

The Dependence of Organic Bulk Heterojunction Solar Cells Efficiency on The Charge Carrier Mobility

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Abstract

The power conversion efficiency of organic solar cells based on donor-acceptor blends is governed by two competing processes, extraction and recombination of charge carriers. Both processes are strongly dependent on the charge carrier mobility. Using microscopic effective medium simulation, we demonstrate that the best device efficiencies are achieved in the mobility range $10^{-6} - 10^{-4} m^2/Vs$. For lower mobilities lead to losses by bimolecular recombination and higher mobilities lead to a reduction of the open circuit voltage, and consequently a drop in efficiency.

Keywords: Organic solar cells, BHJ solar cells, Efficiency of organic solar cells.

اعتماد كفاءة الخلايا الشمسية العضوية على حركية ناقلات الشحنة

الخلاصة

تتنافس على التحكم بكفاءة الخلايا الشمسية العضوية، المرتكزة على مزيج الواهب/المستقبل) donor-acceptor blends عمليتان؛ الاولى استخلاص ناقلات الشحنة والثانية إعادة اتحادهما. وتعتمد كلتا العمليتين بشدة على حركية ناقلات الشحنة. باستخدام نموذج رياضي لتمثيل هكذا خلايا، نوضح في هذا البحث ان افضل كفاءة يمكن تحقيقها تكون ضمن قيم للحركية تتراوح بين $(10^{-6} - 10^{-4} m^2/Vs)$ حيث تؤدي القيم الاقل من هذا المدى الى خسائر بسبب إعادة الاتحاد الجزيئي الثنائي (bimolecular recombination) والاعلى من هذا المدى الى نقصان في فولتية الدائرة المفتوحة، وبالتالي هبوط الكفاءة. متوسط يستطيع اختراق الفقاعة ولكن قد لا يكسرها.. وكل هذه الظواهر كانت متوقعة للموديل المقترح.

1.Introduction

The efficiency of solar cells based on bulk heterojunction (BHJ) of organic semiconductors has shown promising increases in recent years [1-6]. A major focus now lies in finding a viable strategy for further optimization of the conversion efficiency, guided by a deeper understanding of the fundamental processes. Device simulations are useful tools to assist in finding such routes, as they allow the extrapolation of possible but not yet implemented device concepts. In this study the influence of charge carrier mobility on dissociation and transport processes, which govern the efficiency of solar cells, will be investigated. For this purpose we have built up a simulation model of polymer:fullerene solar cell based on an effective medium approach.

In addition to previously published models [7,8] where a reduced recombination rate has been considered, Our simulation program solves the following differential equations system by finite difference method;

- The Poisson equation

$$\frac{\partial^2}{\partial x^2} \psi(x) = \frac{q}{\epsilon_0 \epsilon_r} [n(x) - p(x)] \dots (1)$$

where q is the elementary charge, ϵ_0 is the permittivity of free space and ϵ_r is the relative dielectric constant of the semiconductor, relates the potential $\psi(x)$ to the electron and hole densities $n(x)$ and $p(x)$, respectively.

- The electron and hole current continuity equations

$$\frac{\partial}{\partial x} J_n(x) = -q U(x) \dots (2a)$$

$$\frac{\partial}{\partial x} J_p(x) = q U(x), \dots (2b)$$

where $J_{n(p)}(x)$ is the electron(hole) current density and $U(x)$ is the net generation rate, i.e.,the difference between the generation and recombination of free charge carriers [9].

$$U = PG_{max} - (1 - P)R, \dots (3)$$

where P is the dissociation probability of excitons, G_{max} is the maximum generation rate of bound electron-hole pairs, and R is the recombination rate.

- The drift-diffusion equations

$$J_n(x) = -qn\mu_n \frac{\partial}{\partial x} \psi(x) + qD_n \frac{\partial}{\partial x} n \dots (4a)$$

$$J_p(x) = -qn\mu_p \frac{\partial}{\partial x} \psi(x) - qD_p \frac{\partial}{\partial x} p \dots (4b)$$

where D is the carrier diffusion coefficient, which is assumed to obey the Einstein relation [10]

$$D = \mu V_t \dots (5)$$

with $V_t = k_B T / q$, the thermal voltage, where k_B is Boltzmann's constant and T is the absolute temperature.

Gummel iterative method [11] has been used to solve the coupled equations and Scharfetter-Gummel approximations [12] for the discretization of the continuity equations

Unlike inorganic solar cells, light absorption in BHJ organic solar cells results in the production of a mobile excited state (excitons) rather than free electron-hole pair. These photogenerated excitons are subsequently dissociate at a

heterojunction interface via an ultrafast charge transfer (≈ 45 fs) from the excited donor to the acceptor [13]. However, the ultrafast charge transfer to the acceptor does not directly result in free carriers, but in a bound electron-hole pair due to the Coulomb attraction between the carriers. This pair also needs to be dissociated, assisted by temperature and by the internal electric field, before it decays to the ground state [14]. As proposed by the Braun model [14], this bound pair is metastable, enabling multiple dissociations and being revived by the recombination of free charge carriers. Finally, the free carriers are transported to the electrodes, a process governed by charge mobility.

It has been shown that the bimolecular recombination of free carriers in organic semiconductors, which is a loss process in the solar cells, is of the Langevin type [15]. The recombination rate is given by

$$R = k_r (np - n_{int}^2), \quad (6)$$

where n (p) is the free electron (hole) density, n_{int} is the intrinsic carrier density, and k_r is the Langevin recombination constant. The recombination constant for a pristine material is governed by the sum of electron and hole mobility [15]

$$k_r = \frac{q}{\epsilon} (\mu_n + \mu_p) \quad \dots(7)$$

where ϵ is the dielectric constant. In case of a blend it was proposed that the spatial average of the electron and hole mobility should be used, in order to compensate for the eventual mobility differences of carriers in the different components of the blend [14], but Koster *et al.* [9] have shown that the slowest carrier mainly governs the recombination process in

the blend; since the fastest carrier cannot cross the interface due to the energy offset between the donor and the acceptor, it must wait for the slowest carrier in order to recombine [9], in which case the recombination constant is given by

$$k_r = \frac{q}{\epsilon} \min(\mu_n, \mu_p) \quad (8)$$

As a result, solar cells made of organic semiconductors are special in the sense that the two competing processes, extraction and recombination of charge carriers, are both governed by the mobility of the charge carriers. An increase in carrier mobility would have a positive effect on transport, facilitating carrier extraction, but on the other hand it will increase the bimolecular recombination strength as well.

2. Simulation results and analysis:

i. Carrier recombination rate

In solar cells based on *PPV:PCBM* blends (1:4 wt. ratio), the hole mobility, which is one order of magnitude lower than electron mobility [16], governs the recombination. With annealed *regioregular poly(3-hexylthiophene) (P3HT)* blended with *[6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM)* solar cells (1:1 wt. ratio), higher efficiencies have been obtained [3], not only due to an increased light absorption because of a higher polymer fraction in the blend, but in this case also the dissociation process is more efficient [17]. The carrier mobilities for the *P3HT:PCBM* blend (1:1 wt. ratio) are comparable to the *PPV:PCBM* (1:4 wt. ratio) blends [17], with $\mu_n \sim 10^{-7} \text{ m}^2/\text{Vs}$ and $\mu_p \sim 10^{-8} \text{ m}^2/\text{Vs}$. To investigate the effect of reducing the mobility on

the efficiency of such devices, all other device parameters are kept the same, including a 10:1 ratio of electron-to-hole mobility. A lower mobility of both carriers will lead to a slower extraction of the charge carriers as well as a reduced Langevin recombination, leading to a longer lifetime of the photogenerated carriers. The combination of these two effects strongly affects the steady-state build-up of charge carriers in the solar cell. In Figure 1 the electron and hole densities in the solar cell are calculated for electron mobility of $1 \times 10^{-10} \text{ m}^2/\text{Vs}$ (hole mobility of $1 \times 10^{-11} \text{ m}^2/\text{Vs}$) and $1 \times 10^{-5} \text{ m}^2/\text{Vs}$ (hole mobility of $1 \times 10^{-6} \text{ m}^2/\text{Vs}$). In this calculation all device parameters have been taken identical as the ones found for annealed P3HT:PCBM devices, table 1 [17].

As shown in Figure 1 the steady-state carrier concentrations under 1 Sun illumination ($100 \text{ mW}/\text{cm}^2$) typically increase by 5 orders of magnitude in the middle region of the device, when the mobility is lowered by 5 orders of magnitude. It can be seen from equations (6) and (7) that the strong increase of the carrier densities leads to a strong enhancement of the carrier recombination; since n and p vary each as much as the mobility, the reduction of the Langevin recombination constant k_r by a lower mobility is overruled by the product of n and p (equation 6).

In Figure 2 the amount of bimolecular recombination is calculated at short-circuit. For an electron mobility of $1 \times 10^{-10} \text{ m}^2/\text{Vs}$ (hole mobility

of $1 \times 10^{-11} \text{ m}^2/\text{Vs}$), 45% of the carriers recombine at short circuit conditions, as compared to only 0.38%, in case of an electron mobility of $1 \times 10^{-5} \text{ m}^2/\text{Vs}$ (hole mobility of $1 \times 10^{-6} \text{ m}^2/\text{Vs}$).

ii. Dissociation efficiency and optimum mobility

The dissociation of a bound electron-hole pair is a field and temperature dependent process, with a probability given by [16]

$$P(E, T) = k_D(E, T) / (k_D(E, T) + k_f) \quad (9)$$

where k_D is the dissociation rate constant of the electron-hole pair and k_f is the decay rate to the ground state. The dissociation rate constant k_D is proportional to the Langevin constant k_r of charge carriers () [16], a process which revives the electron-hole pair, and as mentioned above, is governed by the carrier mobility. As a result, the dissociation efficiency is also governed by the charge carrier mobility.

Figure 3 shows the dissociation probability at the maximum power point () as a function of electron mobility. It appears that for mobilities lower than the dissociation probability starts to decrease. As a result, at low mobilities not only the increased recombination reduces the solar cell performance, but also the fact that many of the photogenerated bound electron-hole pairs will not dissociate into free carriers and recombine to their ground state. These results indicate that high charge carrier mobility would be beneficial for the performance of an organic solar cell.

Therefore, the effect of an increasing carrier mobility is

evaluated, starting from a mobility of . As can be seen in Figure 3, the dissociation probability at maximum power point () approaches 1 at this mobility, and will not further increase, so the dissociation will not be further improved by a higher mobility value. However, a low mobility leads to a build-up of charge carriers in the solar cell. Following the same reasoning one can expect that a high mobility, giving rise to an efficient extraction, will lead to a depletion of charge carriers in the solar cell. Thus, sweeping carriers efficiently out of the device will lead to low quasi-Fermi levels for electrons and holes. The quasi-Fermi levels are a measure of the deviation from equilibrium of the system, and are related to the carrier densities by [18].

$$(10)$$

where $n(p)$ is the non-equilibrium (under illumination) electron (hole) concentration, n_i is the intrinsic carrier concentration, V is the applied voltage. At the open-circuit voltage , the carrier densities are given by [18]

$$(11)$$

equation (11), shows that a high mobility, which lowers the carrier densities due to fast carrier extraction, implicitly lowers the open-circuit voltage of the solar cell. In Figure 4 the quasi-Fermi levels in case of a very high mobility of are compared with the ones at . It is clear that V_{oc} , represented by the difference between the quasi-Fermi levels, is reduced from 0.55V to 0.1V when the mobility is increased from $\mu_n = 1 \times 10^{-5} \text{ m}^2/\text{Vs}$ to $\mu_n = 1 \times 10^3 \text{ m}^2/\text{Vs}$. This reduction of the V_{oc} leads to a decrease of the solar cell

performance at very high carrier mobilities.

iii. Efficiency and carrier mobility

It can be seen from figure 5 where the power conversion efficiency is calculated as a function of electron mobility that the efficiency shows a distinct maximum in the range of $\mu_n = 1 \times 10^{-6} \text{ m}^2/\text{Vs}$ to $\mu_n = 1 \times 10^{-5} \text{ m}^2/\text{Vs}$, and decreases for both lower and higher mobilities. The increased recombination and reduced dissociation probability at lower mobilities result in a decrease of the efficiency, whereas the loss in V_{oc} at higher carrier mobility is responsible for the decrease of the efficiency.

It should be noted that our results are in complete agreement with those obtained by Mandoc et al. [7]. Also the maximum experimentally measured carrier mobility for *BHJ* solar cells of *P3HT:PCBM*, is $\sim 10^{-7} \text{ m}^2/\text{Vs}$ for values of efficient device [17] which is fairly close to the values of our calculations.

Thus, we expect that further enhancement of the charge carrier transport properties would not lead to much improvement with regard to the efficiency.

3. Conclusions

We conclude that for maximum attainable performance of *BHJ* organic solar cells, charge carrier mobility must be optimized since both extremes, too low or too high mobilities, lead to losses in efficiency. Moreover, for further enhancement of the power conversion efficiency other concepts, such as improving the absorption, either by the use of strongly

absorbing acceptor materials or using tandem solar cells, should be investigated.

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Table (1) Parameters for annealed P3HT:PCBM device used for the simulation [17]

Parameter	Symbol	Value	Units
Active layer thickness	L	100	nm
Generation rate	G_{max}	6×10^{27}	$m^{-3}s^{-1}$
Spatial average of relative dielectric constant	ϵ	3.4	
Effective energy gap	E_g	1	eV
Dissociation parameter	a	1.8	nm
Decay constant	k_f	1.4×10^4	s^{-1}

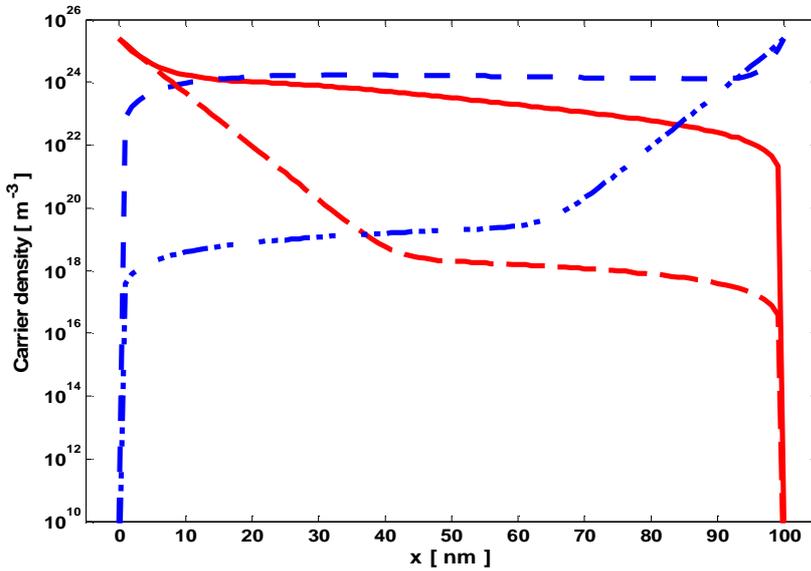


Figure (1) Carrier densities at short circuit versus device thickness, for an electron mobility of $1 \times 10^{-10} \text{ m}^2/\text{Vs}$ (hole mobility of $1 \times 10^{-11} \text{ m}^2/\text{Vs}$) electrons (solid line) and holes (dotted line) and for an electron mobility of $1 \times 10^{-5} \text{ m}^2/\text{Vs}$ (hole mobility of $1 \times 10^{-6} \text{ m}^2/\text{Vs}$): electrons (dashed line) and holes (dash-dotted line).

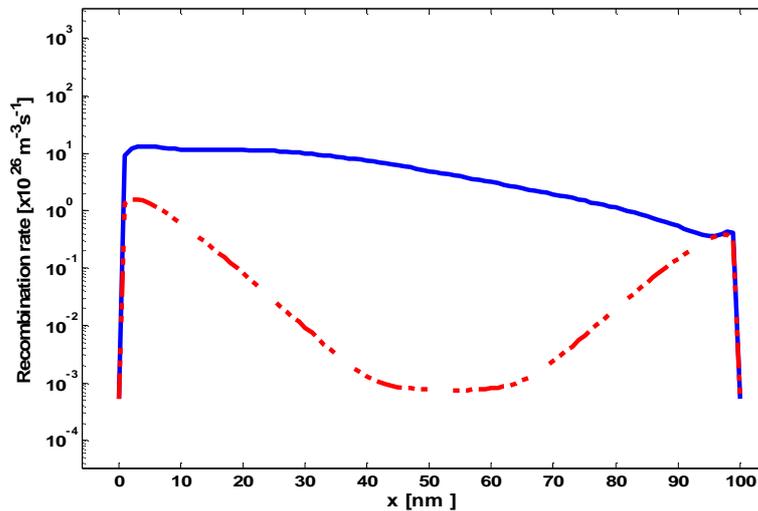


Figure (2) Recombination rate at short circuit versus device thickness for an electron mobility $1 \times 10^{-10} \text{ m}^2/\text{Vs}$ (hole mobility of $1 \times 10^{-11} \text{ m}^2/\text{Vs}$) (solid line) and for $1 \times 10^{-5} \text{ m}^2/\text{Vs}$ (hole mobility of $1 \times 10^{-6} \text{ m}^2/\text{Vs}$) (dash-dotted line).

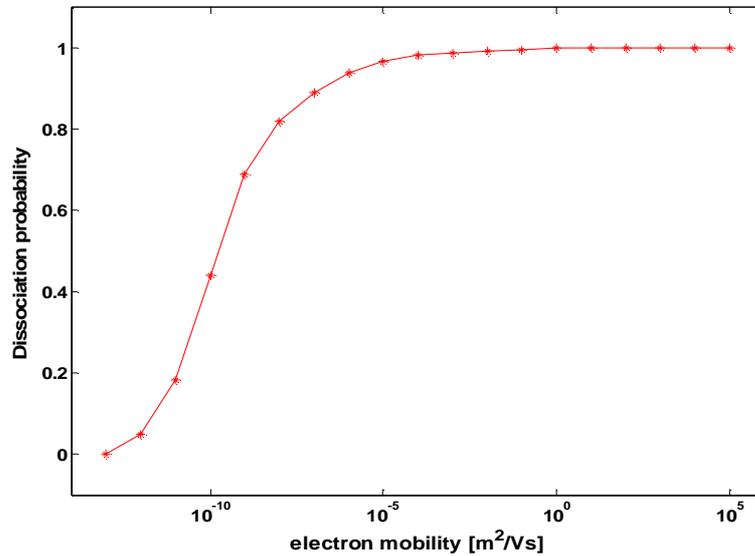


Figure (3) The dissociation probability at M_{pp} versus electron mobility, corresponding to efficiency values in Figure 5.

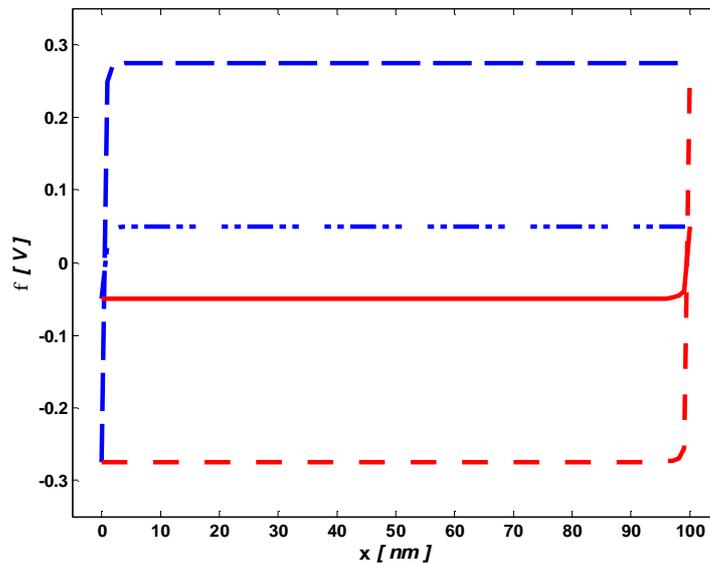


Figure (4) Quasi-Fermi levels versus the active layer thickness for $\mu_n = 1 \times 10^{-5} \text{ m}^2/\text{Vs}$ ($\mu_p = 1 \times 10^{-6} \text{ m}^2/\text{Vs}$), for electrons (dotted line) and for holes (dashed line), and in case of $\mu_n = 1 \times 10^3 \text{ m}^2/\text{Vs}$ ($\mu_p = 1 \times 10^2 \text{ m}^2/\text{Vs}$), for electrons (solid line) and for holes (dash-dotted line).

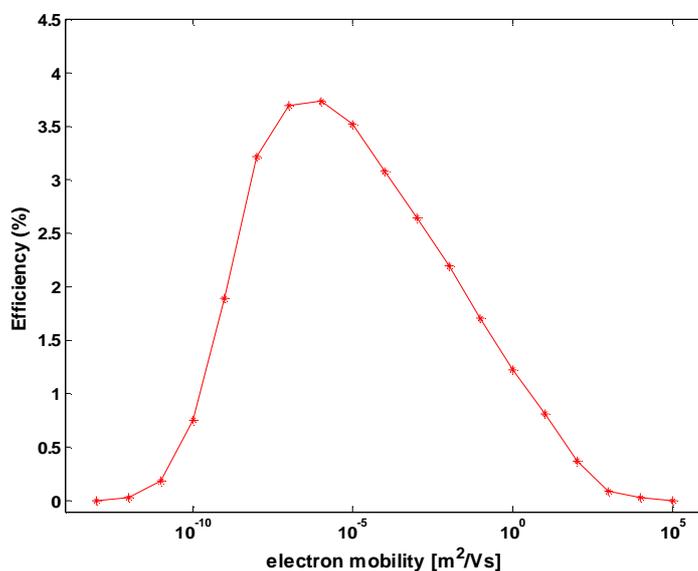


Figure (5) Efficiency as a function of electron mobility.