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Published in:
Advances in Solid State Physics

DOI:
[10.1007/3-540-45618-X_39](https://doi.org/10.1007/3-540-45618-X_39)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2002

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):
van Woudenberg, T., Blom, P. W. M., & Huiberts, J. N. (2002). Charge injection in polymer light-emitting diodes. In *Advances in Solid State Physics* (Vol. 42, pp. 495-503). Springer. https://doi.org/10.1007/3-540-45618-X_39

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Charge Injection in Polymer Light-Emitting Diodes

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Abstract. The injection-limited hole current from Ag into poly-dialkoxy-p-phenylene vinylene (PPV) exhibits a weak dependence on temperature, in spite of the presence of a large injection barrier of 1 eV. The measured field- and temperature dependence of the hole injection is explained by a hopping model in which energetic disorder is taken into account. In a PPV-based light-emitting diode it is demonstrated that the hole injection is enhanced by the presence of electrons. As a mechanism for this enhanced hole injection an increase of the electric field at the hole injecting contact due to trapped electrons is proposed.

1 Introduction

Directly after the discovery of polymer light emitting diodes (PLEDs) [1], charge injection has been recognized as an important process for the performance of a PLED [2]. An unbalanced charge injection leads to an excess of one of the two charge carrier types, leading to poor device efficiencies. However, the mechanisms of charge injection into conjugated polymers are poorly understood, compared with the knowledge of inorganic semiconductors. For classical semiconductors the current density J for injection from an electrode into a semiconductor or insulator has been described by thermionic or Richardson-Schottky emission [3], given by

$$J = A^* T^2 \exp\left(\frac{-q\phi_B}{kT}\right) \quad (1)$$

arising from the band offset between the semiconductor and the electrode. However, it was pointed out by Simmons [4] that for low mobility materials this expression is not valid: due to the low mobility a large amount of charge builds up at the contact and as a result back-flow from the semiconductor to the electrode will occur. In that case, the diffusion-limited regime, J is

$$J = qp(0)mE(0) = qN_c \exp\left(\frac{-q\phi_B}{kT}\right) mE(0) \quad (2)$$

with $p(0)$ the charge carrier density at the contact, m charge carrier mobility, and N_c the effective density of states.

Contrary to inorganic semiconductors like Si, with charge carrier mobilities of typically $1000 \text{ cm}^2/\text{Vs}$, the charge transport in conjugated polymers is determined by tightly bound charge carriers on transporting sites that are subject to energetic and spatial disorder [5]. Typical mobilities for PPV-based polymers are in the range 10^{-6} to $10^{-7} \text{ cm}^2/\text{Vs}$. As a result of this low mobility, it is expected that the charge injection into PPV is diffusion-limited, indicating that the charge carrier mobility will play an important role in the injection process. As a result, in order to disentangle the contributions from the mobility m and injection barrier f_B to the injection process, the field and temperature dependence of both the mobility and the energy barriers have to be known.

2 Hole Mobility of PPV

The hole mobility m_p of PPV is strongly dependent on electric field E and temperature T [6], given by

$$m_p(E, T) = m(T) \exp(g\sqrt{E}) \quad (3)$$

with

$$m(T) = m_0 \exp\left(-\frac{D}{kT}\right) \quad (4)$$

and

$$g = B \left(\frac{1}{kT} - \frac{1}{kT_0} \right) \quad (5)$$

with $D = 0.50 \text{ eV}$, $B = 3.1 \cdot 10^{-5} \text{ eV}(\text{V/m})^{-1/2}$, $T_0 = 420 \text{ K}$, and $m_0 = 1.0 \cdot 10^{-2} \text{ m}^2/\text{Vs}$. This functional form of the field E and temperature T dependence of the charge carrier mobility (3) is an intriguing feature of disordered organic semiconductors. The stretched exponential form has first been observed for poly(N-vinyl carbazole) by Gill in 1972 [7]. Numerous experimental studies on molecularly doped polymers, pendant group polymers and amorphous molecular glasses have revealed a similar behavior [8,9,10].

Charge transport in disordered organic conductors is thought to proceed by means of hopping in a Gaussian site-energy distribution. This density of states (DOS) reflects the energetic spread in the charge transporting levels of chain segments due to fluctuation in conjugation lengths and structural disorder. Bässler and co-workers [5,11] have performed numerical simulations of charge transport in a regular array of hopping sites with a Gaussian distribution of site energies. In this Gaussian disorder model (GDM) the following

Fig. 1. Schematic representation of the initial carrier jumps at the metal-polymer interface. The dotted line shows the potential distribution due to the applied electric field, the solid line includes the potential lowering due to the image force. The dashed line represents the transport energy level

functional dependence of m has been proposed [5],

$$m_{GDM} = m_{\infty} \exp \left[- \left(\frac{2s}{3kT} \right)^2 + C \left(\left(\frac{s}{kT} \right)^2 - 2.25 \right) \sqrt{E} \right], \quad (6)$$

with m_{∞} the mobility in the limit $T \rightarrow \infty$, s the width of the Gaussian DOS and C a constant (depending on, e.g., the site spacing). The simulations revealed that in principle the transport in the Gaussian DOS is governed by two energy levels: an equilibrium level to which the charge carriers relax, located at $-s^2/kT$ (zero energy is the maximum of the Gauss), and a transport level E_{tr} located at $-5/9s^2/kT$, as shown in Fig. 1. As a result, the charge transport (6) is governed by an activation energy of $4/9s^2/kT$. Using (6) the phenomenological parameters D and g (3) may be related to the microscopic material parameter s . From the zero-field mobility of our PPV a width of the Gaussian DOS of $s = 0.11$ eV and a typical hopping distance of 1.2 nm have been obtained [12].

3 Mechanism of Charge Injection

In order to discriminate between the contributions of the charge carrier mobility and the energy barrier at the interface the temperature dependence of contact-limited currents in PPV has been investigated [13]. As an electrode silver (Ag) has been used, which for hole injection has an energy barrier f_B of nearly 1 eV. As a result, from the diffusion-limited injection model (2) a thermally activated behavior is expected, according to $\sim \exp(-(D + f_B)/kT)$, with $D + f_B \sim 1.5$ eV. However, the experimental injection-limited J - V characteristics revealed a very weak temperature dependence, even weaker than

the thermal activation D , which is in strong contrast to the diffusion-limited injection model. However, an injection model based on thermally assisted hopping from the electrode into the localized states of the polymer [14] consistently describes the experimental results [13].

The mechanism for charge injection into a disordered conductor is schematically depicted in Fig. 1. The potential distribution U in which the charge carrier is injected is the sum of the barrier height f_B , the image potential and the external potential relative to the Fermi level of the metal

$$U(x) = f_B - \frac{e^2}{16\pi\epsilon_0\epsilon_r x} - eFx \quad (7)$$

where the potential is given as a function of the distance x , measured from the metal/polymer interface, F is the applied electric field. The essential assumption of the analytical model is, that the first upward jump is rate limiting. The next jumps can in that case be treated as a diffusive escape from the interface. The minimum distance for a carrier to pass from the contact is limited by the spacing of transport sites and will therefore be close to the nearest neighbor distance a .

As the carriers will jump immediately to the transport energy E_{tr} for an upward jump, the criterion for the regime of upward jumps is given by

$$U(a) - E_{tr} = f_B - \frac{e^2}{16\pi\epsilon_0\epsilon_r a} - eFa - E_{tr} \geq 0 \quad (8)$$

The current j_{inj} is given by the integral of the net hopping onto states at x multiplied with the total injection probability to all energy states at x , given by the Gaussian distribution $g(U(x) - E)$ of the target sites, E being the extra site energy measured from the center of the Gauss, and assuming a Boltzmann occupation of energies, $Bol(E)$. This gives [14]

$$j_{inj} = ev_0 \int_a^\infty dx \exp(-2gx) w_{esc}(x) \int_{-\infty}^\infty dE Bol(E) g(U(x) - E) . \quad (9)$$

The exponential factor $2gx$ determines the hopping probability to a distance x , where g is the inverse localization radius, which is $g \equiv 10/\text{nm}$. This probability is multiplied by the escape probability w_{esc} from x . In order to compare this hopping based model with experiments it should be realized that the injection-limited current is determined by four parameters: the energetic width s , the dielectric constant ϵ , the nearest neighbor distance a , and the energy barrier f_B at the Ag/PPV interface. From the field- and temperature dependence of the hole mobility of our OC₁C₁₀ - PPV, $s = 0.11$ eV and $a = (1.2 \pm 0.1)$ nm have been extracted [12].

Furthermore, from impedance measurements $\epsilon = 2.1$ has been found [15]. The only remaining parameter in the random hopping model is the potential barrier f_B . This barrier can be estimated from the difference between the HOMO level of the PPV (5.3 eV) and the Fermi level of Ag of (-4.3 eV) [16],

Fig. 2. Injection limited hole current density J versus electric field E for an ITO/Ag/PPV/Ag device at $T = 300$ K and $T = 195$ K. The calculated J - V characteristics for a barrier height $f_B = 0.95$ eV are plotted as solid lines. For our OC₁C₁₀ - PPV an energy width of $s = 0.11$ eV, a nearest neighbor distance of $a = (1.2 \pm 0.1)$ nm, and a dielectric constant of $\epsilon = 2.1$ have been used

thus $f_B = 1.0$ eV. As a result all input parameters are fixed. In Fig. 2 it is demonstrated that the observed field- and temperature dependence of the hole injection from Ag into PPV is in good agreement with the predictions of the model.

4 PLED with an Injection Limited Hole Contact

Charge injection is an important process with regard to the performance of PLEDs. Especially for materials with a large energy gap, as applied for blue PLEDs, large energy barriers at the injecting interface are expected. So far, experimental results on PLEDs with Ohmic electron- and hole contacts have been modeled [17]. By incorporating the injection model based on thermally assisted hopping into the PLED device model also PLEDs with strongly hindered hole injection can be investigated. The injection-limited PLED devices that have been investigated consist of dialkoxy-PPV (OC₁C₁₀ - PPV) sandwiched between two electrodes on top of a glass substrate. The OC₁C₁₀ - PPV polymer is spin coated on top of a silver (Ag) bottom electrode and is covered by a Ca contact. The Ca top electrode has a work function which is close to the conduction band energy of OC₁C₁₀ - PPV [16], resulting in an Ohmic contact for the electron injection. The Ag-contact at the other hand, makes an injection barrier of 1 eV with the valence band of the PPV [16]. As a result, the hole injection into PPV from the Ag contact is strongly hindered.

Furthermore, for comparison also bulk-limited PLED devices have been made, where the OC₁C₁₀ - PPV has been spin coated on top of an ITO contact. As the device current of a PLED based on PPV is hole dominated [18], it

Fig. 3. Hole current density J versus voltage V at room temperature of an ITO/PPV/Ag hole-only device with thickness $L = 240$ nm. For hole injection from ITO the current is space-charge limited (SCLC), for hole injection from Ag the current is injection limited (ILC)

is expected that a reduction of the hole current by a high hole contact barrier will strongly reduce the device current. In Fig. 3 it is demonstrated that for hole injection from Ag the hole current is reduced by 4 orders of magnitude as compared to the bulk space-charge limited hole current. Therefore, the number of holes in the injection-limited PLED (IL-PLED) is also reduced by a factor 10^4 .

The current-density voltage (J - V) characteristics for both the IL-PLED and the PLED are shown in Fig. 4a, measured at room temperature. It is observed that the current-density of the IL-PLED is, as expected, strongly reduced compared with the current density of the PLED. The electron current in the PLED is about two to three orders of magnitude lower than the SCLC hole current [18], and consequently larger than the injection-limited hole current. As a result it is expected that the current of the IL-PLED will behave as a space-charge limited electron-only device. From Fig. 4a it is observed that the IL-PLED indeed follows the electron-only current at low voltages. However, at an applied bias V of typically 7 V, the current starts to increase rapidly from the electron current.

The current of the IL-PLED has been calculated by numerically solving the current density equation together with the Poisson equation and applying the proper boundary conditions for the Ohmic electron contact and the injection-limited hole contact. The result of the calculation, also shown in Fig. 4a, confirms that the calculated current is nearly equal to the electron-only current. Due to the strong reduction of the number of holes the electron space-charge is not compensated by holes and as a result the current of the electron-only device is the maximum current a device can support. In Fig. 4b the experimental and calculated light-output of a PLED and an IL-PLED

Fig. 4. (a) Current density J versus voltage V at room temperature for an ITO/PPV/Ca polymer light emitting diode (PLED), a Ag/PPV/Ca injection limited PLED (IL-PLED) and a Ca/PPV/Ca electron-only device, all with thickness $L = 240$ nm. Also shown is the numerically calculated J - V characteristic for the IL-PLED, using a barrier height $f_B = 0.95$ eV for the hole injection. (b) Light output of the ITO/PPV/Ca (PLED) device and the Ag/PPV/Ca (IL-PLED) device at room temperature, together with the calculated light output (solid lines)

are compared. Again, for $V > 7$ V the experimental light-output of the IL-PLED is strongly enhanced and strongly exceeds the predictions from the model. Clearly, the experimental J - V and light-output characteristics of the IL-PLED strongly disagree with the predictions of the device model.

As stated above, with a limited number of holes the space-charge limited electron current is the maximum possible current in the IL-PLED. As a result, the observed increase for $V > 7$ V must originate from an enhanced hole current. From the hopping injection model [14] it is found that the injection current grows rapidly with increasing electric field. A possible origin of an enhanced electric field at the hole-injecting contact might be tunneling through an interface barrier or the trapping of electrons at the interface, as schematically indicated in Fig. 5. Enhancement of charge injection by a tunnel barrier has recently been demonstrated by Murata et al. [19]. Such a tunnel barrier will prevent the electrons to flow into the hole injection contact. Consequently, a large electric field across the tunnel barrier builds up, which gives rise to an increased hole injection. However, the presence of such an electron-blocking tunnel barrier is not in agreement with the fact that we observe the bulk-limited electron current at low voltages in our IL-PLEDs.

An alternative explanation is the presence of electron traps at the Ag/PPV interface. The trapped electrons will increase the electric field at the Ag/PPV interface, leading to an enhanced hole injection. Furthermore, in a hole-only device, as is used in our study of hole injection from Ag into PPV, these electron traps remain unfilled and therefore do not play a role. In

Fig. 5. Possible origin of the enhanced hole injection: **(a)** electron blocking barrier at the hole contact, **(b)** small interfacial region with electron traps near the hole contact. In case (a) the hole tunneling through the barrier is enhanced by strong band bending of the tunnel barrier, in case (b) the hole injection is increased by the extra lowering of the effective barrier

order to model the influence of electron interface traps we incorporate in our model a small interfacial region of a few nm which contains interface traps. In this region the relation between trapped electrons n_t and free electrons n is

$$n_t = \frac{n}{q} \quad (10)$$

Thus, we have added one additional parameter q to our PLED device model. In Fig. 6a the calculated J - V characteristics are shown for $q = 5 \times 10^{-5}$.

Fig. 6. **(a)** Current density J versus voltage V at room temperature for the Ag/PPV/Ca injection limited PLED (IL-PLED). The calculation (*solid line*) includes an electron trap in a small interfacial region near the hole contact, with a ratio q between free and trapped electrons, $q = 5 \times 10^{-5}$. **(b)** Light output of the ITO/PPV/Ca (PLED) and the Ag/PPV/Ca (IL-PLED) device at room temperature, together with the calculated light output (*solid lines*) from the device model incorporating an electron trap near the hole contact

The calculated J-V characteristics consistently describe the experimental results of the IL-PLED. Furthermore, in Fig. 6b the light-output is shown, inclusion of an interface trap also gives good agreement between model and experiments. In order to find out more about the nature of the interface traps the temperature dependence of the IL-PLED will be investigated, which is a subject of further study.

5 Conclusions

In conclusion, it is found that the injection-limited hole current in a polymeric LED is significantly enhanced by the presence of electrons. The increase of the hole current is quantitatively explained by an electron trap near the PPV interface, which enlarges the electric field at the interface resulting in a strong enhancement of the hole injection.

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