Carrier mobility, structural order, and solar cell efficiency of organic heterojunction devices

R. A. Streeta
Palo Alto Research Center, Palo Alto, California 94304, USA

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The loss mechanisms limiting solar cell efficiency in organic heterojunction photodiodes are discussed. We show that the energy loss when the exciton is split, and absence of Langevin recombination at the interface, are related to the magnitude of the electron-phonon interaction and the wavefunction extent of the electron and hole. In contrast to several recent publications, it is argued that well-ordered, high mobility organic materials will provide higher efficiency cells.


Bulk heterojunction (BHJ) organic solar cells are a promising solar cell technology. The BHJ diode derives its improved efficiency over a uniform thin film diode, from the large surface area to split the exciton into an electron-hole (e-h) pair and the short exciton diffusion length. However although the cell efficiency has reached 5%–6%, it is still too low for commercial power generation, for which an efficiency of 10% is expected to be a minimum requirement, irrespective of a low fabrication cost. In order to improve the efficiency it is essential to understand in detail the various loss mechanisms so that these might be overcome by better materials or better device geometry. The loss mechanisms are easily identified but the underlying explanation is under considerable debate. One of the advantages of organic electronics is the ability to design new molecules with specific properties, but the chemists need to know what properties to design for. Hence it is important to understand what might be possible as well as to understand the deficiencies of the existing materials systems.

The principal loss mechanisms involve the splitting of the exciton at the heterojunction, and the subsequent processes of recombination and charge collection. Koster et al. demonstrated by modeling that the cell efficiency increases rapidly with closer band alignment, but did not consider band offsets below 0.5 eV, raising the question of how the energy loss can be made smaller. Recombination after exciton splitting has been the subject of much debate, mostly based on the Langevin recombination mechanism. BHJ cells that have reached ~5% efficiency seem to largely avoid Langevin recombination for reasons that are not clear. Koster et al. proposed that the Langevin recombination rate at the interface was controlled by the carrier with the lowest mobility, unlike bulk recombination which was controlled by the faster carrier, suggesting low mobility of at least one carrier is helpful. However, studies have found that the recombination rate can be orders of magnitude below the usual Langevin rate so the difference would have to be very large. Arkhipov et al. proposed that the zero-point energy for a specific alignment of the polymer chain provides an energy barrier preventing recombination. The presence of a depletion field at the interface due to inadvertent impurities might separate the carriers before recombination can occur. However, the BHJ is so thin that there should be no significant electric field. An alternative explanation is that the polymer region immediately next to the interface is disordered and hence has a larger band gap due to reduced conjugation which will push the hole away from the interface. Again, this model suggests that low mobility, disordered materials provide the highest efficiency cell. In considering the charge collection, Mandoc et al. argued that there is an optimum mobility of ~10⁻² cm²/V s because lower mobility causes recombination from a very high carrier concentration, but higher mobility reduces the open circuit voltage, VOC, essentially because carriers are collected too rapidly.

The idea that low carrier mobility is generally beneficial to solar cell operation is counterintuitive and also contrary to the known properties of inorganic solar cells. Low mobility might help mitigate a particular loss mechanism in a certain material, but we argue here that it should be possible to find organic materials to give higher solar cell efficiency, and the common characteristic is that they should be high mobility, highly ordered materials.

Consider an exciton with energy EX and with binding energy EB to separate the electron and hole in a uniform material. The band offsets of the hetero-junction reduces the e-h energy by EH, when the pair separates to the different sides of the junction, so that the condition that the separated e-h pair has lower energy than the exciton is EH > EB. The energy of the e-h pair is then

\[ E_{EH} = EX + EB - EH. \]

The reverse reaction to the higher energy exciton state is reduced by a thermal activation factor \( \exp\left[-(EX - E_{EH})/kT\right] \). In principle, therefore, EH only needs to be larger than EB by a few kT to prevent the reverse reaction, so that \( E_{EH} = EX - n kT \), with \( n \) small and the reverse reaction is suppressed by \( e^{-n} \). These energies are illustrated in Fig. 1.

The issue with the solar cell efficiency is not the exciton energy per se but the optical absorption edge since the loss of cell efficiency arises from the inability to use photons in the energy range, \( \Delta E \), between \( E_{EH} \) and the optical gap, because VOC should be as close as possible to the optical gap. The magnitude of \( \Delta E \) depends on the physical situation, specifically on the electron-phonon coupling. The exciton binding energy in a typical organic has two components, the Coulomb energy of the electron and hole and the additional binding energy from the electron-phonon interaction. For the case that the exciton has negligible electron-phonon cou-
pling, the optical absorption edge is coincident with the exciton energy (assuming a direct gap semiconductor), irrespective of the magnitude of the exciton binding energy (see Fig. 1). In this case \( \Delta E = E_H - E_L = \hbar kT \), and the energy loss introduced by the exciton splitting can be minimal, perhaps no more than 0.1 eV (i.e., \( 4kT \) at room temperature). However, when the exciton has strong electron-phonon coupling, the optical absorption is no longer coincident with the exciton energy but is shifted up in energy by half the Stokes shift, \( E_S \), which is the difference between the energy of the exciton absorption and emission. The Stokes shift varies significantly from material to material but can be about 1 eV in the organics so the energy loss in the BHJ is \( \sim 0.5 \) eV plus the \( E_S - E_{EH} \) term. The two situations are illustrated in Fig. 1.

In the solar cells that organics must compete with, \( V_{OC} \) is \( \sim 0.4-0.5 \) eV below the optical gap (and \( \sim 0.7 \) eV below the gap in a-Si), the difference being largely due to the positions of the quasi-Fermi energies, \( E_{QFN} \) and \( E_{QFP} \), with respect to the band edge. For band gaps in the preferred range \( \sim 1.5 \) eV, the added reduction in \( V_{OC} \) when there is a strong electron-phonon coupling cuts \( V_{OC} \), and the cell efficiency in half, but by much less when there is only Coulomb binding. For the PCBM/P3HT BHJ cell, the optical gap is \( \sim 2 \) eV and \( V_{OC} \sim 0.6 \) eV, which is even worse than our estimate.

The conclusion is that two mechanisms reduce \( V_{OC} \)—the band offsets at the heterojunction and the Stokes shift—and both contribute about 0.5 eV in present BHJ solar cells. It is therefore important to minimize the energy loss at the heterojunction by choosing materials with appropriate energy levels with respect to the exciton energy, and to find an organic semiconductor with as small as possible electron-phonon coupling of the exciton so that the optical gap is as close as possible to the exciton zero-phonon energy. Increased conjugation length in well-ordered polymers is known to give delocalized excitons with smaller Stokes shift.\(^1\) The effect of structural order to reduce the phonon coupling is also known for polarons in the organic semiconductors.\(^1\)

According to the Langevin recombination mechanism, recombination across the heterojunction should be expected even after the exciton has split. Langevin recombination applies to a material with short carrier mean free paths, in which case recombination occurs whenever a carrier is bound by the Coulomb attraction of an opposite carrier or a charged trap. The capture radius corresponds to a Coulomb energy of \( kT \), and the capture rate is then only dependent on the carrier mobility and the dielectric constant. For a typical polymer at room temperature, the capture radius is 10–20 nm. Since the electron and hole split at the heterojunction are closer, recombination should occur.

The Langevin model is a classical model which assumes that the Coulomb well binds the electron and hole with ever increasing energy as they become indefinitely close so that recombination is certain once the carriers are bound by more than \( kT \). In the quantum mechanical description, however, the electron and hole have a finite binding energy which corresponds to the formation of an exciton. Whether or not the Langevin model applies depends on the relative rates of exciton recombination, \( P_E \) or thermal ionization. Hence, the Langevin model applies when

\[
P_E > \omega_0 \exp(-E_B/kT), \quad E_B > kT \ln(\omega_0/P_E).
\]

When this condition is not satisfied, the Langevin recombination model does not apply and the recombination rate is smaller. For a typical situation, \( \omega_0 \sim 10^{13} \) s\(^{-1} \) and for a single exciton, \( P_E \sim 10^9 \) s\(^{-1} \), so that the condition is \( E_B > 10kT - 0.25 \) eV at room temperature. The lower recombination rate of triplets makes ionization relatively much more favorable. Thus the exciton binding energy has to be quite large before the Langevin mechanism applies. The Langevin recombination actually has less to do with the low mobility, but rather is determined by the exciton binding energy and consequently on the magnitude of the electron-phonon coupling.

Langevin recombination of the split exciton is even less favorable. The Coulomb energy of an e-h pair on either side of a junction at their point of closest approach is

\[
E_C = \frac{e^2}{4 \pi \varepsilon_0 (R_E + R_H)},
\]

where \( R_E \) and \( R_H \) are the wavefunction extent of the electron and hole. The physical separation of the electron and hole also reduces the split exciton recombination rate by a tunneling factor \( \exp(2R/R_0) \), where \( R \) is the separation of the charges and \( R_0 \) is the parameter of the exponential decay of the wavefunction into the other side of the heterojunction. The condition for exciton ionization to dominate over recombination becomes

\[
\omega_0 \exp\left[-\frac{e^2}{4 \pi \varepsilon_0 (R_E + R_H)kT} \frac{E_P}{kT} \right] > P_E \exp\left[-\frac{2(R_E + R_H)}{R_0}\right],
\]

or

\[
\ln\left[\frac{\omega_0}{P_E}\right] - \frac{e}{4 \pi \varepsilon_0 (R_E + R_H)kT} \frac{E_P}{kT} + \frac{2(R_E + R_H)}{R_0} > 0.
\]

\( E_P \) is the contribution to the binding energy from the electron-phonon coupling in addition to the polaron energies of the free carriers. Increasing \( R_E + R_H \) rapidly makes the left side of Eq. (5) more positive, as illustrated in Fig. 2. The tunneling term is substantial since \( R_0 \) should be small, as it
represents the wavefunction decay in a potential well \( \sim -0.5 \) eV deep. On the other hand, \( E_p \) probably contributes very little, as the extra phonon coupling should be negligible until the electron and hole are very close together.

When the left side of Eq. (5) is positive, the split exciton is in thermal equilibrium with the free carriers. The rate of exciton recombination depends on the occupancy of the exciton state, and hence on its energy, \( E_{XS} \), relative to the free energy of the free electron and hole. Hence recombination is increasingly suppressed when \( E_{XS} \) is larger than \( E_{QFN} + E_{OFF} \). The electron and hole can easily be more than 1 nm apart so that the binding energy is \(<0.4\) eV, while \( E_{QFN} \) and \( E_{OFF} \) together can be more than 0.5 eV from \( E_{EH} \) so that it is very reasonable that recombination is highly suppressed.

The relative probability of recombination compared to charge collection is therefore very sensitive to the extent of the electron and hole wavefunction on either side of the junction. An extended electron and hole wavefunction rapidly favors charge separation, and therefore the best strategy to enhance carrier collection is to maximize the wavefunction. The wavefunction extent is larger in a more ordered polymer material, and polythiophenes can have crystallite sizes of 10 nm or more. Hence rather than a disordered material at the interface to separate the e-h pair, our analysis suggests that a more ordered material is needed.

Finally, the analysis that high carrier mobility leads to low \( V_{OC} \) seems incorrect. The proposed argument is that if carriers are extracted rapidly, their concentration is low so that the quasi-Fermi energy level, \( E_{QF} \), is far below the band edge. Therefore \( V_{OC} \) is consequently small since it arises from the difference in electron and hole \( E_{QF} \). Instead, the following argument is offered. When the cell is biased at \( V_{OC} \), the current is zero and no charge is collected. The positions of the electron and hole \( E_{QF} \) is therefore determined by recombination, not by the rate of charge extraction, and so the carrier mobility plays no direct role in \( V_{OC} \). A high fill factor requires that charge is extracted as efficiently as possible at voltages close to \( V_{OC} \), where the extraction field is very small. Hence a high mobility is beneficial to the fill factor.

Recombination at a bias near \( V_{OC} \) may be by e-h recombination across the junction or by the Auger-like recombination of an exciton with a free carrier. Both are enhanced by the high carrier concentration—high concentration increases the quasi-Fermi energy, which favors recombination across the junction as discussed above.

In summary, consideration of exciton splitting, recombination, and charge collection all suggest that highly ordered organic materials are more likely to give higher efficiency cells, in contrast to other models that suggest low mobility materials would be better. In particular, organic materials are needed that minimize the exciton electron-phonon coupling by specific molecular design and/or having a highly ordered structure in the device. It is important to resolve the mechanisms of recombination and charge collection in detail so that materials can be synthesized and studied that have the best chance of organic solar cell optimization.


\[ 10 \] P. Peumans (unpublished).

