

## Mobility-Dependent Charge Injection into an Organic Semiconductor

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Measurements of charge injection from indium tin oxide (ITO) into the organic semiconductor, tetraphenyl diamine doped polycarbonate (PC:TPD), were carried out. The current injected at the contact was measured as a function of the hole mobility in the organic semiconductor, which was varied from  $10^{-6}$  to  $10^{-3}$   $\text{cm}^2/\text{V} \cdot \text{s}$  by adjusting the concentration of the hole transport agent, TPD, in the PC host. These experiments reveal that the current injected at the contact is proportional to the hole mobility in the bulk. As a result, the ITO/PC:TPD contact is found to limit current flow in all samples, regardless of the hole mobility in PC:TPD.

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The operation of organic electronic devices, such as light-emitting diodes [1–3], thin film transistors [4–6], photodetectors, and solar cells [7–9] involves injection of charge from a metallic electrode into the organic semiconductor, a process that often plays a dominant role in determining device performance. The efficiency of light-emitting diodes, for example, is directly related to the ability of the contacts to supply the organic bulk with charge [10]. Despite the great technological importance of charge injection, the physics of this process is not understood in any real detail. This may be ascribed to the fact that transport in organic semiconductors, which occurs by hopping between localized electronic states, is very different from the band motion in their inorganic counterparts. A variety of models that incorporate hopping transport in the injection process have been proposed [11–15], sometimes giving conflicting predictions, even in terms of the influence of disorder on the magnitude of the injected current [13,16]. The morphology [17,18], energetics [19–25], and electrical properties [13,26–28] of metal/organic interfaces are also under intensive experimental scrutiny, as we do not yet have a thorough understanding of the dependence of charge injection on material parameters.

The charge injection process can be viewed as a supply vs demand problem. The maximum current density that a depleted, trap-free semiconductor with thickness  $L$  can carry is space-charge limited (SCL) and given by the Mott-Gurney law [29]:

$$J_{\text{SCL}} = \left(\frac{9}{8}\right)\epsilon\epsilon_0\mu V^2/L^3, \quad (1)$$

where  $\epsilon_0$  is its dielectric constant,  $\mu$  is the charge carrier mobility, assumed here to be field independent, and  $V$  is the applied voltage. By definition, an Ohmic contact poses no limitation to the current flow and therefore supplies the semiconductor with space-charge limited current. Otherwise, if the supply from the contact is not adequate to satisfy the demand of the bulk, the contact is injection limited and the current is lower than  $J_{\text{SCL}}$ . A figure of merit (for trap-free materials) is the injection efficiency,  $\eta = J_{\text{INJ}}/J_{\text{SCL}}$ , where  $J_{\text{INJ}}$  is the current density that is injected from the contact [26].

The energetics at the contact play an important role in determining the injection efficiency. Although formation effects have been reported for contacts made by evaporating the metal on the organic [28], and although certain metals have been found to react with certain organic semiconductors [21,22], the energy barrier at the interface is generally found to scale with the difference in the appropriate energy levels of the metal and the organic [19–25]. Abkowitz *et al.* [26] have recently measured the injection efficiency from various metal electrodes into tetraphenyl diamine doped polycarbonate (PC:TPD) (containing 40% TPD) and found that it decreases exponentially with the difference between the ionization potential of TPD and the Fermi energy of the metal.

It was shown by Emtage and O'Dwyer [30], and recently rederived by Scott and Malliaras [15] using a different approach, that the rate of injection at a contact limited electrode is also proportional to the charge mobility in the organic material. Specifically, the net injected current into the bulk of the film ( $J_{\text{INJ}}$ ) is the difference between the injected flux and a surface recombination rate [15]:

$$J_{\text{INJ}} = 4\psi^2 N_0 e \mu E \exp(-\varphi_B/kT) \exp(f^{1/2}), \quad (2)$$

where  $\psi$  is a slowly varying function of electric field,  $N_0$  is the density of charge hopping sites, and  $\varphi_B$  is the Schottky energy barrier. The exponential in the square root of the electric field,  $f = e^3 E / [4\pi\epsilon\epsilon_0(kT)^2]$ , represents the usual Schottky barrier lowering effect. [In deriving Eq. (2), the mobility is assumed to be independent of the electric field.] The mobility dependence of the thermionic injection rate, first predicted by Emtage and O'Dwyer and extended by two of us, introducing the field-dependent prefactor  $\psi$ , seems to have been overlooked in much of the recent literature on organic electronics. This may be due to the lack of experimental verification of Eq. (2). It is therefore the goal of the present study to test this theoretical prediction.

In the experiments to be described in this paper, the approach used is to keep the energetics at the interface the same and to vary the mobility of the semiconductor bulk. This is possible in a molecularly doped polymer

such as tetraphenyl diamine doped polycarbonate, an organic semiconductor used in electrophotography [31]. TPD  $\{N, N'$ -diphenyl- $N, N'$ -bis(3-methylphenyl)-[1, 1'-bisphenyl]-4, 4'-diamine $\}$  is a prototypical unipolar organic transport material (holes are the mobile species) whose charge transport properties have been extensively studied in the past [31]. Transport in this material takes place via hopping of holes among TPD molecules, permitting the mobility to be varied over several orders of magnitude by adjusting the TPD concentration in the host polymer [32]. In this Letter, we take advantage of this property of PC:TPD and study hole injection as a function of mobility. Indium tin oxide (ITO), a commonly utilized electrode in organic light emitting diodes, was used as the hole injection contact.

Injection was studied in several samples with a concentration of TPD in PC equal to 30%, 40%, 50%, 60%, 80%, and 100% by weight. ITO coated glass substrates were bought from Thin Film Devices and cleaned by UV/ozone treatment at slightly elevated temperatures. Immediately after cleaning, the PC:TPD films were cast on the ITO substrates by screen coating from a tetrahydrofuran solution. The pure TPD films were prepared by direct vacuum deposition on the ITO substrates at  $10^{-6}$  mbar. A semi-transparent Al layer was vacuum deposited on all samples as the back contact, defining a device area of  $3 \text{ mm}^2$ . The thickness of the organic layers was about  $10 \text{ }\mu\text{m}$ . The pure TPD samples had the tendency to crystallize a few weeks after preparation; all the measurements reported here were done before any crystallization was visible. The electrical characteristics of the contacts reported here did not change significantly over that period of time.

The mobility was measured by the photoinduced time-of-flight technique. A nanosecond nitrogen laser was used as the excitation source, incident through the Al electrode that was biased positive with respect to the ITO. It was established experimentally that hole injection from Al was negligible. Nondispersive transients with well-defined plateaus were observed and the mobility was determined from the time at which the current reached half of its plateau value. The resulting mobilities were found to exhibit the usual  $\ln\mu \sim E^{1/2}$  electric field dependence and were in agreement with literature data [32].

The experiment consisted of three steps: First, the mobility of a sample was measured. Second, the space-charge limited current was calculated for that sample [33]. Third, the polarity of the bias voltage was reversed and the current due to hole injection from ITO was measured. Typical data for two samples are shown in Fig. 1. The upper two curves are for pure TPD. The injected current (solid circles) is 2 orders of magnitude lower than the space-charge limited current (solid line), indicating that the ITO/TPD contact is injection limited. The lower two curves in Fig. 1 are for the sample with 50% TPD. The mobility of this sample is about 2 orders of magnitude lower than that of pure TPD, which is reflected in the calculated value of the

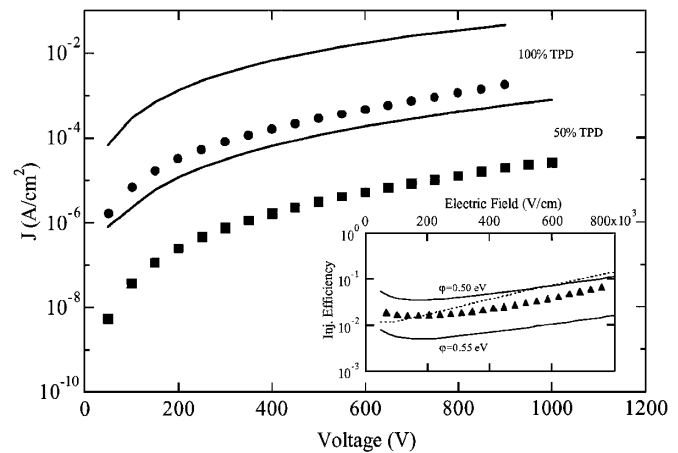


FIG. 1. Voltage dependence of the space-charge limited (solid lines) and injected (solid circles and solid squares) current densities. The top two curves are for a pure TPD film, while the bottom two curves are for a sample with 50% TPD in PC. Inset: Electric field dependence of the injection efficiency for the sample containing 60% TPD. The solid lines are the predictions of the theory for  $\varphi_B = 0.50$  and  $0.55 \text{ eV}$ . The dotted line shows the electric field dependence of the Schottky effect alone, calculated for a barrier height of  $\varphi_B = 0.55 \text{ eV}$ .

space-charge limited current. Even so, the current injected from the ITO contact remains injection limited and the injection efficiency is practically identical to that in the pure TPD sample.

The electric field dependence of the injection efficiency is shown in the inset of Fig. 1 for the sample with 60% TPD. Similar curves were obtained from the other samples. The solid lines are calculated using Eqs. (1) and (2) for  $\varphi_B = 0.50$  and  $0.55 \text{ eV}$  and  $N_0$  equal to the number density of TPD molecules. The theory gives a rather good description of the main features of the experimental data, namely, the shallow minimum in the efficiency (due to the factor  $\psi$ ) and the slower rise with electric field than that given by the Schottky effect alone. The only adjustable parameter, the barrier height of about  $0.52 \text{ eV}$ , is consistent with the expected energy difference between the Fermi energy of ITO (work function approximately  $5.0 \text{ eV}$ ) [34] and the ionization potential of TPD ( $5.5 \text{ eV}$ ) [26].

The dependence of injection on mobility is shown in Fig. 2, which summarizes data from all samples. The densities of the space-charge limited and the injected current are plotted as a function of mobility at a constant electric field ( $0.4 \text{ MV/cm}$ ). The space charge limited current (solid squares) is proportional to the mobility, according to Eq. (1). The injected current (solid circles) is also proportional to the mobility, in agreement with the prediction of Eq. (2). The lower solid line in Fig. 2 is a fit that gives a slope of  $0.91 \pm 0.07$ . As a result, the ITO/PC:TPD contact remains injection limited in all samples, with an injection efficiency of the order of  $10^{-2}$ .

It is worth commenting on the fact that the simple theory leading to Eq. (2), which ignores field dependence of the

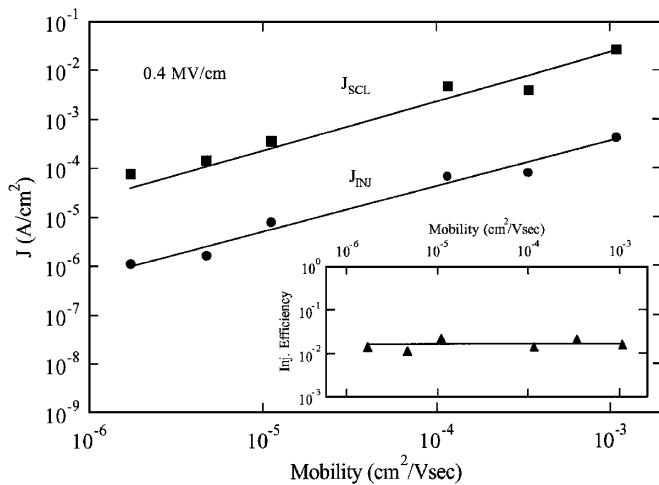


FIG. 2. Mobility dependence of the space-charge limited and injected current densities for six PC:TPD samples at 0.4 MV/cm. The relative TPD concentration in PC was equal to 30%, 40%, 50%, 60%, 80%, and 100%, respectively. The solid lines are fits with slopes of 1 and  $0.91 \pm 0.07$ , respectively. Inset: Mobility dependence of the injection efficiency in the PC:TPD samples at 0.4 MV/cm. The line is a guide to the eye.

mobility, nevertheless predicts the field dependence of the injection efficiency (inset of Fig. 1) quite accurately. In part, this is because we have chosen to present the data as the ratio of  $J_{INJ}/J_{SCL}$  so that the explicit dependence on the mobility, and its field dependence, is suppressed. Further details of the field and temperature dependence of the injection current are under investigation, and will be presented in future publications [35].

In conclusion, we have varied the mobility in the amorphous organic semiconductor PC:TPD and measured the current injected from an ITO electrode. The current is found to be proportional to the mobility, as predicted by Emtage and O'Dwyer and by Scott and Malliaras. Thus, at all concentrations, the ITO/PC:TPD contact remains injection limited in its ability to supply charge to the organic layer. The ratio of injected current to (predicted) space-charge limited current is therefore also independent of concentration.

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- [1] R. H. Friend *et al.*, *Nature (London)* **397**, 121–128 (1999).
- [2] M. A. Baldo *et al.*, *Nature (London)* **395**, 151–154 (1998).
- [3] D. G. Lidzey, D. D. C. Bradley, S. F. Alvarado, and P. F. Seidler, *Nature (London)* **386**, 135 (1997).
- [4] J. H. Schon, S. Berg, C. Kloc, and B. Batlogg, *Science* **287**, 1022–1023 (2000).
- [5] B. Crone *et al.*, *Nature (London)* **403**, 521–523 (2000).
- [6] C. D. Dimitrakopoulos, S. Purushothaman, J. Kymissis, A. Callegari, and J. M. Shaw, *Science* **283**, 822–824 (1999).
- [7] J. H. Schon, C. Kloc, E. Bucher, and B. Batlogg, *Nature (London)* **403**, 408–410 (2000).
- [8] G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, *Science* **270**, 1789–1791 (1995).
- [9] J. J. M. Halls *et al.*, *Nature (London)* **376**, 498–500 (1995).
- [10] G. G. Malliaras and J. C. Scott, *J. Appl. Phys.* **83**, 5399–5403 (1998).
- [11] M. A. Abkowitz and H. A. Mizes, *Appl. Phys. Lett.* **66**, 1288–1290 (1995).
- [12] E. M. Conwell and M. W. Wu, *Appl. Phys. Lett.* **70**, 1867–1869 (1997).
- [13] V. I. Arkhipov, E. V. Emelianova, Y. H. Tak, and H. Bassler, *J. Appl. Phys.* **84**, 848–856 (1998).
- [14] M. N. Bussac, D. Michoud, and L. Zuppiroli, *Phys. Rev. Lett.* **81**, 1678–1681 (1998).
- [15] J. C. Scott and G. G. Malliaras, *Chem. Phys. Lett.* **299**, 115–119 (1999).
- [16] Y. N. Gartstein and E. M. Conwell, *Chem. Phys. Lett.* **255**, 93–98 (1996).
- [17] F. J. Esselink and G. Hadziioannou, *Synth. Met.* **75**, 209–212 (1995).
- [18] S. Conalves-Conto, M. Carrard, L. Si-Ahmed, and L. Zuppiroli, *Adv. Mater.* **11**, 112–115 (1999).
- [19] I. H. Campbell, T. W. Hagler, D. L. Smith, and J. P. Ferraris, *Phys. Rev. Lett.* **76**, 1900–1903 (1996).
- [20] K. Seki, E. Ito, and H. Ishii, *Synth. Met.* **91**, 137–142 (1997).
- [21] W. R. Salaneck and M. Lönglund, *Polym. Adv. Technol.* **9**, 419–428 (1998).
- [22] V.-E. Choong, M. G. Mason, C. W. Tang, and Y. Gao, *Appl. Phys. Lett.* **72**, 2689–2691 (1998).
- [23] G. G. Malliaras, J. R. Salem, P. J. Brock, and J. C. Scott, *J. Appl. Phys.* **84**, 1583–1587 (1998).
- [24] R. Schlaf, C. D. Merritt, L. A. Crisafulli, and Z. H. Kafafi, *J. Appl. Phys.* **86**, 5678–5686 (1999).
- [25] H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater.* **11**, 605–625 (1999).
- [26] M. Abkowitz, J. S. Facci, and J. Rehm, *J. Appl. Phys.* **83**, 2670–2676 (1998).
- [27] C. Glebeler, H. Antoniadis, D. D. C. Bradley, and Y. Shirota, *Appl. Phys. Lett.* **72**, 2448–2450 (1998).
- [28] A. Ioannidis, J. S. Facci, and M. A. Abkowitz, *J. Appl. Phys.* **84**, 1439–1444 (1998).
- [29] M. A. Lambert and P. Mark, *Current Injection in Solids* (Academic, New York, 1970).
- [30] P. R. Emtage and J. J. O'Dwyer, *Phys. Rev. Lett.* **16**, 356–358 (1966).
- [31] P. M. Borsenberger and D. S. Weiss, *Organic Photoreceptors for Xerography* (Marcel Dekker, New York, 1998).

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- [32] H.-J. Yuh and D.M. Pai, *Mol. Cryst. Liq. Cryst.* **183**, 217–226 (1990).
- [33] The electric field dependence of the mobility was properly accounted for in the calculation of the space charge limited current [G. G. Malliaras and J. C. Scott, *J. Appl. Phys.* **85**, 7426–7432 (1999)].
- [34] J. C. Scott *et al.*, *Appl. Phys. Lett.* **74**, 1510–1512 (1999).
- [35] L. Bozano, S. A. Carter, P. J. Brock, and J. C. Scott (unpublished).