Charge Injection Model in Organic Light-Emitting Diodes Based on a Master Equation

Ling Li, Gregor Meller, and Hans Kosina

Institute for Microelectronics, TU Wien, 1040 Vienna, Austria
{li|meller|kosina}@iue.tuwien.ac.at

Abstract

A master equation model is developed for dark injection from a metallic electrode into a random hopping system, representing a conjugated polymer or a molecularly doped polymer. A master equation allows for the inclusion of the image force effect on the charge injection process and for a separate analysis of the forward hopping and backflow components. This model yields the injection current as a function of electric field, temperature, energy barrier between metal and organic layer, and energetic width of the distribution of hopping sites. Good agreement with experimental data is found.

1 Introduction

Over the past decade, the interest in organic semiconductors has increased dramatically. Devices such as organic light emitting diodes (OLED) and organic field effect transistors have been realized. In spite of these successful applications, the physical processes underlying the charge injection in OLED are not well understood. Commonly the injection-limited condition is described either by the Fowler-Nordheim (FN) model for tunneling or by the Richardson-Schottky (RS) model for thermionic emission [1]. However, these two models were developed for semiconductor materials with perfect band structure, and cannot directly be applied to disordered organic materials, where charge carriers are localized and transport involves discrete hopping within a distribution of energy states. Arkhipov presented an analytical model based on hopping theory [2]. However, this model neglected the backflow current from the semiconductor towards the electrode, which can play an important role for the injection current. In this work we develop an analytical master equation model to describe the injection process in OLED including the backflow current.

2 Model Theory

The system to be considered here is an energetically and positionally random hopping system in contact with a metallic electrode. At an arbitrary distance x away from the metal-organic layer interface, located at $x = 0$, the electrostatic potential is given by the sum of the image charge potential and the applied potential described by electric field F as [3]

$$E = \Delta - \frac{e}{16\pi\varepsilon\varepsilon_0 x} - Fx \tag{1}$$

where e is the elementary charge, Δ is the difference between the workfunction of the metal and the electron affinity of the organic semiconductor, and $\varepsilon\varepsilon_0$ is the dielectric permittivity. Since the rapid variation of potential (1) takes place in front of the cathode, and space-charge effects can be ignored altogether in the calculation of the cathode characteristics [2,4], the field F may be regarded as being nearly constant.
Assuming no correlations between the occupation probabilities of different localized sates, the net electron flow between two states is given as

$$I_{ij} = f_i\,(1-f_j)\,\omega_{ij} - f_j\,(1-f_i)\,\omega_{ji} \tag{2}$$

with f_i denoting the occupation probability of site i and ω_{ij} the electron transition rate of the hopping process between the occupied state i to the empty state j. The probabilities (2) are then employed in a master equation for describing charge transport. With the electrochemical potential μ_i' at the position of state i the occupation probability is described by a Fermi-Dirac distribution as

$$f_i = \frac{1}{1+\exp\left(\frac{E_i'-\mu_i'}{k_B T}\right)}. \tag{3}$$

For the metal electrode we assume a fixed electron concentration P_0 and a Fermi-level of zero. All injected carriers are hopping from the metal Fermi-level. Under the effect of a constant electric field F and the Coulomb field binding the carrier with its image charge on the electrode the energy and the electrochemical potential of a localized state are given by

$$\begin{aligned} E_j' &= E_j + \Delta - e\varphi\,(R_j,\theta)\,, \\ \mu_j' &= \Delta - e\varphi\,(R_j,\theta) \\ \varphi\,(R_j,\theta) &= F R_j \cos\theta + \frac{e}{16\pi\varepsilon R_j\cos\theta} \end{aligned}$$

where R_j denotes the distance of state j from the interface, θ the angle between F and R_j, Δ the barrier height, and E_j the energy at state j without electric field. According to Mott's formalism [5], the transition rate ω_j from the metal Fermi-level to state j reads as

$$\omega_j \propto \begin{cases} \exp\left[-2\gamma R_j - \frac{E_j'}{k_B T}\right] & : \quad E_j' \geq 0 \\ \exp\left(-2\gamma R_j\right) & : \quad E_j' \leq 0 \end{cases} \tag{4}$$

where γ is the localization parameter of the states. We assume a Gaussian density of states.

$$g(E_j) = \frac{N_t}{\sqrt{2\pi}\sigma}\exp\left(-\frac{E_j^2}{2\sigma^2}\right) \tag{5}$$

N_t denotes the total concentration of localized states and σ the width of the distribution. The net current across the metal-organic contact can be written as

$$I = I_{\text{inj}} - I_{\text{rec}} = e\nu_0\,(I_1 + I_2 - I_3 - I_4) \tag{6}$$

where ν_0 is the attempt-to-jump frequency and

$$I_1 = \int_1^{+\infty} dr \int_\alpha^\infty dR_j \int_{-\infty}^0 dE_j \frac{P_0\left(1-f_j\right)}{\sqrt{2\pi}\sigma} \exp\left(-2\gamma R_j - \frac{\left(E_j-\left(\Delta - e\varphi\left(R_j,r\right)\right)\right)^2}{2\sigma^2}\right)$$

$$I_2 = \int_1^{+\infty} dr \int_\alpha^\infty dR_j \int_0^\infty dE_j \frac{P_0\left(1-f_j\right)}{\sqrt{2\pi}\sigma} \exp\left(-2\gamma R_j - E_j - \frac{\left(E_j-\left(\Delta - e\varphi\left(R_j,r\right)\right)\right)^2}{2\sigma^2}\right)$$

$$I_3 = \int_1^{+\infty} dr \int_\alpha^\infty dR_j \int_0^\infty dE_j \frac{N_t f_j}{\sqrt{2\pi}\sigma} \exp\left(-2\gamma R_j - \frac{\left(E_j-\left(\Delta - e\varphi\left(R_j,r\right)\right)\right)^2}{2\sigma^2}\right)$$

$$I_4 = \int_1^{+\infty} dr \int_\alpha^\infty dR_j \int_{-\infty}^0 dE_j \frac{N_t f_j}{\sqrt{2\pi}\sigma} \exp\left(E_j - 2\gamma R_j - \frac{\left(E_j-\left(\Delta - e\varphi\left(R_j,r\right)\right)\right)^2}{2\sigma^2}\right)$$

where $r = 1/\cos\theta$ and $f_j = \left(1+\exp\left(\frac{E_j-\mu_j}{k_BT}\right)\right)^{-1}$. I_1 and I_2 describe the charge injection downwards and upwards from the electrode, respectively. I_3 and I_4 describe the backflow of charge to the electrode. The net current can be calculated by evaluating I_1, I_2, I_3 and I_4 numerically.

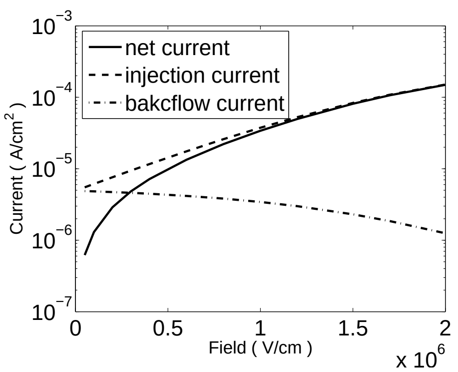

Figure 1: Field dependence of the net, injection, and backflow currents.

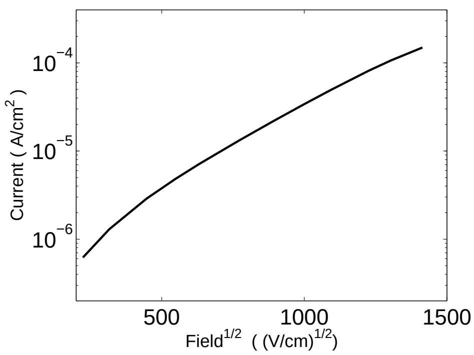

Figure 2: Relation between injection current and $F^{1/2}$.

3 Results and Discussion

With the model presented we calculate the field dependence of the net, injection and backflow current. The parameters are $\Delta = 0.3$eV, $N_t = 1\times10^{22}$cm^{-3}, $T = 300$K, ε=3, $\alpha = 0.6$nm, $\gamma = 2\times10^8$cm^{-1}, $\sigma = 0.08$eV and $\nu_0 = 1\times10^{11}$s^{-1}. Fig. 1 shows that with electric field the injection current increases and the backflow current decreases, as intuitively expected. As a result, the net current increases with electric field quickly in the low field regime.
Fig. 2 shows the semilogarithmic plots of the current versus $F^{1/2}$ with the same parameters as used in Fig. 1. This presentation is appropriate for testing RS behavior as

$j \propto \exp\left(\sqrt{eF/4\pi\varepsilon\varepsilon_0}\right)$. Since the dependence of $\log j$ versus $F^{1/2}$ is not linear, a deviation from the RS characteristics is observed. Fig. 3 shows current-field characteristics at different Δ and $N_t = 9 \times 10^{22}\mathrm{cm}^{-3}$, the other parameters are the same as in Fig. 1. The injection current increases with decreasing barrier height Δ and with electric field. The comparison between calculation and experimental data of DASMB sandwiched between ITO and Al electrodes [2] is given in Fig. 4. The parameters are $\Delta = 0.4$eV and $T = 123$K, the other parameters are the same as in Fig.1. The agreements is quite good at low electric fields. The discrepancy between calculation and experimental data comes from the resistance of the ITO contact at high electric field [2].

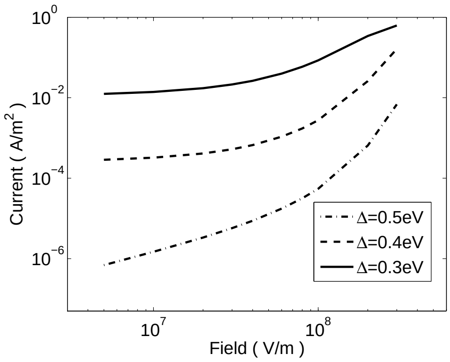

Figure 3: Barrier height dependence of the injection current.

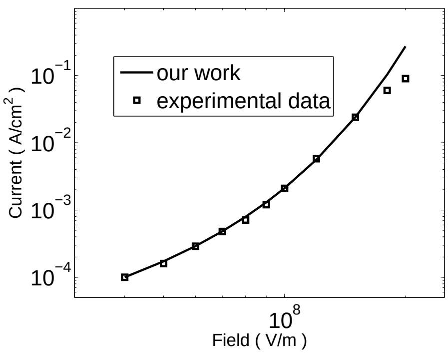

Figure 4: Comparison between calculation and experimental data at $T = 123K$.

Acknowledgments

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