

Chapter 2

Charge Transport and Recombination in Organic Solar Cells (OSCs)

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2.1 Basic Concepts of Charge Transport in Organic Semiconductors

Organic compounds are mainly hydrocarbon compounds with a backbone of carbon atoms. The strong bonds that form the molecular backbone are a result of overlap of sp^2 hybridized atomic orbitals of adjacent carbon atoms, yielding a bonding σ and an antibonding σ^* orbitals. The remaining unhybridized p orbitals overlap and form π and π^* orbitals. The energies of π orbitals are higher than those of σ orbitals, whereas energies of π^* orbitals are lower than those of σ orbitals. Based on Pauli exclusion principle and Hund's rule, the energies of π and π^* orbitals are defined as highest occupied molecular orbital (HOMO), and lowest unoccupied molecular orbitals (LUMO), respectively.

For charge transport to take place in organic solids, there must be a charge on the molecular unit. This may either be an additional electron that is accommodated in an antibonding orbital, or one that is removed from bonding orbital. The molecule is then no longer in the ground state but rather in a charged excited state.

There are a number of factors that can influence charge carrier mobilities, including molecular packing, disorder, temperature, impurities, electric field, and pressure [1].

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2.1.1 General Approach to Charge Transfer Mechanisms

For inorganic semiconductors such as silicon (Si) and germanium (Ge), which involve covalent bonds with high-bonding energy, charge carriers move as highly delocalized plane waves and carrier mobilities are often far larger than $1 \text{ cm}^2/\text{Vs}$. In these systems, as a result of carrier scattering, increasing temperature reduces the carrier mobilities. On the other hand, in the case for organic semiconductors, they consist of π -conjugated units and they are kept together mainly by weak van der Waals forces with weak bonding energies on the same order as molecular vibrational energies at room temperature. In addition, the separations between molecules are sufficiently large for molecular orbitals to overlap. Therefore, charge transport in organic semiconductors takes place in the form of hopping mechanism. In contrast to inorganic semiconductors, elevated temperature increases the charge carrier mobilities for organic semiconductors. Understanding the fundamental charge transport mechanisms at both molecular and device levels are of special importance to organic semiconductors. There are several excellent review articles to cover this topic. For example, interested readers can find these recent reviews regarding charge transport in organic semiconductors [1, 2].

Typically, it is believed that semiconductors with carrier mobilities higher than $1 \text{ cm}^2/\text{Vs}$ involve carrier transport via delocalized plane waves, whereas carrier mobilities less than $0.1 \text{ cm}^2/\text{Vs}$ are suggestive of hopping conduction between localized states across different molecules. For hopping transport, the relationship between carrier mobility and temperature follows Eq. (2.1).

$$\mu = \mu_0 \exp \left[- \left(\frac{T_0}{T} \right)^{\frac{1}{\alpha}} \right], \alpha \text{ is between 1 and 4.} \quad (2.1)$$

The exact charge transport mechanisms in organic semiconductors are still under debate. The most commonly used model is the Holstein's small-polaron model [3]. In covalent π -conjugated organic systems, the distribution of electronic cloud in molecules is highly delocalized. Self-trapping occurs via the creation of localized states in the gap between conduction band and valence band, which results in the formation of polarons. The Holstein model simplifies the charge transport as a 1D, one-electron model. The total energy in the system consists of three elements: (i) lattice energy E_L which is a sum of N number of harmonic oscillator at a single frequency, ω_0 , in the form of:

$$E_L = \sum_{n=1}^N \frac{1}{2M} \left(\frac{\hbar}{i} \frac{\partial}{\partial u_n} \right) + \frac{1}{2} M \omega_0^2 u_n^2 \quad (2.2)$$

where u_n is the displacement of n th molecule from its equilibrium position and M is the reduced mass of each molecular site; (ii) the energy dispersion of the electron which can be written in the form of:

$$E_k = E_0 - 2J \cos(ka) \quad (2.3)$$

where J is the electron transfer energy and a is the lattice constant; (iii) the electron-lattice coupling in the form of $\varepsilon_n = -Au_n$, where A is a constant.

Another important parameter to consider is the polaron-binding energy, E_b , which is described as the energy gain of an infinitely slow carrier due to polarization and deformation. It can be described as:

$$E_b = A^2 / (2M\omega_0^2) \quad (2.4)$$

When electronic bandwidth, $2J$, is smaller than E_b , the small-polaron model faces its limit. In such condition, the electronic term of the total Hamiltonian can be treated as a small perturbation, and the mobility of the small polaron can be described as a time-dependent Schrödinger equation. At high temperature ($T > \Theta$, Θ is the Debye temperature), mobility is obtained through:

$$\mu = \sqrt{\frac{\pi}{2}} \frac{ea^2}{\hbar} \frac{J^2}{\sqrt{E_b}} (kT)^{-\frac{3}{2}} \exp\left(-\frac{E_b}{2kT}\right) \quad (2.5)$$

where $\frac{ea^2}{\hbar}$ has the dimension of a carrier mobility, and is close to 1 cm²/Vs for most organic crystals.

It is also worth noting that at high field ($> 10^5$ V/cm), the carrier transport in organic materials is field-dependent. This is because the external field can alter the columbic potentials near localized-energy levels, thus increasing the electron tunnel transfer rate between sites. This phenomenon is described as Poole–Frankel mechanism. The field-dependent mobility, $\mu(F)$, can be described as:

$$\mu(F) = \mu(0) \exp\left(\frac{q}{kT} \beta \sqrt{F}\right) \quad (2.6)$$

Where $\mu(0)$ is the mobility at zero field, and β is the Poole–Frankel constant, which can be obtained from:

$$\beta = \left(\frac{e}{\pi\epsilon\epsilon_0}\right)^{\frac{1}{2}} \quad (2.7)$$

Where ϵ is the dielectric constant and ϵ_0 is the vacuum dielectric constant [3].

The multiple trapping and release (MTR) model is most widely used in describing charge transport in amorphous silicon. MTR model assumes that: (i) the probability of carrier arriving at a trap site and being trapped is close to unity; (ii) the release of trapped carrier is a thermally activated process. The relationship between drift mobility, μ_D and the mobility in the delocalized band, μ_0 , can be described as:

$$\mu_D = \mu_0 \alpha \exp\left(-\frac{E_t}{kT}\right) \quad (2.8)$$

Where E_t is the energy difference between trap and band edge of delocalized band, and α is the ratio between the effective density of states at delocalized band–band edge to the concentration of traps.

Various other models have been employed for describing charge transport in organic semiconductors [4–6]. For example, Borsenberger et al. [4] described the charge transport in disordered molecular solids in the form of hopping transport between the Gaussian DOS of hopping sites. Meijer et al. [6] in the studies of pentacene and α -hexathiophene, discovered that the carrier transport follows Meyer–Neldel rule (MNR), in which the carrier transport mobility can be described as:

$$X = X_{00} \exp - E_a \left(\frac{1}{k_B T} - \frac{1}{E_{MN}} \right) \quad (2.9)$$

Where E_{MN} is the Meyer–Neldel energy, and E_a is the activation energy.

2.2 Operation of Organic Photovoltaic (OPV)

In this section, some basics of OPV are outlined. First, the fundamentals of photovoltaic effect known from conventional semiconductor models are outlined. Then, equivalent circuit models widely used for describing different solar cell systems are presented. Next, we outline the unique processes occurred in OPVs and the origins of V_{OC} , J_{SC} , and fill factor (FF) are described. Last, we focus on the two types of recombination dynamics, geminate and nongeminate recombination, which are the two dominating loss mechanisms limiting the performance of OPVs.

2.2.1 Photovoltaic Effect

2.2.1.1 Photon Absorption

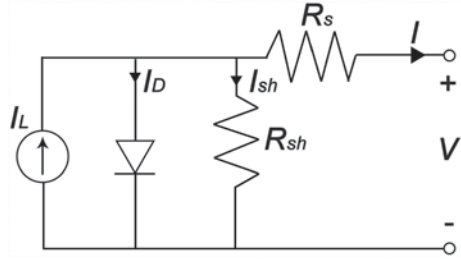
The basic relationship between photon wavelength, λ , and energy is:

$$\lambda = \frac{C}{\nu} = \frac{hc}{h\nu} = \frac{1.24}{h\nu} (\mu\text{m}) \quad (2.10)$$

where C is the speed of light in vacuum, ν is the frequency of light, h is Planck's constant.

When a semiconductor interacts with incident light, photons can be absorbed under these circumstances: (i) when $h\nu = E_g$ electrons are activated from the valence band to the conduction band; (ii) when $h\nu > E_g$, in addition to the formation of electron-hole pair, the excess energy $h\nu - E_g$ is released in the form of heat; (iii) when $h\nu < E_g$, the photons can be absorbed only if there exist deep level states as a result of chemical impurities or physical defects.

Fig. 2.1 Equivalent circuit of a practical solar cell



2.2.1.2 Semiconductor Photovoltaic Effect and Charge Transport Equations

The transport of electrons and holes in inorganic semiconductors can be described using field current and diffusion current. The one-dimensional drift-diffusion equation follows:

$$J_n = q\mu_e n \frac{\partial E_c}{\partial x} + qD_n \frac{\partial n}{\partial x} \quad (2.11)$$

$$J_p = q\mu_h p \frac{\partial E_v}{\partial x} - qD_p \frac{\partial p}{\partial x} \quad (2.12)$$

Where $J_{e,h}$ is the electron/hole current density, $\mu_{e,h}$ is the electron/hole mobilities, and $D_{e,h}$ is the electron/hole diffusion coefficients. Assuming an electric field $E = -grad\phi$ and uniform distribution of electrons and holes, the total charge, j_Q , can be written as:

$$j_Q = \frac{\sigma_e}{e} grad\eta_e - \frac{\sigma_h}{e} grad\eta_h \quad (2.13)$$

For conventional *pn*-junction solar cells, the space charge forms a stable electric field in the direction of *n*-type toward *p*-type, with the diffusion voltage being:

$$\psi_0 = \psi_n - \psi_p = V_T \ln \frac{N_d N_a}{n_i^2} \quad (2.14)$$

Where N_a is the majority carrier concentration, N_d is the donor impurity concentration, n_i is the intrinsic carrier concentration, and V_T is the thermoelectric field.

2.2.2 Solar Cell Equivalent Circuit Model

For an ideal solar cell, the I-V characteristics can be described using equivalent circuit (Fig. 2.1):

When ignoring the effect of series resistance (R_s) and shunt resistance (R_{sh}) ($R_s=0$ and $R_{sh}=\infty$) for ideal solar cell, current can be represented by the difference between short circuit photocurrent, I_L , and the forward current of pn -junction, or dark current,

$$I_D = \left(1 - e^{\frac{V}{V_T}} \right) \quad (2.15)$$

$$I = I_L - I_D = I_L + I_0 \left(1 - e^{\frac{V}{V_T}} \right) \quad (2.16)$$

where I_0 is the saturation current. Therefore, the voltage on pn -junction is given by:

$$V = V_T \ln \left(1 + \frac{I_L - I}{I_0} \right) \quad (2.17)$$

Under short-circuit condition ($V=0$), the current output is the short-circuit current: $I = I_L = I_{sc}$. Whereas under open-circuit condition ($I=0$), the open-circuit voltage is given by:

$$V_{oc} = V_T \ln \left(1 + \frac{I_L}{I_0} \right). \quad (2.18)$$

Based on the equivalent circuit diagram of solar cell, the solar cell output power is given simply by:

$$P = IV = (I_L - I_D)V = I_L V + I_0 V \left(1 - e^{\frac{V}{V_T}} \right) \quad (2.19)$$

To further include the discussion of R_s and R_{sh} for practical solar cells, the I-V characteristics are modified from ideal solar cell condition:

$$I = I_L + I_0 \left(1 - \frac{e(V - IR_s)}{V_T} \right) - \frac{V - IR_s}{R_{sh}} \quad (2.20)$$

The power conversion efficiency (PCE) is represented by the ratio between solar cell maximum power output, P_m , and input power from incident light, P_{in} :

$$\eta = \frac{P_m}{P_{in}} \times 100\% \quad (2.21)$$

Here, according to Eq. 2.19, P_m can be further represented as:

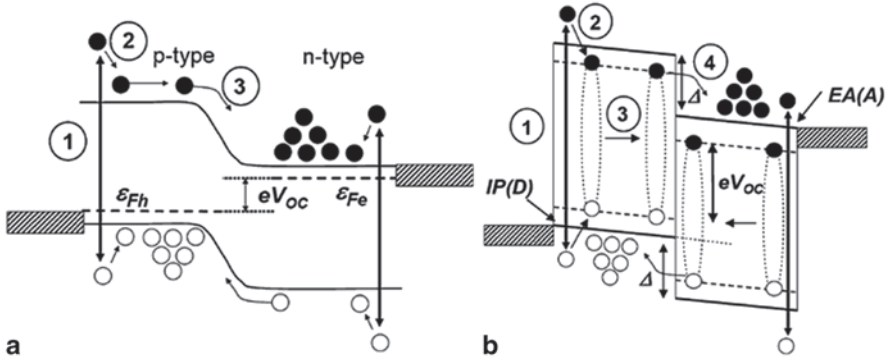


Fig. 2.2 Comparison of the typical energy diagrams of **a** an inorganic solar cell and **b** an organic solar cells. **a** In inorganic *p-n* junction solar cells, absorption of photon energy leads to thermalization of the holes and electrons near the top of the valence and conduction bands (*step 1*), followed by the diffusion of minority carriers to the junction (*step 2*) and they are eventually swept away and accumulate on the other side of the junction where they become the majority carriers (*step 3*). V_{oc} of *p-n* junction solar cells is determined by the difference between the quasi-Fermi level energies of *n*- and *p*-type semiconductors (denoted as \mathcal{E}_{Fe} and \mathcal{E}_{Fh} , respectively). **b** In organic solar cells, absorption of photons (*step 1*) lead to the formation of a bound electron-hole pair, exciton, (*step 2*) which diffuse to the donor/acceptor interface (*step 3*). As a result of energy difference between electron affinity of the donor and the acceptor materials, excitons can dissociate and form free-charge carriers (*step 4*). In this process, the maximum V_{oc} is determined between ionization potential of donor ($IP(D)$) and electron affinity of acceptor ($EA(A)$). Reproduced from ref [7]

$$P_m = V_{mP} I_{mP} = \frac{V_{mP}^2 I_L}{V_{mP} + V_T} \left(1 + \frac{I_0}{I_L} \right) \quad (2.22)$$

where V_{mP} and I_{mP} are the voltage and current at the maximum power point per unit area. It is obvious that high solar cell efficiency requires high I_{sc} and V_{oc} . Another important factor, FF also contributes to the solar cell efficiency. FF is defined as the ratio between P_m and the product of V_{oc} and I_{sc} : $FF = \frac{V_{mP} I_{mP}}{V_{oc} I_{sc}}$. Finally, according to Eq. 2.21, the PCE is therefore defined as:

$$\eta = \frac{V_{oc} \times I_{sc} \times FF}{P_{in}}$$

2.2.3 Organic Photovoltaic Cells

In the simple picture of an energy diagram, a *p*-type semiconductor and an *n* type semiconductor is placed adjacent to each other, forming an abrupt interface. (Fig. 2.2) Different from traditional *p-n* junction type solar cells, in OPV operation, the absorption of a photon does not directly lead to a free electron and a free hole.

This entity in which electron and hole are still bound to each other by Coulomb forces is called an exciton, and it requires a relatively large driving force to be separated [1].

The basic light absorption process in OPV can be simply summarized as following: charge pairs are generated throughout the device with the generation rate proportion to the optical absorption profile $Q(x)$, calculated as [8]

$$Q(x) = \frac{1}{2} c \varepsilon_0 \alpha n |E(x)|^2 \quad (2.23)$$

where c is vacuum speed of light, ε_0 is the vacuum permittivity, n is the refractive index, α is the absorption coefficient. Charge-pair separation efficiency is then determined via the Onsager–Braun formula that depends on the local strength of the internal electrical field (see more further).

Another important property of OPV active layer is that they are macroscopically homogeneous mixtures and cannot differentiate charge transport direction without selective contacts. Usually, a combination of a low-work function and a high-work function electrode, as well as common n -type and p -type interfacial layers are used to differentiate electron and hole transport. A standard model for charge collection in bulk heterojunction (BHJ) OPV is illustrated in a recent review by Bisquert et al. [9]. In principle, the transport of separated charges to the electrodes can be modeled via drift-diffusion equations as described previously with the additional possibility of the trapping and detrapping of electrons from deep trap states. In the following sections, the exciton dissociation and charge collection processes involving two key recombination mechanisms: geminate recombination and nongeminate recombination will be discussed in more details.

2.2.4 Basic Charge Transport Expressions in Organic Solar Cells

Similar to inorganic-type solar cells described previously, the fundamental relationship between charge and electric field can be described by Poisson's equation:

$$\frac{dE}{dx} = \frac{\rho}{\varepsilon} = \frac{q}{\varepsilon} (p(x) - n(x) + N_D - N_A) \quad (2.24)$$

At any given position x in solar cell photoactive layer, the exciton-generation rate (the number of exciton generated) can be represented as:

$$G(x) = \frac{Q(x)}{E_e} = \frac{Q(x)}{h\nu} = Q(x) \frac{\lambda}{hc} \quad (2.25)$$

where $E_e = \frac{hc}{\lambda}$ is the exciton energy,

where E is the electric field, ρ is the charge density and ε is the material permittivity. The electron and hole continuity equations are:

$$\frac{1}{q} \frac{dJ_n(x)}{dx} + G(x) - R(x) = 0 \quad (2.26)$$

$$\frac{1}{q} \frac{dJ_p(x)}{dx} + G(x) - R(x) = 0 \quad (2.27)$$

At any given position x in solar cell photoactive layer, the short-circuit current density $J(x)$ is the difference between carrier generation rate and recombination rate.

2.2.5 Origin of V_{oc} , J_{sc} , and FF

2.2.5.1 V_{oc}

V_{oc} of OPV is a result of splitting electron and hole quasi-Fermi energy levels triggered by illumination.

$$V_{oc} = \frac{1}{q} (E_{Fn} - E_{Fp}) \quad (2.28)$$

Where E_{Fn} and E_{Fp} are the electron and hole quasi-Fermi energies, respectively. Scharber et al. [10] summarized a series of OPV active layers and propose the empirical relationship between the HOMO of the donor materials and LUMO of the acceptors, proposed by Scharber et al.,

$$V_{oc} = \frac{1}{q} (E_{HOMO,D} - E_{LUMO,A} - 0.3V) \quad (2.29)$$

It should be noted that the V_{oc} loss of 0.3 eV is empirical, and the loss could be greater or smaller.

There are a number of factors that can adversely affect the V_{oc} of OPV devices. Consideration on disorder-induced V_{oc} loss and carrier recombination induced V_{oc} loss, V_{oc} can be expressed: [11]

$$qV_{oc} = \Delta E_{DA} - \frac{\sigma^2}{k_B T} - k_B T \ln \left(\frac{N_A N_D}{np} \right) \quad (2.30)$$

In Eq. 2.30, the first term is the effective bandgap, ΔE_{DA} , the second term is the disorder-induced V_{oc} loss, and the third term represents carrier recombination induced V_{oc} loss.

Experimentally, the dependence of V_{oc} on temperature and light intensity has profound effect on identifying basic OPV properties. By linearly fit V_{oc} with respect to temperature, it was found that $V_{oc} = \Delta E_{DA}$ when T approaches 0 K [12, 13]. However, this linear dependence is only valid at low temperature. V_{oc} was rather

found to saturate at elevated temperatures and started to decrease at certain temperature. This effect can be easily simulated according to Eq. 2.30 [11]. Therefore, by measuring V_{oc} saturation experimentally, one can estimate the degree of disorder in OPVs.

The steady-state light intensity dependence of V_{oc} is widely used to fit to a logarithmic relationship:

$$V_{oc} = S \ln(I / I_0), \quad (2.31)$$

where I_0 is the light intensity under 1 sun condition [14–16]. Here the slope, S , can be compared to nkT/q , where n is the ideality factor. For p - n junction-based inorganic solar cells, n is often observed to be close to 1 since bimolecular recombination is the predominant loss mechanism. Whereas $n > 1.5$ is often found in several OPV systems [7, 17], indicating the presence of possible other recombination mechanisms, i.e., trap-assisted recombination.

2.2.5.2 J_{sc}

J_{sc} is directly related to the spectral response, and it can be simply calculated by integrating the external-quantum efficiency, η_{EQE} , against the AM 1.5G spectrum. (where $N_{ph}(\lambda)$ is the photon flux density at wavelength (λ))

$$J_{sc} = \int_{AM\,1.5} e \eta_{EQE}(\lambda) N_{ph}(\lambda) d\lambda \quad (2.32)$$

Where E is the photon energy, q is the elementary charge [7].

Similar to V_{oc} , light intensity dependent J_{sc} measurement is also good indicator of recombination orders [18].

2.2.5.3 FF

Unlike V_{oc} and J_{sc} which can be estimated relatively easily through material-energetic alignment of D and A , i.e., lowering optical bandgap to maximize J_{sc} , while lowering the HOMO energies of donor materials to increase V_{oc} . Note, however, that HOMO lowering will also increase the bandgap, underscoring the problematic tradeoff between V_{oc} and J_{sc} . Realizing high FFs has proven elusive, although there is evidence that carrier mobility, active-layer microstructure, and also interfacial and bulk charge recombination play a role [19, 20].

After solving equivalent circuit model, a common expression for ideal FF_0 (no resistance considered) can be written as:

$$FF_0 = \frac{\tilde{v}_{oc} - \ln(\tilde{v}_{oc} + 0.72V)}{\tilde{v}_{oc} + 1} \quad (2.33)$$

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