

$\alpha$ being a constant, has now been observed for PPV and a couple of its derivatives.\(^7\)\(^8\)\(^9\) This field dependence is a result of disorder. An appropriate model for treating transport in these systems for low injection is the disorder model pioneered by Bässler and associates.\(^10\) The distribution in energy of hopping sites, in this case the polaron states, is taken as a Gaussian with variance $\sigma$.\(^10\) Comparison of disorder theory with various experimental data for PPV leads to $\sigma \sim 0.1$ eV for that case.\(^11\)

The behavior of a contact depends critically on the location of the polaron states relative to the Fermi energy, $E_F$, of the metal. Internal photoemission measurements, such as those of Campbell et al.\(^12\) yielding the energy required to inject an electron from a metal into a polymer, give the energy difference between $E_F$ and some average state in the polaron distribution. We denote this energy by $W$. In section II we discuss $I$-$V$ characteristics for a case of large $W$, which means small injection, using the results of a Monte Carlo simulation based on the disorder model.\(^13\) In section III we carry out calculations for $W \sim 0$, or ohmic contacts, first for the case of only one contact injecting,\(^14\) then for both contacts injecting. We use the classical approach of Lampert for both cases.\(^15\),\(^16\) In the former case we obtain good agreement with the current $I$ vs. voltage $V$ characteristic of poly(2-methoxy, 5-(2′-ethyl-hexyloxy)-1, 4 $p$-phenylene vinylene), MEH-PPV, samples with only electrons injected, from a Ca contact\(^12\) for which photoemission gives $W \sim 0$.\(^12\) This calculation requires taking into account trapping of the electrons. A calculation of $I$ vs. $V$ for electrons only injected, including trapping, was carried out for poly(dialkoxy phenylene vinylene).\(^17\) The steep experimental variation of $I$ with $V$ was fitted by assuming a distribution of traps exponential in energy. These results are not meaningful, however, because mobility was taken as constant rather than varying with field according to Eq. (1). In later work by some of the same authors calculations were carried out for poly(dialkoxy PPV) samples with hole injection only, for which trapping may be neglected, with $\mu$ given by Eq. (1) and the contacts assumed ohmic.\(^9\) These calculation give good agreement with experimental $I$ vs. $V$ despite the fact that $W \neq 0$ for the ITO contact that was used. The agreement supports the assumption that this contact was nevertheless not emission-limited for the range of fields in the study.\(^9\)
3. I-V CHARACTERISTIC FOR LARGE $W$

Large $W$ implies emission-limited contacts, which in turn usually means space charge effects may be neglected. Current variation with field may then be obtained by the usual Monte Carlo simulation for transport in disordered materials. We followed the treatment of Ref. 13. Taking $E_F$ of the metal as the zero of the energy scale and the metal-polymer interface as $x = 0$, we may write the energy $U$ of a polaron site in the electric field:

$$U(x) = W - e E x - \frac{e^2}{4 \kappa x}$$

(2)

where the last term represents the image force, $\kappa$ being the dielectric constant, taken as 3. In the presence of energetic disorder $U(x)$ gives the mean energy $\bar{\varepsilon}(x)$ of a polaron site at $x$. The energy $\varepsilon$ is assumed to have a Gaussian-distribution around $\bar{\varepsilon}$ given by $P(\varepsilon, \bar{\varepsilon}) = \frac{1}{(2\pi\sigma^2)^{1/2}} \exp\left[-\frac{(\varepsilon - \bar{\varepsilon})^2}{2\sigma^2}\right]$. The rate of carrier tunneling into a polaron state of energy $\varepsilon$ at $x$ is assumed to be $v_m(x) e^{-\varepsilon/kT}$, where the last factor represents the probability of the carrier having thermal energy $\varepsilon$ above $E_F$. The total number of carriers tunneling into polaron levels at $x$ per second is then $v_m(x) \exp\left[-(\bar{\varepsilon}(x) - \sigma^2/2kT)/kT\right]$. It is reasonable to assume that this represents the initial population in the first layer of the polymer. Thus, as expected for large $W$, the mean energy of the initially populated sites is below $\bar{\varepsilon}$, specifically by the amount $\sigma^2/kT$. It is apparent from this that increase in $\sigma$, i.e., broadening the energy distribution of transport sites by disorder, increases the current tunneling into the polymer. This effect was found experimentally by Vestweber et al., who noted that the LED current increased with increase in $\sigma$, indicating that the increased injection dominates over the decreased $\mu$ that also results from increase in disorder.

Given the rate of carriers initially tunneling into the polymer and their distribution in energy, we can determine by Monte Carlo simulation the yield, i.e., the fraction of these carriers that escapes the return to the electrode and reaches the other boundary of the sample. Even in the absence of disorder the image force results in the great majority of carriers returning to the electrode at low fields. An analytic solution for small injection (space charge neglected) in the ordered case based on Eq. (2) gives the yield as 0.3 % in a field of $1.25 \times 10^5$ V/cm at 300 K for the parameters of Ref. 13. The results for the Monte Carlo simulation for $\sigma = 0$ were in good agreement with the analytic solution. In the disordered case the carriers have to overcome the random barriers due to disorder as well as the image force. The result is that at fields $\sim 10^5$ V/cm mild disorder ($\sigma = 0.08$ eV) results in a yield smaller by a couple of orders of magnitude even though as pointed out above, large $\sigma$ makes the injection larger. In addition the yield increases more strongly with increasing field, at least partially the result of increasing $\mu$ with increasing field.

To calculate current vs. field it is necessary to multiply the yield by the number of carriers entering the polymer per second. The result of this for the parameters of Ref. 13 and a sample length of 120 nm is a current increase by a factor of $10^5$ as the applied voltage goes from 1 to 20 eV. For PPV the increase obtained should be even larger because indications are that $\sigma \sim 0.1$ rather than 0.08...
4. I-V CHARACTERISTIC FOR OHMIC INJECTING CONTACTS

We consider first the case where only electrons are injected. Possion’s equation may then be written

\[(\kappa/e) \frac{dE}{dx} = \rho\]

where

\[\rho = (n - \bar{n}) + (n_t - \bar{n}_t)\]  

Here \(e\) is the charge on the electron, \(n\) and \(n_t\) the densities of free and trapped electrons, respectively, and \(\bar{n}\) and \(\bar{n}_t\) their respective average values for the sample in thermal and electrical equilibrium (no applied voltage). Following Lampert \(^{15}\) we simplify the equation for current density \(J\) by neglecting the diffusion terms. For electrons only, with Eq. (1) incorporated, the steady current density is given by

\[J = ne\mu_0 \exp(\alpha E^{1/2})E\]

With the simplification of neglecting the diffusion current the boundary condition at the cathode interface \(x = 0\) is \(E = 0\). \(^{15}\) I-V characteristics with only electrons injected were obtained by Parker on MEH-PPV samples with one Ca electrode and the other electrode Nd, Mg or Ca. As shown in Ref. 14 we were able to fit Parker’s data with the calculations described above for both trap-free \((n_t = \bar{n}_t = 0)\) and all-traps-filled \((n_t = N_t, \text{ the total trap density})\) cases. \(^{14}\) In the latter case there is a threshold for current flow because the repulsion of the charges in the traps prevents injection of additional charge at low fields. However, beyond the threshold, above \(\sim 5\) V or \(4 \times 10^5\) V/cm for the particular samples, there is a good fit to the data under the assumption that all traps are filled. For the trap-free case the parameters for the fit were \(\mu_0 = 5 \times 10^{-11}\) cm\(^2\)/Vs, \(\alpha = 8 \times 10^{-3}\) cm\(^{1/2}\)/V\(^{1/2}\). For the trap-filled case the best fit was obtained with \(\mu_0 = 5 \times 10^{-9}\) cm\(^2\)/Vs, \(\alpha = 4.5 \times 10^{-3}\) cm\(^{1/2}\)/V\(^{1/2}\) and \(N_t = 10^{17}/\text{cm}^3\). (It is reasonable to assume \(\bar{n} = \bar{n}_t = 0\)). The latter set of parameters, particularly \(\mu_0\), appears to be in better agreement with values determined by other methods. Hole mobility vs. field, measured for PPV by observing the time delay after injection for the appearance of luminescence, yields by extrapolation \(\mu_0 = 5 \times 10^{-9}\) cm\(^2\)/Vs. \(^{6}\) Electron mobility in PPV and its derivatives is generally found at not too high fields to be a couple of orders of magnitude smaller than hole mobility, \(\mu_p\), the differences attributed to trapping, by carbonyls for example. \(^{11}\)

It is reasonable that \(\mu_n\) increases as \(E\) increases and thus trap-filling increases. The finding that \(\mu_n \sim \mu_p\) in the trap-filled limit is not unexpected because bandstructure is similar for electrons and holes in PPV. \(^{21}\) It is interesting to note that \(\mu_0\) is different for different PPV derivatives. For
dialkoxy-PPV, for example, Blom *et al.* obtained $\mu_0 = 5 \times 10^{-7}$ cm$^2$/Vs for holes.\(\text{[7]}\) We suggest that the differences reflect different degrees of disorder. Support for this is the fact that in dialkoxy-PPV $\mu$ can be measured by traditional time-of-flight technique, in which the arrival time at the other electrode of an injected pulse of carriers is observed, whereas transport in PPV and MEH-PPV is too dispersive for that method to work. The value of $\alpha$ found by Karg *et al.* is $6 \times 10^{-3}$ cm$^{1/2}$/V$^{1/2}$, close to the value of $4.5 \times 10^{-3}$ cm$^{1/2}$/V$^{1/2}$ found here, and also to the value $5.4 \times 10^{-3}$ cm$^{1/2}$/V$^{1/2}$ found for dialkoxy-PPV.\(\text{[8]}\) The value of $N_t$ for the particular sample used is, of course, unknown but is similar to the value estimated by Campbell *et al.* for MEH-PPV from the change in capacitance with forward bias.\(\text{[22]}\) From the good fit at high voltage we conclude that the current there is space-charge limited. It does not vary as $V^2$ because of the strong field-dependence of $\mu$.

We consider now the case of both electrons and holes injected. For this analysis we simplify Possion’s equation by taking

$$\rho = n - p + N_d,$$  \((6)\)

where $N_d$ is the density of traps filled by electrons. For the current density we use Eq. \((3)\) with $\mu_0$ replaced by $\mu_n^0$, and a similar term added for holes with $\mu_p^0$ replaced by $\mu_p^0$. We assume $\alpha$ is the same for electrons and holes. Steady state requires that

$$\frac{dJ}{dx} = \frac{dj_n}{dx} + \frac{dj_p}{dx} = 0,$$  \((7)\)

where $j_n = n\mu_n(E)E$ and $j_p = p\mu_p(E)E$. For the steady state, on the simplifying assumption that the lifetime for recombination $\tau$ is a constant, independent of $x$, we obtain\(\text{[4]}\)

$$\frac{dj_n}{dx} = -n(x)/\tau_n,$$  \((8)\)

$$\frac{dj_p}{dx} = n(x)/\tau_n.$$  \((9)\)

Eliminating $n$ and $p$ from Eqs. \((3)\), \((6)\), \((8)\) and \((9)\), and using Eq. \((1)\), we obtain\(\text{[4]}\)

$$Ee^{\alpha\sqrt{E}} \frac{d}{dx} \left( Ee^{\alpha\sqrt{E}} \frac{dE}{dx} \right) - \frac{1}{\mu_p^0\tau_n} Ee^{\alpha\sqrt{E}} \frac{dE}{dx} = -\frac{J}{\epsilon\mu_p^0\mu_n^0\tau_n}.$$  \((10)\)

This equation can be solved by assuming

$$Ee^{\alpha\sqrt{E}} \frac{d}{dx} = \frac{d}{dy}.$$  \((11)\)

The solution is

$$E(y) = C_1e^{by} - \left( A/b \right)y + C_2$$  \((12)\)

where $b = 1/\mu_p^0\tau_n$, $A = -J/\epsilon\mu_p^0\mu_n^0\tau_n$ and $C_1$, $C_2$ arbitrary constants to be determined by the boundary conditions.

We assume both contacts are ohmic, so the condition at the cathode is
\[ E(y = 0) = E(x = 0) = 0 \]  \hspace{1cm} (13)

and at the anode
\[ E(x = L) = E(y = y_c) = 0 \]  \hspace{1cm} (14)

where \( y_c \) is determined from
\[ L = \int_0^{y_c} E(y) e^{\alpha \sqrt{E(y)}} dy . \]  \hspace{1cm} (15)

With these boundary conditions
\[ C_1 = (A/b)y_c(e^{by_c} - 1)^{-1}, \hspace{0.5cm} C_2 = -C_1 . \]  \hspace{1cm} (16)

The applied voltage is given by
\[ V = \int_0^L E(x) dx = \int_0^{y_c} E^2(y) e^{\alpha \sqrt{E(y)}} dy . \]  \hspace{1cm} (17)

These equations have been used to fit data for an MEH-PPV diode with one Ca contact and the other contact Au or ITO, all of which may reasonably be considered ohmic. Shown in Fig. 1 is the fit for \( N_d = 0 \) and the parameters for that fit. It should be noted that the \( \mu_0^p \) value is similar to that obtained earlier for the trap-free single carrier case. To further elucidate the meaning of the results we calculated \( j_n \) and \( j_p \), the electric field, \( n \), \( p \) and the ratio \( p/n \) as functions of \( x \) for a particular current density, \( J = 0.2 \text{ mA/mm}^2 \) corresponding to \( V = 7.4 \text{ V} \). It was found that the large ratio \( \mu_0^p/\mu_0^n \) causes \( p >> n \) over 2/3 of the sample. This results in \( j_p >> j_n \) except in the immediate vicinity of the cathode. To maintain constant current given the large ratio of \( \mu_p \) to \( \mu_n \) requires that the electric field be larger near the cathode than the anode, rising more rapidly from \( E = 0 \) at the cathode than at the anode. If we allow \( N_d \neq 0 \) and \( \mu_p = \mu_n \) as expected for the trap-filled case, the curves become more symmetrical in \( n \) and \( p \) and the field is more symmetrical about the middle of the sample.

5. CONCLUSIONS

Because of the short conjugation lengths, characteristic of PPV and other conducting polymers, there are no broad continuous bands and carriers are most likely to tunnel into polaron levels with little or no hindrance by a barrier. Random variation in conjugation lengths, and thus site energies, as well as other sources of disorder, result in the hopping mobility of polarons increasing exponentially with \( \sqrt{E} \), as has been shown exponentially for several PPV derivatives. This increase of \( \mu \) with \( E \) contributes to the strong increase of \( I \) with \( V \) observed for LEDs, for example. We have studied the variation of \( I \) with \( V \) for polymer samples with emission-limited contacts and with ohmic contacts. In the former case we did not assume any \( \mu \) variation with \( E \) but relied on the usual Monte Carlo simulation to determine first the number of carriers that make it across the sample to the other
electrode as a function of $E$, and then the current. We find that $I$ increases steeply as $V$ increases, both because carriers can better overcome the image force and more easily surmount barriers due to random site energy variations.

In the case of ohmic contacts, space charge effects also contribute to the steepness of $I$ vs. $V$. It is now documented that the $I$ vs. $V$ characteristic is well fitted by the use of Poisson’s Equation and the current continuity condition, with insertion of the $\mu$ dependence on $E$, for hole only transport in dialkoxy PPV. Fits to Parker’s $I$ vs. $V$ data for hole transport only and electron transport only in MEH-PPV suggest that trapping is important in both those cases. A good fit has been obtained for high enough fields that all traps should be filled, with parameters that are in reasonable agreement with the values found from other experiments. More work is needed to fit $I$ vs. $V$ for the case where both carriers contribute.

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Fig. 1. Fit of theory (solid curve) to data (dots) of Ref. 1 (Fig. 13) for MEH-PPV with electrons injected at Ca contact, holes injected from ITO. The parameters for the fit are $N_d = 0$, $\alpha = 7 \times 10^{-3}$ cm$^{1/2}/$V$^{1/2}$, $\mu_p^0 = 10^{-9}$ cm$^2$/Vs, $\mu_n^0 = 0.01\mu_p^0$, $\tau = 1.4 \times 10^{-4}$ s.