

Temperature dependence of open-circuit voltage in organic solar cells from generation–recombination kinetic balance

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ABSTRACT

The variation in the open-circuit voltage of bulk-heterojunction organic solar cells with temperature and light intensity is analyzed based on the kinetic balance between photogeneration and recombination rates, by determining the Fermi level displacement with temperature and occupancy of the density-of-states. In good accordance with experimental observations, a negative temperature coefficient of order $dV_{oc}/dT \approx -1 \text{ mV K}^{-1}$ is obtained at temperatures higher than a critical value T_c , which signals the transition between high- to low-occupancy conditions. This temperature dependence is valid for carriers obeying Boltzmann statistics at low-occupancy level, in similarity to that occurring for inorganic solar cells.

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1. Introduction

Organic conducting materials are at the heart of bulk heterojunction (BHJ) organic solar cells, a promising alternative to silicon-based solar cells [1–3] because of their optical, electronic and mechanical properties [4,5]. Despite the progress in device physics some fundamental issues are still unclear and require further investigation, for instance the origin of the open-circuit voltage V_{oc} and the limits of conversion efficiency [6,7], and the kinetics of recombination [8,9]. Particularly interesting is the analysis of V_{oc} dependence on light intensity and temperature. Experimental results using several BHJ configurations [10–13], and flexible roll-to-roll coated modules [5] found that V_{oc} linearly decreases with temperature exhibiting a temperature coefficient of order -1 mV K^{-1} around room-temperature (see Table 1). No definitive explanation exists about the physical mechanism behind the observed temperature dependence of V_{oc} . Such temperature behavior was related for instance to the temperature dependence of the built-in voltage [13]. Other authors, however, qualitatively interpreted this behavior relying on the response of inorganic p–n junction to temperature [11]. Additionally, V_{oc} is known to be related to fundamental thermodynamic parameters such as the statistics of occupancy of transport and trap states. Here, we show the calculation of V_{oc} as a function of temperature and light intensity using a recently

published model [14], which integrates carrier density-of-states (DOS) and generation–recombination kinetic balance. Our approach then regards V_{oc} as determined by inner, bulk material parameters such as occupancy statistics and recombination mechanisms [14]. The results of the calculation will be compared with experimental temperature coefficients of V_{oc} reported for BHJ organic solar cells.

2. Open-circuit voltage calculation

In every solar cell, the open-circuit photovoltage, which can be achieved assuming large enough carrier mobilities, equals the difference between the electron and hole chemical potentials (quasi-Fermi levels) in the active layer under steady-state illumination [15]

$$qV_{oc} = E_{Fn} - E_{Fp} \quad (1)$$

where q is the elementary charge. Hence, the output voltage measured in open-circuit conditions monitors the splitting of the Fermi levels, which in turn are stated by the charge-carrier concentrations. In the case of crystalline silicon solar cells, the free carrier density follows the Fermi statistics, which can in most cases well be approximated by the Boltzmann distribution. This entails that V_{oc} can be expressed as

$$qV_{oc} = E_g - k_B T \ln \left(\frac{N_c N_v}{np} \right) \quad (2)$$

Here E_g corresponds to the energy gap, N_c (N_v) the effective conduction band (valence band) density-of-states, n (p) the free

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Table 1

Temperature coefficient of the open-circuit voltage of different bulk-heterojunction organic solar cells (and other kinds of photovoltaic devices for comparison) measured around room temperature and 100 mW cm⁻² of light intensity.

Solar cell	Temperature coefficient (mV K ⁻¹)	Reference
Bulk-heterojunction organic		
P3HT ^a :PCBM ^b	~ -0.6	[11]
P3HT ^a :PCBM ^b	~ -0.7	[5] ^c
MDMO-PPV ^d :PCBM	-1.1	[12]
MDMO-PPV:PCBM	-1.4 to -1.6	[10]
MDMO-PPV:PCBM	-1.5	[13]
Solid-state dye-sensitized		
TiO ₂ :SpiroMeOTAD ^e	-1.4	[31]
Crystalline Si		
p-n junction	-1.9 to -2.5	[17]

^a P3HT=poly(3-hexylthiophene).

^b PCBM=[6,6]-phenyl C₆₁-butyric acid methyl ester.

^c per cell in a module.

^d MDMO-PPV=poly [2-methoxy, 5-(3',7'-dimethyl-octyloxy)]-p-phenylene-vinylene.

^e SpiroMeOTAD=2,2',7,7'-tetrakis(N, N-di-methoxyphenyl-amine)-9,9'-spiro-bifluorene.

electron (hole) concentration and $k_B T$ stands for the thermal energy. The temperature coefficient of V_{oc} is derived as follows

$$q \frac{dV_{oc}}{dT} = \frac{dE_g}{dT} - k_B \ln \left(\frac{N_c N_v}{np} \right) + k_B T \left(\frac{1}{n} \frac{dn}{dT} + \frac{1}{p} \frac{dp}{dT} \right) \quad (3)$$

The third summand in Eq. (3) has a minor contribution to the derivative because the terms dn/n and dp/p are likely to be very small. The second summand can be expressed in a more useful form [16]

$$\frac{dV_{oc}}{dT} \approx \frac{dE_g/q}{dT} + \frac{V_{oc} - E_g/q}{T} \quad (4)$$

From Eq. (4) it is inferred that the temperature dependence is mainly related to the term $(V_{oc} - E_g/q)/T$, which after integration provides a linear relationship $V_{oc} \propto -T$ [Eq. (2)] as observed experimentally [17]. The main result is that $dV_{oc}/dT < 0$, being the negative temperature coefficients larger in the case of small V_{oc} values. It should be noted here that this temperature coefficient is originated by the temperature dependence of the Boltzmann function. In addition, heating reduces the size of the energy gap [17].

When the occupancy deviates from the simpler Boltzmann statistics because of the existence of DOS distributions in the transport levels or tail states penetrating the band gap, able to capture free carriers, the determination of V_{oc} is only feasible by numerical calculation. In such cases a useful strategy to evaluate the output V_{oc} has been the determination of carrier concentration resulting from the kinetic balance between photogeneration and recombination rates. This scheme was applied to estimate the maximum V_{oc} reachable in case of amorphous silicon solar cells [18] in which tail states caused by the intrinsic energy disorder play a determining role as trap and recombination centers. More recently a similar procedure has been used in the calculation of the output V_{oc} in BHJ organic solar cells [14].

Let us briefly outline the model in Ref. [14]. We assumed DOS distributions of both donor highest-occupied molecular orbital (HOMO) and acceptor lowest-unoccupied molecular orbital (LUMO) manifolds. The energy disorder common for organic conductors is modeled by means of Gaussian DOS with mean energy E_{LUMO} and width σ_n for the acceptor fullerene (and E_{HOMO} and width σ_p for the donor polymer) [19]. The effective energy gap is then determined as $E_g = E_{LUMO}(A) - E_{HOMO}(D)$. The effective bandgap can be alternatively defined as the energy corresponding the charge-transfer state at the molecular donor:acceptor

interface [20]. For the sake of simplicity we assume a temperature-independent effective bandgap. Gaussian distributions are accessible by using a variety of experimental methods: from cyclic voltammetry [21] to transient microwave signal relaxation [22]. A broad distribution of the Gaussian DOS is considered because $\sigma \approx 2k_B T - 4k_B T$

$$g_n(E_n) = \frac{N_n}{\sqrt{2\pi}\sigma_n} \exp \left[-\frac{(E_n - E_{LUMO})^2}{2\sigma_n^2} \right] \quad (5)$$

$$g_p(E_p) = \frac{N_p}{\sqrt{2\pi}\sigma_p} \exp \left[-\frac{(E_p - E_{HOMO})^2}{2\sigma_p^2} \right] \quad (6)$$

N_n (and N_p) represent the total density of electron (hole) states. The carrier density can be calculated by considering the Fermi-Dirac function

$$f(E_F, E) = \frac{1}{1 + \exp((E - E_F)/k_B T)} \quad (7)$$

as photogenerated electrons n in the fullerene (and holes p in the polymer) depending on the position of the respective Fermi level E_{Fn} (E_{Fp})

$$n(E_{Fn}) = \int_{-\infty}^{+\infty} g_n(E_n) f(E_{Fn}, E_n) dE_n \quad (8)$$

$$p(E_{Fp}) = \int_{-\infty}^{+\infty} g_p(E_p) [1 - f(E_{Fp}, E_p)] dE_p \quad (9)$$

Recombination is described by a charge-transfer between an occupied electron state of the LUMO manifold and an unoccupied hole state of the HOMO distribution [23]. We adopted the Marcus model approach [24], which involves a reorganization energy λ . The charge-transfer rate is given by

$$v_{rec}(E_n - E_p) = k_0 \exp \left[-\frac{(E_n - E_p - \lambda)^2}{4k_B T \lambda} \right] \quad (10)$$

where k_0 is a parameter with dimension (cm³ s⁻¹). The total recombination rate is calculated by integration of all charge-transfer events following a bimolecular-like process as

$$R(E_{Fn}, E_{Fp}) = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} g_n(E_n) f(E_{Fn}, E_n) g_p(E_p) [1 - f(E_{Fp}, E_p)] \times v_{rec}(E_n - E_p) dE_n dE_p \quad (11)$$

This is a general expression of the recombination rate, which substitutes the simplified version $R = knp$ (being k the recombination rate) by considering energy distributions and occupancy [9]. Alternative approaches as those related to Langevin-like recombination with reduced prefactor could be also incorporated in our calculation [25].

In the steady state under continuous irradiation, the photogeneration rate G equals the recombination rate because no direct current is allowed

$$R(E_{Fn}, E_{Fp}) = G \quad (12)$$

We assume that bulk recombination is dominant over outer interface recombination. Several recent studies suggest that this is indeed the case [9,26]. Assuming that the photogenerated carriers exceed intrinsic carrier densities $n > n_0$ ($p > p_0$), the following electroneutrality constraint applies:

$$n(E_{Fn}) = p(E_{Fp}). \quad (13)$$

The Fermi level positions can be evaluated by requiring the system of equations to satisfy the previously mentioned conditions: first photogeneration rate must be balanced by the recombination rate [Eq. (12)], and the absorber layer should be space-charge free [Eq. (13)]. The actual Fermi level position is

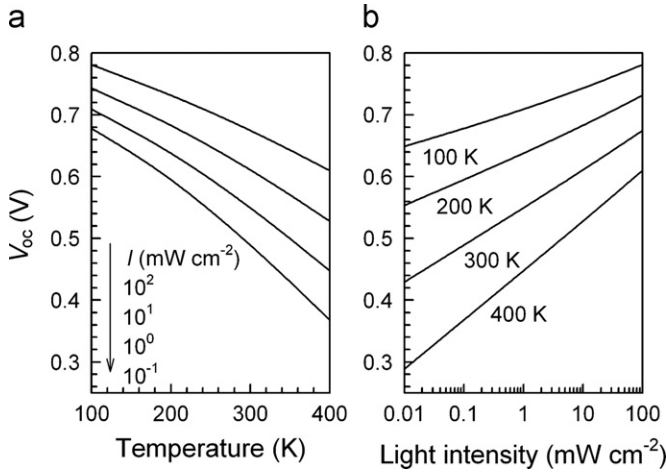


Fig. 1. Open-circuit voltage resulting from model simulations as a function of (a) temperature and (b) light intensity. Parameters used in the simulation: $E_g = E_{\text{LUMO}}(A) - E_{\text{HOMO}}(D) = 1$ eV, $N_n = N_p = 10^{20} \text{ cm}^{-3}$, $\sigma_n = \sigma_p = 50 \text{ meV}$, $k_0 = 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $\lambda = 1$ eV and $G = 7.5 \times 10^{16} / L \text{ cm}^3 \text{ s}^{-1}$ (layer thickness $L = 100 \text{ nm}$) corresponds to $I = 100 \text{ mW cm}^{-2}$. Other parameters marked in each curve.

finally governed by the kinetic balance, which in turn depends on the statistics of occupancy. It is assumed in this calculation that contact barriers have a minor effect and are perfectly selective [27].

A uniform absorption along the layer thickness L is also assumed, so that the photogeneration rate is given by

$$G = \phi(1 - \beta)/L \quad (14)$$

where ϕ is the photon flux and β stands for the ratio of geminate electron-hole pairs, which recombine before charge separation. It is adopted the value $\beta = 0$ for the sake of simplicity. In order to estimate the generation rate at standard AM1.5 G conditions (1000 W m^{-2} of integrated power density) a short-circuit current of 12 mA cm^{-2} (reported for bulk heterojunction organic practical cells [4]) is adopted which entails $\phi = 7.5 \times 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$.

3. Results and discussion

Results of the model simulations are presented in Fig. 1(a) using a typical set of parameters. V_{oc} calculated from the splitting of the Fermi levels [Eq. (1)] exhibits the expected dependence on temperature: it is found to decrease when T increases. At lower temperatures V_{oc} seems to saturate as reported in some studies [12]. At higher T values near room-temperature the coefficient is more pronounced for low light-intensity values (low V_{oc}) in good accordance with experiments [12] and that derived from the simpler case of Eq. (4). Moreover, an approximately linear relationship like $V_{oc} \propto -T$ is encountered in this high-temperature range. The temperature coefficient obtained for the set of simulation parameters results $dV_{oc}/dT \approx -0.6 \text{ mV K}^{-1}$ at 300 K, which results within the order of magnitude reported for most BHJ solar cell devices (Table 1). V_{oc} dependence on light-intensity follows the usual experimentally observed behavior $V_{oc} \propto \log I$ [Fig. 1(b)]. The influence of the recombination kinetics is drawn in Fig. 2(a) by varying the order of magnitude of the prefactor k_0 . It is observed that slower recombination produces higher values of the output photovoltage because higher carrier concentrations are achieved. k_0 also influences the temperature coefficient at high temperatures.

In steady-state conditions and low occupancy ($n/N_n < 10^{-2}$) [28], the photogenerated carriers, which are initially distributed along DOS shape, thermalize in the Gaussian tail following a

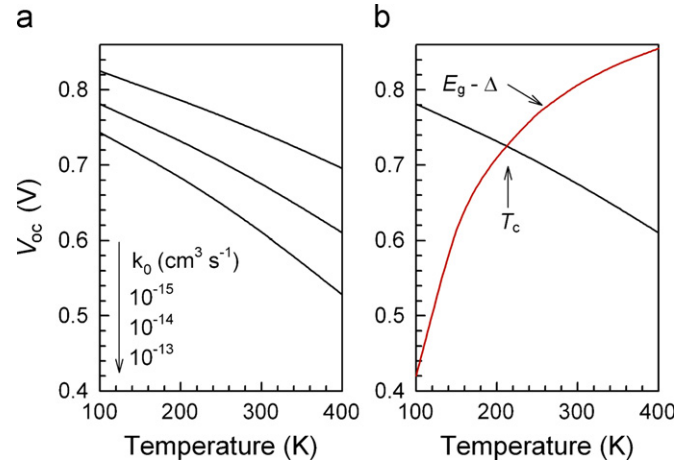


Fig. 2. (a) Open-circuit voltage resulting from model simulations as a function of temperature for different values of the recombination prefactor k_0 as indicated. Parameters used in the simulation: $E_g = E_{\text{LUMO}}(A) - E_{\text{HOMO}}(D) = 1$ eV, $N_n = N_p = 10^{20} \text{ cm}^{-3}$, $\sigma_n = \sigma_p = 50 \text{ meV}$, $T = 300 \text{ K}$, $\lambda = 1$ eV and $G = 7.5 \times 10^{16} / L \text{ cm}^3 \text{ s}^{-1}$ (layer thickness $L = 100 \text{ nm}$) corresponds to $I = 100 \text{ mW cm}^{-2}$. (b) Transition between high- to low-occupancy conditions at $T = T_c$ using the same set of parameters and $k_0 = 10^{-14} \text{ cm}^3 \text{ s}^{-1}$. The position of the equilibration energy as $E_g - \Delta (\Delta = (\sigma_n^2 + \sigma_p^2)/k_B T)$ is drawn.

Boltzmann statistics with an average, equilibration energy $E_{mn} = \sigma_n^2/k_B T$ below E_{LUMO} . Such energy signals the mean energy level of the charge carriers and is located above the concentration-dependent Fermi level, i.e. $E_{Fn} < E_{mn}$ [19]. This situation corresponds to high-temperature occupancy curve in Fig. 3. Similarly, for holes one can define $E_{mp} = \sigma_p^2/k_B T$ above E_{HOMO} [14]. Because of the lower location of the Fermi level in case of low occupancy, the equilibration energy $\sigma^2/k_B T$ establishes an upper limit to the achievable photovoltage, which is found to be lower than the effective bandgap E_g [29].

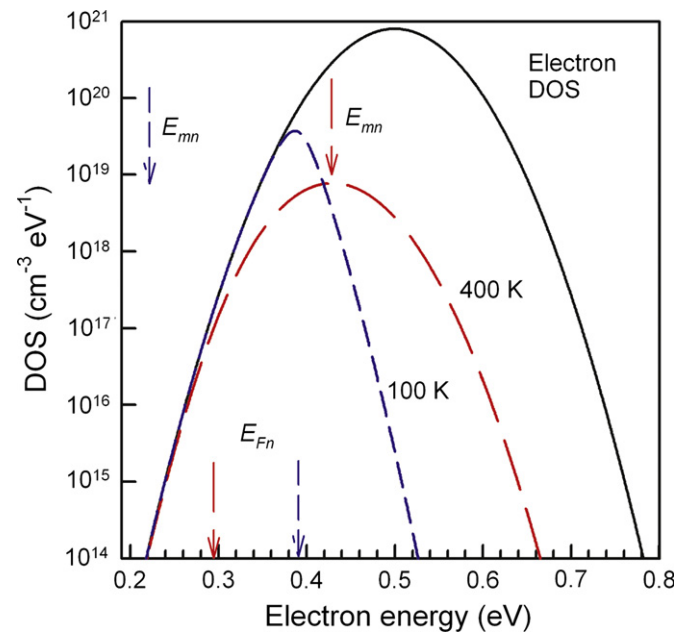


Fig. 3. Electron density-of-states (solid line) and occupancy (dashed line) at high and low temperatures as indicated. Arrows mark the position of electron Fermi level and the equilibration energy $-\sigma_n^2/k_B T$ respect to the LUMO mean. Parameters used in the simulation: $E_g = E_{\text{LUMO}}(A) - E_{\text{HOMO}}(D) = 1$ eV, $N_n = N_p = 10^{20} \text{ cm}^{-3}$, $\sigma_n = \sigma_p = 50 \text{ meV}$, $k_0 = 10^{-14} \text{ cm}^3 \text{ s}^{-1}$, $\lambda = 1$ eV and $G = 7.5 \times 10^{16} / L \text{ cm}^3 \text{ s}^{-1}$ (layer thickness $L = 100 \text{ nm}$) corresponds to $I = 100 \text{ mW cm}^{-2}$.

It is worth noting that similar to that occurring for inorganic p–n junction solar cells, organic bulk heterojunctions also exhibit a negative temperature coefficient of V_{oc} near room temperature. This similar response of organic and inorganic photovoltaic devices is related to the fact at high temperature ($T > T_c$ in Fig. 2(b)) charge-carriers in organic compounds obey Boltzmann statistics because low-occupancy conditions are satisfied. T_c is a critical temperature at which $E_{Fn} = -\sigma_n^2/k_B T$ respect to the LUMO mean and $E_{Fp} = \sigma_p^2/k_B T$ respect to the HOMO mean [30]. At lower temperatures ($T < T_c$) reduction in the activated recombination rate and displacement of the equilibration energies induce a transition to high-occupation conditions (see Fig. 3), which entails that the Fermi level is situated at energies higher than $\sigma^2/k_B T$. Focusing our attention to the high-temperature, Boltzmann regime at $T > T_c$, a straightforward calculation allows determining the Fermi level positions [30] from which an expression for V_{oc} can be readily given

$$qV_{oc} = E_g - \frac{\sigma_n^2 + \sigma_p^2}{2k_B T} - k_B T \ln \left(\frac{N_n N_p}{np} \right). \quad (15)$$

This last expression contains the term related to the electron and hole equilibration energies as discussed above. Note here that the second summand is not present in the Fermi level splitting calculation for inorganic solar cells in Eq. (2). It appears as a distinctive feature of organic disordered compounds related to the Gaussian DOS occupancy. At high-temperature (Boltzmann regime) the last expression is valid regardless the specific recombination mechanism. The second summand in Eq. (15) introduces a positive correction into the temperature coefficient as $(\sigma_n^2 + \sigma_p^2)/2k_B T^2$ that corresponds to 0.3 mV K^{-1} at 300 K, assuming the parameter values of our simulation. This additional contribution explains the slightly minor negative temperature coefficient reported for organic cells in comparison with their inorganic counterparts (see Table 1).

4. Conclusions

In summary we have presented the calculation of V_{oc} as a function of temperature and light intensity, which integrates carrier DOS and generation-recombination kinetic balance. Our approach then regards V_{oc} as determined by inner, bulk material parameters such as occupancy statistics and recombination mechanisms. For carriers obeying Boltzmann statistics at temperatures higher than the critical value T_c , the calculated temperature coefficient of V_{oc} coincides with that reported experimentally.

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