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Research Paper

Investigation and Simulation of Recombination Models in Virtual Organic Solar Cells

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Abstract

As fossil fuels cause environmental problems and begin to become depleted, research into developing renewable energy is on the rise. As fossil fuels begin to deplete and the cost of energy rises, there is more and more need for a renewable, clean energy source. One such possible alternative are Organic Solar Cells. Experimental results have reported 8.3% efficiency in lab tests. The development of OSC efficiency is an important step in reducing our carbon footprint. The absorption of photons is not a problem in most OSC because normally 96% of light is absorbed and organic semiconductors have high absorption coefficients even for very thin specimen. After the photons are absorbed, an exciton consisting of a hole and an electron with a binding energy of 0.1 - 1.4 eV is formed. In this article, three different models for the bimolecular recombination of solar cells are explored and a simulation is run and compared to experimental results.

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1. INTRODUCTION

Inorganic solar cells, usually manufactured using doped silicon, do not have high enough efficiencies to be cost effective in today's energy market because they are expensive to manufacture and have reached a plateau in their efficiency. However, there is another possibility for a replacement of silicon based solar cells. Organic solar cells, or OSC*, are solar cells created from carbon-based polymers. [1,2] They have been developed over the last ten years. Starting in 2000, Alan Heeger, et al were given the Nobel Prize in Chemistry for developing conductive polymers. Since then, OSC have taken shape. Now, OSC are shown to be much less expensive to manufacture and show promise in being able to reach ten percent efficiency. 8.3% efficiency of OSC has been reported in lab testing already. OSC also are flexible, making them more versatile than inorganic solar cells. [3]

However, in order to make OSC viable, the efficiency needs to be improved. The efficiency of OSC is dependent on many different parts of the energy generation process. The absorption of photons, transportation and separation of excitons, and the transportation of electrons and holes to their respective electrodes all contribute to the efficiency of OSC. [4,5]

A possible shortcut to improved efficiency of solar cells is creating a virtual model with the capabilities of changing parameters to model real situations and thus idealizing OSC setups. This will eliminate the time of creating a specific OSC and running experimental tests, which take time and resources to carry out.

However, the model is in need of an equation that will describe the bimolecular recombination effects. Three different equations are presented: Langevin's equation, the Interface model, and Koster's model. [6,7]

2. THEORY AND MODEL

The problem is that the exciton needs to be separated and the exciton has a short diffusion length of three to ten nanometers. This is solved by using two different materials that have a high electron affinity and a lower ionization energy. The materials (usually a polymer - fullerene combination) would then be combined to form a bulk heterojunction. At the junction of the materials the exciton will separate, causing the electrons to travel to the cathode and the holes to travel to the anode. [8,9]

* Organic solar cells

The places that energy is lost is when an exciton fails to reach the polymer - fullerene junction, when an electron and a hole recombines with one another, and when electrons and holes get trapped in the dangling bonds of the polymer between the OSC and the electrodes or defects in the material. When holes and electrons recombine after separating at the interface it is called bimolecular recombination and when holes or electrons get caught in traps due to defects or disorder in the material it is called monomolecular material. In the model used, monomolecular recombination is neglected because the polymer/fullerene mixture of P3HT:PCBM has few defects. [10]

In this model, drift and diffusion of charge carriers, bimolecular recombination, and the effect of field and temperature dependent generation of free charge carriers is included. The steady state continuity equation for electrons is given by:[11]

$$\frac{1}{q}\frac{\partial}{\partial x}J_n(x) = PG - (1-p)R \qquad (1)$$

Where $J_n(x)$ is the electron current density, G is the generation rate of bound electron- hole pairs , and P is the probability for dissociation of a bound electron- hole pair. The dissociation probability is dependent on the initial electron- hole separation distance(a) and the decay rate of the bound pair. The factor 1-P appears in Eq.(1) since the recombination of electrons and holes in a blend systems dose not directly lead to loss of charge carriers. Instead, a bound electron- hole pair is created, analogous to the creation of a bound pair after electron transfer across the materials interface, effectively lowering the recombination constant to (1-P) γ .[12]

Solar cells are usually characterized by three parameters: The current density under short-circuit conditions (J_{sc}), the open-circuit voltage (V_{oc}), defined as the voltage for which the current in the external circuit equals zero, and the fill factor (FF) Eq.(3).

In order to determine the energy lost, models are created to represent recombination, electron-hole diffusion and generation rate of holes and electrons. Using a model will help determine what is the ideal combination of polymer and fullerene as well as being able to test individual aspects of the model by holding other variables constant. [13,14]

The ultimate goal is to create a model that will closely estimate the efficiency of OSC. This efficiency is determined by the energy produced by the OSC divided by the amount of light energy or photons available for absorption. This efficiency is calculated with the following equation, [15]

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{in}} \tag{2}$$

with η as the efficiency and P_{in} representing the light energy absorbed. The fill factor, FF, is the maximum amount of power a OSC can produce given specific open circuit voltage, V_{oc}, and short circuit current, I_{sc}. The equation,

$$FF = \frac{J_{mpp} V_{mpp}}{J_{sc} V_{oc}} \tag{3}$$

J_{mpp} and V_{mpp} represent the voltage and current density when the power output is greatest. Graphically, the fill factor is the largest square inside the current density/applied voltage curve. [16]

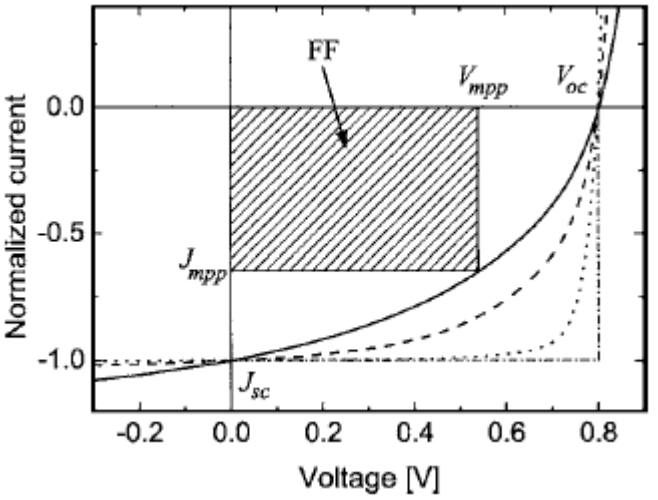

Fig. 1. Current-voltage characteristics of a bulk heterojunction photovoltaic device[5]

Fig.1 shows simulated current-voltage characteristics for various recombination strengths and two orders of magnitude difference between electron and hole mobility ($\mu_e = 3\times10^{-7}\, m^2/Vs$ and $\mu_h = 3\times10^{-9}\, m^2/Vs$). Whiout bimolecular recombination the fill factor is 84% (Fig.1, dotted line), but the FF

drops from 57% to 44% when increasing γ from taking only the slowest carrier Eq.(6) to the spatial average result Eq.(4). This sensitivity of the FF on the recombination strength allows us to determine whether the slowest carrier determines the Langevin rate instead of the spatial average of the mobilities.[17,18]

In order to be more specific with the model, a recombination rate needs to be incorporated, particularly for bimolecular recombination . Previously, Langevin's recombination model has been used to represent the recombination. [19,20] Using

$$\gamma = \frac{q}{\varepsilon}(\mu_e + \mu_h) \tag{4}$$

where γ is Langevin's recombination constant, q is the elementary charge, ε is the dielectric constant, and μ_e and μ_h represent the electron and hole mobilities, respectively. The recombination, R, will then be defined by

$$R = \gamma(np - n_{\text{int}}\, p_{\text{int}}) \tag{5}$$

where n and p are the free electron and hole densities, respectively, and n_{int} and p_{int} being the intrinsic electron and hole densities, respectively[21]

Lately, γ_L has been described as being four orders of magnitude greater than the experimental results. Langevin's model usually holds true for room temperature, but OSC operate at a variety of temperatures. Koster *et al*. proposed that bimolecular recombination can only occur at the junction of the two materials and thus will only happen if the slowest charge carrier reaches the interface. [14,15] The equation,

$$\gamma_k = \frac{q}{\varepsilon} \times \min(\mu_e, \mu_h) \tag{6}$$

incorporates only the slowest carrier. [22,23]

Another explanation is that, due to the two different materials, there will be two different dielectric constants. Known as the interface recombination coefficient,

$$\gamma_I = \left|\frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + \varepsilon_2}\right| \frac{e\mu_1}{\varepsilon_0 \varepsilon_1} \tag{7}$$

ε1 and ε2 represent the different static permittivities and μ1 is the mobility of the carriers in the ε1 permittivity medium. For example, the mixture P3HT:PCBM has a dielectric constant of 3.9 for PCBM while P3HT is 3.0. Langevin's model uses the spatial average of the two dielectric constants. [24,25]

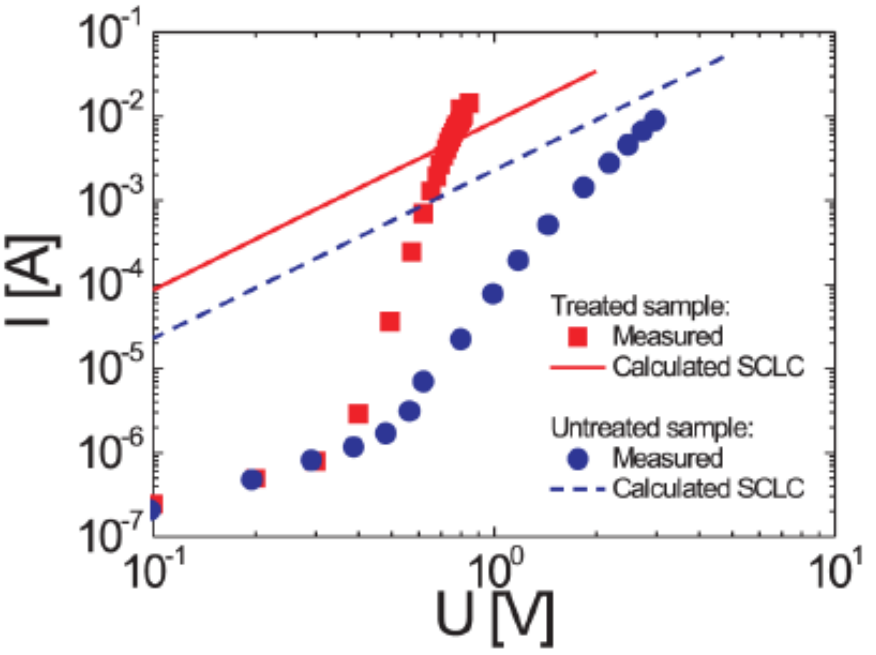

Fig.2. Current- voltage characteristics in treated and untreated devices[8]

In Dark Injection technique has been measured the steady-state current-voltage characteristics, as shown in Fig.2. The experimentally measured(bipolar) current (data points) is compared with the calculated unipolar SCLC(straight lines).The high current density in the treated films confirm that the electron and hole injection are not limited by the contacts, but the carrier recombination in the

bulk of the film. By comparing the result of this work with our work, we get the approved results.[26,27]

3. RESULTS AND DISCUSSION

Using the three different models, certain parameters must be defined to fit with experimental data. Two different combinations of materials were used in the model. The fullerene that was used is PCBM in both cases. In the first combination, P3HT is the polymer was used. Monomolecular recombination can be neglected as long as illumination intensity is kept low. The combination of high illumination intensity and large differences in hole and electron mobility will cause space charge limited photocurrent and will decrease the efficiency. Using parameters defined by Koster, the results are shown in Fig.3.

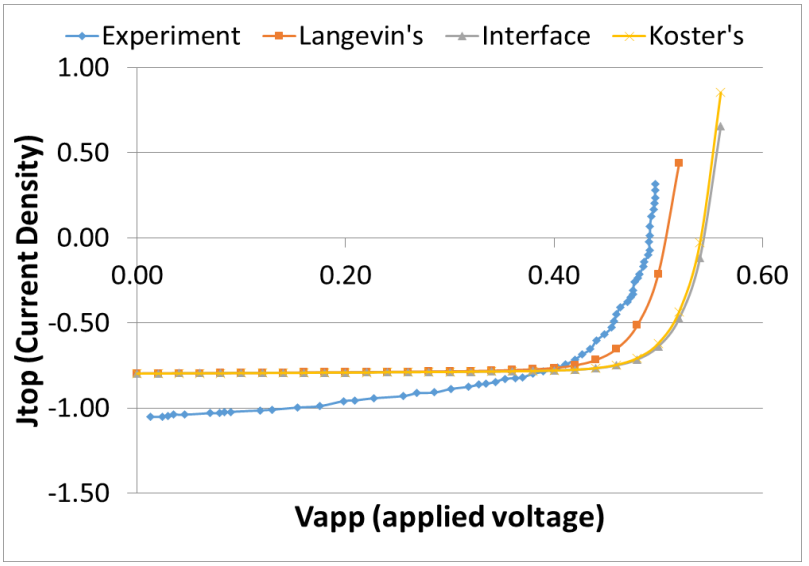

Fig. 3. Comparison of Experimental and Virtual Values for P3HT:PCBM

All three recombination models used the same parameters. The temperature was set at room temperature (300K) so it was expected that Langevin would be a more precise model. However, the large error between the experimental data and the models can probably be attributed to certain estimated parameters.

Another model was run using the same recombination models with a different polymer: PPV. The results are graphed in Fig.4.

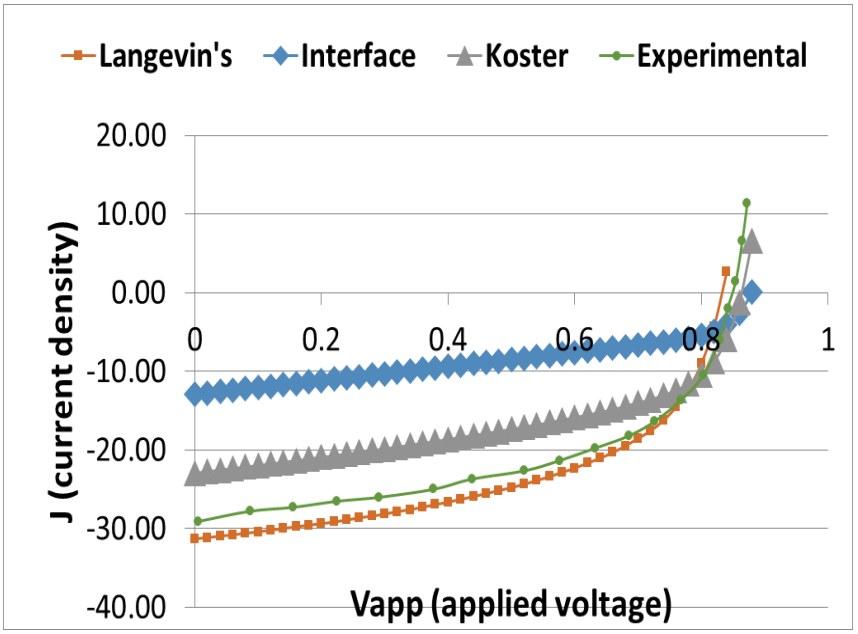

Fig. 4. Comparison of Experimental and Virtual Values for PPV:PCBM

These virtual models were also run at room temperature. It is obvious that Langevin's equation has a small margin of error compared to experimental values.

4. CONCLUSION

The information that can be gathered from this data is that at room temperature, Langevin's model is most accurate. However, in the P3HT:PCBM mixture, none of the recombination models represented the experimental data accurately enough. Curve fitting code could be used to estimate parameters in order to more closely match experimental data. The sensitivity of the FF of the current-voltage characteristics of solar cells and the infeasibility to obtain a good fit with the original Langvein rate allow us to discriminate between the original (spatially averaged) Langvein rate and the rate dominated only by the slowest charge carrier. Moreover, recent measurement of recombination rate in a conjugated polymer/PCBM blend quantitatively confirm this reduction of the Langevin recombination constant.

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