One-Dimensional Device Model for Bulk Heterojunction Solar Cells

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Shortly after the initial discovery of organic photovoltaic devices, it became apparent that, despite sharing many similarities with traditional inorganic silicon p-n type solar cells, these new cells could not be assessed in the same manner due to some fundamental physical differences which dictate the mechanisms by which energy is generated [9]. For this, many years have been spent trying to better understand these devices so that they can be improved upon and be made to function more efficiently, but only in the more recent years has the practice of modeling such cells really begun to take form. Here, we look at basic solar cell function, followed by an assessment of polymer solar cells overall and an explanation of our one-dimensional device model for bulk heterojunction devices.

I. INTRODUCTION

Solar cells, though still highly underutilized, have been on the minds of scientists seeking new energy sources since the middle of the twentieth century when the first silicon solar panels were constructed [8]. These first cells were inefficient, expensive, and only somewhat understood, but still seen as a promising renewable and completely unused power source. Now, after years of study, we are able to produce fairly efficient silicon solar cells; however, these cells remain quite expensive and therefore impractical for more widespread use. Nonetheless, as the costs of other nonrenewable energy sources soar higher than ever and the environmental consequences of burning oil evidence an urgent need for change, solar power seems like a perfect alternative. Thus, recently, solar study has taken off in two distinct directions, attempting to both increase efficiency dramatically and also to find a way to create cheaper solar cells, so as to attain a reasonable watt to dollar ratio that might make widespread commercial usage more practical.

II. SOLAR CELL FUNCTION AND DESIGN

A conventional solar cell, for example the silicon cells which we see most commonly, uses a doped semiconductor to form a p–n junction. Light comes in and generates electrons and holes in the semiconductor material, which then are led to the proper electrodes by the electric field generated by the excesses of electrons and holes on the n and p sides of the device [3], thus producing a negative current through the device and charging a battery placed in the circuit.

Naturally, design of any power-supply device is based around optimization of efficiency, \( \eta = \frac{P_{\text{out}}}{P_{\text{in}}} \), which we can calculate without much trouble. \( P_{\text{in}} \) is simply the power of the photons coming into the device from the sun, and can therefore be expressed as an integral over all photon frequencies \( \nu \) of the blackbody spectrum

\[
P_{\text{in}} = C \int_{0}^{\infty} \frac{h \nu^3}{e^{h \nu / kT} - 1} d\nu
\]

where \( k \) is the Boltzmann constant, \( T \) is the sun’s temperature, \( h \) is Planck’s constant, and \( C \) is just a normalization constant. Then, with \( N(\nu) \) as the number of incident photons to the cell with frequency \( \nu \), we arrive at

\[
P_{\text{in}} = \int_{0}^{\infty} h\nu N(\nu) d\nu.
\]

In order for a photon to excite an electron to mobilize, it must come in with an energy higher than the material’s band gap, which is just the difference in energy between the valence band and the conduction band of the material. Because of this, we assume that any photon coming into the cell with an energy greater than \( E_g \) is potentially able to produce current within the device. Therefore, we can take the maximum possible current in the device to be

\[
I_{\text{max}} = \frac{C}{h} \int_{E_g}^{\infty} \frac{\nu^2}{e^{h \nu / kT} - 1} d\nu.
\]

Meanwhile, the voltage within the cell is determined by the difference of the work functions of the contacts at the ends of the device; however, this gap is limited by \( E_g \). If we were to use materials that create a large gap, the current would begin to flow right from one electrode to the other, thus producing a positive current and draining energy from what we are attempting to charge. Given this, we would ideally have the electrodes right at the same levels as the conduction and valence bands, or more realistically, just inside of them. Again, due to the dependence of \( I_{\text{max}} \) on \( E_g \), we cannot simply find a material with a large band gap either, and instead must find the optimal balance for the best efficiency.

So finally, the ideal power output can be written as

\[
P_{\text{out}} = E_g I_{\text{max}} = E_g \int_{E_g}^{\infty} N(\nu) d\nu
\]

which fills in the last piece needed to calculate our ideal efficiency for the basic single gap device. With this, we can graph the ideal efficiency as a function of \( x_g = E_g / kT_{\text{sun}} \) (see FIG. 1) and find that \( \eta \) peaks at \( x_g = 2.17 \), which translates to \( E_g = 1.1eV \) (hence the
FIG. 1: Ideal solar cell efficiencies for a standard cell (lower points) and a tandem cell arrangement (upper points). Though this figure does not account for dark currents (those that exist inherently in the cell even when there is no incident light upon the device), the numbers remain similar to predictions which take them into account. Note that the peak of the lower curve occurs at roughly $x_g = 2.2$ which corresponds to the band gap $E_g$ of silicon.

typical use of silicon, which has a band gap of 1.1$eV$). Still, this idealized case only gives a theoretical efficiency of about 44%

Generalizing efficiency for a more actual case, wherein not every single photon above the proper energy results in the creation of an electron-hole pair that contributes to the device current, we must turn to a more realistic view. Though the analysis varies widely from cell to cell, the end goal is simple, and unchanging: to find the current density at the end of the cell, which will be the effective current through the system. If we calculate (or measure) this current for a number of different values of $V_a$, we can find the $J-V$ curve for the device. Given the fact that we are working with negative current, we will be concerned with the portion of this graph that appears beneath the positive x-axis.

Because the curve enters this quadrant at the short circuit current $J_{SC}$ where $V_a = 0$ and leaves the quadrant at $V_a = V_{OC}$ where $J = 0$, we can use a rectangle formed by $V_{OC}$ and $J_{SC}$ as a sort of standard for which we strive, as this demonstrates the ideal possible power output of the device with no exciton recombination [3]. Therefore, we define the fill factor (FF)

$$FF = \frac{J_{max}V_{max}}{J_{SC}V_{OC}}$$

(5)

which relates directly to the efficiency of the device

$$\eta = \frac{FFJ_{SC}V_{OC}}{P_{sun}}$$

(6)

where $J_{max}V_{max}$ is defined as the current and voltage values that result in the highest possible power (basically, the largest rectangle that can be inscribed within the J-V curve).

FIG. 2: A simple diagram of the tandem solar cell arrangement with light coming into the device from above (through a transparent top contact). Note the required one to one ratio of charge carrier generation between the two materials so that the holes from the top layer annihilate with the electrons from the bottom layer. If this were not the case, we would have low-voltage electrons from layer 2 reaching the top contact and degrading the efficiency of the cell

III. TANDEM SOLAR CELLS

This general concept, however, can be greatly expanded upon, depending on materials used, to drastically change the performance of a photovoltaic device. Today, one of the most successful methods for improving upon this efficiency limit is the use of tandem cells.

In tandem cell construction, the focus is shifted to taking complete advantage of all the light incident upon the cell, by using multiple materials with different band gaps. Recalling that the integral in Eq. (4) goes from $E_g$ up to infinity, one notes that all the photons coming into the device with energy less than $E_g$ are completely unused. However, if we stack a second material (FIG. 2), with a lower band gap $E_{g2}$ than that of the first $E_{g1}$, beneath the first material in our cell, we will additionally absorb all photons with an energy higher than $E_{g2}$.

In this arrangement, the two absorbing materials sandwich a conductor between them. Then, as light enters the cell, photons above $E_{g1}$ are absorbed by the top material to create electron-hole pairs, and then photons with energies less than $E_{g1}$ and greater than $E_{g2}$ are absorbed by the second material. Due to the electric field of the device, the electrons from the first material travel towards the top electrode, while the holes move into the conductor between the layers. Similarly following the field, the holes from the second material move towards the bottom electrode while the electrons move to the conductor where they annihilate with the holes from the first material. Because of this set-up, wherein the holes and electrons from the first and second materials, respectively, annihilate, it is extremely important that the same number of holes and electrons be produced in each material, in
order to take full advantage of the arrangement and not lose any current. To ensure this, the current output of each material must be equivalent, and $E_{g2}$ is not chosen arbitrarily, but rather is specifically picked based on the spectrum of light entering the device (the spectrum of light emitted by the sun). Therefore, $E_{g1}$ and $E_{g2}$ have to satisfy

$$
\int_{E_{g2}}^{E_{g1}} N(\nu) d\nu = \int_{E_{g1}}^{\infty} N(\nu) d\nu.
$$

(7)

Then, in place of $E_g$ in Eq. (4) as the maximum voltage out in front of the integral, we have $E_{g1} + E_{g2}$, which greatly increases the power output of the cell, giving

$$
P_{out-Tandem} = (E_{g1} + E_{g2}) \int_{E_{g2}}^{E_{g1}} N(\nu) d\nu.
$$

(8)

and subsequently increasing the efficiency of the device, leading to the higher curve in FIG.1.

In fact, this can be expanded upon further still, and more than two layers can be used in order to fully use the spectrum of photon energies that enter the device, so long as the same principle of current-matching between layers is obeyed throughout the device.

However, this option, despite great efficiencies, is completely impractical for widespread commercial application as these modifications only further increase the already-expensive cost of standard silicon cells. Nonetheless, a whole new, and rather different branch of photovoltaic device construction has come about that uses cheaper organic materials in place of the typical inorganic semiconductor materials.

IV. POLYMER PHOTOVOLTAIC DEVICES

The use of organics in solar cells is an immediately attractive concept simply due to the significantly lower production cost, as well as the ability to create cells that are both thin and flexible as a result of the optical thickness of most organic materials [9]. Still, these devices are not widely used yet because of their low efficiencies which, currently, cannot compete at all with those of more expensive cells. In the near future, however, it is probable that organic cells will begin to rival traditional silicon cells in cost per watt of solar cells, which would naturally increase their popularity significantly.

The most outstanding difference between organic and inorganic photovoltaic devices is the creation of bound electron-hole pairs, called excitons, instead of the free electron-hole pairs generated in inorganic devices. Existing in insulator materials that have a binding energy greater than the thermal energy of the device, these excitons cannot simply dissociate on their own and instead require an interface that provides a more favorable outlet for either the electron or hole to follow, thus allowing the separation of the electron and hole. Therefore, these devices are constructed with selective contacts – one that will accept only electrons and another to accept only holes – but a solution is not quite so straightforward.

Excitons do not have very long lifetimes (usually, $\sim 500$ ps), and if they do not reach an interface at which they can dissociate during their brief lifetimes, they will recombine with the material and no charge carriers will be generated. Because of this, it is crucial that excitons are given the opportunity to dissociate before decaying back into their ground state or else the photons that caused their creation will go to waste. Given their short lifetimes, the excitons will travel only $\sim 10$ nm before they are lost, hence the popularity of bulk heterojunction devices, which attempt to solve this problem.

In a bulk heterojunction photovoltaic device, the donor and acceptor materials are blended together very tightly so that, ideally, an exciton can reach an interface at which it may dissociate without having to travel more than 10 nm. This technique does come with some inherent disadvantages, such as the fact that inexact blending can result in the presence of dead ends in the materials that leave the dissociated charges with no pathway to reach the end terminals and thus contribute to the device current, but refined techniques are constantly improving upon this small roadblock [10].

V. EQUATIONS

Because of this bulk heterojunction arrangement, in considering our model of a one-dimensional device, we can treat the solar cell as a metal-insulator-metal (MIM) device, wherein the polymer blend is represented by an insulator, which we give appropriate physical properties so as to effectively simulate the polymer blend between the electrodes.

Effectively, the electrical behavior inside of the photovoltaic device is governed by the Poisson Equation:

$$
\frac{d^2 \psi(x)}{dx^2} = \frac{q}{\epsilon} [n(x) - p(x)]
$$

and the current continuity equations for both the electrons (here labelled as $n(x)$) and the holes ($p(x)$):

$$
\frac{d}{dx} J_n = q U(x)
$$

(10)

$$
\frac{d}{dx} J_p = -q U(x).
$$

(11)

Here, $\psi(x)$ is the voltage, $q$ is the elementary charge, $\epsilon$ is the dielectric constant, $U(x)$ is the net generation rate of free carriers within the device, and $J_{n,p}$, the current density, can also be written as

$$
J_n = -q n(x) \mu_n \frac{d}{dx} \psi(x) + q D_n \frac{d}{dx} n(x)
$$

and

$$
J_p = q p(x) \mu_p \frac{d}{dx} \psi(x) - q D_p \frac{d}{dx} p(x)
$$

where $\mu_n$ and $\mu_p$ are the mobilities of electrons and holes, and $D_n$ and $D_p$ are the diffusion coefficients of holes and electrons, respectively.
\[ J_p = -q p(x) \mu_p \frac{d}{dx} \psi(x) - q D_p \frac{d^2}{dx^2} p(x) \]

In the above, the first term takes the gradient of the electrostatic potential in order to account for drift of charges in the electric field of the device, while the second term accounts for diffusion of charge carriers due to diffusion gradients resulting from charge concentrations [2].

These equations, along with an expression for \( U(x) \), can be placed in the continuity equations to give a more explanatory equation:

\[ -q \mu_n \frac{d}{dx} \left( n \frac{d \psi(x)}{dx} \right) + q D_n \frac{d^2 n}{dx^2} = q (P G - (1 - P) R) \] (12)

\[ q \mu_p \frac{d}{dx} \left( p \frac{d \psi(x)}{dx} \right) + q D_p \frac{d^2 p}{dx^2} = q (P G - (1 - P) R) \] (13)

with \( \mu_{n,p} \) as the electron (or hole) mobility.

Here, the right hand side has been expanded to account for the excitonic nature of the device. We first calculate the probability \( P \) that a given exciton will dissociate into a free electron-hole pair within the device (which is explained below), and then multiply this by \( G \), the generation rate of bound electron-hole pairs (excitons) to get the generation rate of free electron-hole pairs. However, we must also take into account the fact that the excitons can recombine rather than dissociate, and so we subtract the recombination rate, multiplied by its respective probability of occurrence, from the generation rate in order to get a realistic value for the number of free electron-hole pairs [6]. More quantitatively, we have for the bimolecular recombination rate \( R \) and the carrier diffusion coefficients \( D_{n,p} \)

\[ R = \gamma (n(x)p(x) - n_{int}^2) \]

\[ D_{n,p} = \mu_{n,p} V_t \]

in which \( D_{n,p} \) is assumed to obey the Einstein relation [1].

We have now also introduced the thermal voltage \( V_t = \frac{k_B T}{q} \) (which is just the voltage in the device resulting from the temperature \( T \)) as well as the intrinsic concentration of electrons and holes in the device \( n_{int} = N_C e^{-E_{gap}/2V_t} \), and the recombination strength, denoted as

\[ \gamma = \frac{q \langle \mu \rangle}{\langle \epsilon \rangle} \]

In the above, \( N_C \) is the effective density of states of the conduction and valence band, and \( \langle \mu \rangle \) and \( \langle \epsilon \rangle \) are the spacial averages of \( \mu \) and \( \epsilon \), taken by adding the adding the two components of each together and dividing by two (ie. \( \langle \mu \rangle = \frac{\mu_e + \mu_h}{2} \)).

For a still deeper look at the right hand side of the continuity equations, we begin to expand \( P \), the dissociation probability: Given that an exciton may either decay to ground or dissociate into a free electron-hole pair, the probability of dissociation can be taken as the dissociation rate over the sum of the dissociation rate and the decay rate. However, local disorder within the materials is also accounted for by the the Gaussian distribution \( f(x) \) centered around a typical \( e-h \) separation distance \( a \). Thus leaving us with

\[ P = \int_0^{\infty} \frac{k_{diss}}{k_{diss} + K_f} f(x) \, dx \] (14)

where

\[ f(x) = \frac{4}{\sqrt{\pi a^3}} x^2 e^{-x^2/a^2} \] (15)

and, according to Braun’s derivation based on Onsager’s theory for weak electrolytes [1] [2],

\[ k_{diss} = \frac{3\gamma}{4\pi a^3} e^{-E_B/k_B T} J_1(2\sqrt{-2b}/\sqrt{-2b}) \]

\[ = \frac{3\gamma}{4\pi a^3} e^{-E_B/k_B T} (1 + b + b^2/3 + \cdots) \] (16)

with \( b = \frac{q^2 F}{8\pi e k_B T^2} \), \( \gamma = \frac{q \langle \mu \rangle}{\langle \epsilon \rangle} \), \( J_1 \) as the first order Bessel function, and \( F \) as the field strength at point \( x \): \( F = -\nabla \psi(x) \). (Note: In Eq. (16) Koster et al. list \( R = \gamma (n(x)p(x) - n_{int}^2) \), but the units of \( k_{diss} \) and \( K_f \) do not work out this way.)

VI. ORGANIZATION AND SCALING

Before we can begin to solve these equations, it is important to do all that we can to make them more manageable so that, once we begin the actual calculations, we have a more straightforward set of variables to deal with and can keep most numbers at a low order of magnitude.

Buxton and Clarke propose an excellent scaling of variables in which the following definitions are created in order to make our variables dimensionless:

\[ \psi'(x) = \psi(x)/V_t \]

\[ n'(x) = n(x)/N_C \]

\[ p'(x) = p(x)/N_C \]

\[ \mu' = \mu/\mu_{max} \]
They also define a new step size that we will call $\Delta x$, which, although slightly different from the $\Delta x$ that we use, is still very useful in the simplification of the Poisson Equation.

$$\Delta x^2 = \frac{e k_B T}{q^2 N_C}$$

However, even prior to this reworking our initial equations, let us first work out the boundary conditions of the system required for solving them. Assuming one contact to be electron ohmic and the other to be hole ohmic, which can be verified with current-voltage measurements on the materials, we can use Boltzmann statistics to arrive at our boundary conditions for the continuity equations (here listed normally and in their rescaled forms):

$$n(0) = p(L) = N_C$$
$$n'(0) = p'(L) = 1$$
$$n(L) = p(0) = N_C e^{-E_{gap}/V_t}$$

$$n'(L) = p'(0) = e^{-E_{gap}/V_t}$$

Furthermore, for the voltage, we say that

$$\psi(0) = \psi(L) + E_g - V_a$$
$$\psi'(0) = \psi'(L) + \frac{E_g - V_a}{V_t}$$

Naturally, we set our zero-potential point to be at $\psi(L)$, the lower potential electrode, in order to simplify things.

Now, filling in our dimensionless variables and dropping the $x$-dependence of $n(0)$, $p(0)$, and $n(L)$ for notational convenience, the Poisson Equation becomes

$$\frac{d^2 \psi}{dx^2} = \frac{n' - p'}{\Delta x^2}$$

and the continuity equations become

$$\frac{d}{dx} n(x) \frac{d}{dx} \psi(x) + \frac{d^2 n}{dx^2} = \frac{1}{\mu_N V_t} \left[ P \left( \frac{G}{N_C \mu_{max}} - (1 - P) \gamma' (n' p' - n_{int}^2) N_C \right) \right]$$

and

$$\frac{d}{dx} p(x) \frac{d}{dx} \psi(x) + \frac{d^2 p}{dx^2} = \frac{1}{\mu_P V_t} \left[ P \left( \frac{G}{N_C \mu_{max}} - (1 - P) \gamma' (n' p' - n_{int}^2) N_C \right) \right]$$

VII. DISCRETIZATION

In order to solve three coupled equations such as these, we cannot rely on exact methods and must instead use an iterative solving method in which a discretized adaptation of the equations is used to form a system of matrices that may be used to find the solution to the system (a process described in more detail in a later section).

In order to discretize, we use a simple finite difference technique in which we approximate

$$\frac{d}{dx} f(x) = \frac{f(x + \Delta x) - f(x)}{\Delta x}$$

And if we so desire, we can take a second derivative of this by taking another finite difference, this time in the opposite direction:

$$\frac{d}{dx} \frac{f(x + \Delta x) - f(x)}{\Delta x} \approx \frac{f(x - \Delta x) - 2f(x) + f(x + \Delta x)}{\Delta x^2}$$

But we will take a moment to define $f_i = f(x)$, $f_{i-1} = f(x - \Delta x)$, and $f_{i+1} = f(x + \Delta x)$ to make things a bit less cumbersome as we begin to discretize our equations. Starting with the Poisson Equation, we can simply replace any derivatives with our finite difference expression:

$$\psi_{i-1}' - 2\psi_i' + \psi_{i+1}' = \frac{\Delta x^2}{\Delta x^2} (n_i' - p_i')$$

However, the mixed derivatives of the continuity equations make things slightly more complicated. Still, we just go step by step, beginning with just the left hand
side of the electron equation, we have
\[
\frac{d}{dx} \left(-n'\psi_{i+1} - \psi_{i}'\right) + n'_{i+1} - n'_i
\]
\[
\Delta x
\]
Now, if we just carry through with another finite difference of each term, we arrive at
\[
-\psi_{i+1}n'_i + \psi_{i}n'_i + \psi_{i}n'_{i-1} - \psi_{i-1}n'_{i-1}
\]
\[
\Delta x^2
\]
\[
+ \frac{n'_{i-1} - 2n'_i + n'_{i+1}}{\Delta x^2}
\]
Continuing with a bit of algebra to group like terms and bringing the \(\Delta x^2\) over to the right hand side, we are left with
\[
(\psi_{i}' - \psi_{i-1}') + (\psi_{i}' - \psi_{i+1}') - 2n'_i + n'_{i+1}
\]
\[
(\psi_{i}' - \psi_{i-1}') + (\psi_{i}' - \psi_{i+1}') - 2n'_i + n'_{i+1}
\]
and
\[
(\psi_{i-1}' - \psi_{i}') + (\psi_{i+1}' - \psi_{i}') - 2n'_i + n'_{i+1}
\]
on the left hand sides of the continuity equations for \(n'\) and \(p'\) respectively.

The right hand side, however, takes a bit more care to break down. Beginning with
\[
\frac{\Delta x^2}{\mu'_np_V} \left[ P \frac{G}{N_C\mu_{max}} - (1 - P) \gamma'(n'_p - n'_n)N_C \right],
\]
we find that only \(P\) requires any extra work. Fortunately, our finite difference method allows for a much easier treatment of Eq. (14) in which we transform the integral into a sum over the length of the device:
\[
\sum_{i=0}^{N} \frac{k_{diss}}{k_{diss} + k_f} f(x_i) \Delta x
\]
which, given a uniform mesh, can be rewritten as
\[
\Delta x \sum_{i=0}^{N} \frac{f(x_i)}{1 + k_f/k_{diss}}.
\]

(Note: the seemingly odd \(i = 0\) lower bound and \(i = N\) upperbound of the sum are merely a result of having defined \(N\) to not include the first and last points of the device in order to facilitate the programming of the matrix-solving iterative method.)

Finally, we can collapse the constant terms from \(f(x)\) into a new constant \(\eta = \frac{\alpha}{\sqrt{\pi}}\), and those from \(k_{diss}\) into \(\alpha = \frac{\beta}{\sqrt{\pi}} e^{-E_B/k_{B}T}\). Furthermore, breaking down the gradient of the electric field strength into a finite difference, we can replace \(b\) with \(\beta(\psi_{i}' - \psi_{i+1}') = b\) to see a fully expanded version of the dissociation probability:

\[
P = \eta \Delta x \sum_{i=0}^{N} \frac{x_i^2 e^{-x_i^2/\alpha^2}}{1 + k_f/\alpha[1 + \beta(\psi_{i}' - \psi_{i+1}')/\Delta x] + \frac{\beta^2}{3} (\psi_{i}' - \psi_{i+1}')^2}
\]
or, using our scaled variables:

\[
P = \eta \Delta x \sum_{i=0}^{N} \frac{x_i^2 e^{-x_i^2/\alpha^2}}{1 + \alpha'(1 + \beta'\delta(\psi_{i}' - \psi_{i+1}')/\Delta x) + \frac{\beta'^2}{3} (\psi_{i}' - \psi_{i+1}')^2}
\]
where \(\alpha' = \alpha_{max}\) and \(\beta' = \beta V_t\).

VIII. SPACE CHARGE EFFECTS

Normally, the Fermi energy of one electrode lines up with the conduction band of the center material while the other aligns with the valence band [1]. With any applied voltage, the conduction band remains at the same level as the changing Fermi level, but let us for a moment consider the case of \(V_{SC}\), wherein the applied voltage \(V_a\) is set to 0. In this case, in order for the two contacts to be at the same potential, an excess of holes builds up on the top contact and an excess of electrons builds up on the bottom contact. As a result, electrons in the material gather near the top electrode while holes gather near the bottom electrode. Though the two charge carrier concentrations are roughly equal through the center of the cell, there is a dramatic disparity in concentrations near the ends which means that charge neutrality does not hold [7]. This means that, in some cases, space charge effects may not be negligible, instead being potentially significant enough to limit current through the device.

In cases where the space-charge-limited current is greater than the actual current, no extra considerations need to be made. However, in cases wherein the actual current and space-charge-limited current are similar in magnitude (short circuit conditions, for example), the space-charge-limited current will be the observed current. The effects of space charge can be seen the fact that the voltage in the device loses its linearity near the contacts and instead either climbs or drops off rather sharply (FIG. 3). This sharp change in the voltage then dramatically changes the charge carrier densities, due to their dependence on the first derivative of the voltage. Therefore, in calculations, a constant electric field, which greatly simplifies things, cannot truly be assumed, as it inaccurately would portray a linear voltage.

Unfortunately, due to this sensitivity of the system, and the dramatic rapidity with which the electron and hole concentrations vary near the edges of the device, it is impossible to use the simple discretization laid out here to get a solution that in fact converges. As a result, we will follow a method set forth by Scharfetter and Gummel and used by many others [1] [6] [2] wherein one uses the chain rule to express \(J_n\) as (still using our scaled variables
we get that
\[ B = \frac{n_i' - \frac{J_n}{q\mu_p\mu_{max}V_iNC}}{e^{-E'x_i+1}}. \]

We plug this into the other boundary to get
\[ n_i' = \frac{J_n}{q\mu_p\mu_{max}V_iNC} + \frac{n_{i+1} - \frac{J_n}{q\mu_p\mu_{max}V_iNC}}{e^{-E'x_i+1}} \tag{28} \]

which, when we plug things back into the current density equation and substitute in \(-\Delta \psi'\) for \(E'\Delta x\), leads to
\[ J_{n,i+1/2} = \frac{q\mu_p\mu_{max}V_iNC}{\Delta x}[n_{i+1}'B(\Delta \psi') - n_i'B(-\Delta \psi')] \tag{29} \]

<table>
<thead>
<tr>
<th>Constant</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td>1.3 nm</td>
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<tr>
<td>(T)</td>
<td>300 K</td>
</tr>
<tr>
<td>(E_{gap})</td>
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<tr>
<td>(E_B)</td>
<td>0.20 eV</td>
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<tr>
<td>(V_{SC})</td>
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<tr>
<td>(V_{OC})</td>
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<tr>
<td>(N_C)</td>
<td>(2.5 \times 10^{25}) (m^{-3})</td>
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<td>(G)</td>
<td>(2.7 \times 10^{27}) (m^{-3})</td>
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<tr>
<td>(\mu_p)</td>
<td>(2.5 \times 10^{-7}) (m^2/\text{V}-\text{s})</td>
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<td>(\mu_{max})</td>
<td>(3.0 \times 10^{-8}) (m^2/\text{V}-\text{s})</td>
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<tr>
<td>(\epsilon)</td>
<td>(3.0 \times 10^{-11}) (C/\text{V}-\text{m})</td>
</tr>
<tr>
<td>(kf)</td>
<td>(1.5 \times 10^{6}) (\text{s}^{-1})</td>
</tr>
</tbody>
</table>

where \(B(x) = \frac{x}{x_{i-1}}\) is the Bernoulli function.

Finally, we discretize the continuity equation as
\[ \frac{dJ_n}{dx} \simeq \frac{J_{n,i+1/2} - J_{n,i-1/2}}{\Delta x} \]

and plug in Eq. (29) to arrive at
\[ \frac{dJ_n}{dx} = \frac{q\mu_p\mu_{max}V_iNC}{\Delta x^2}[B(\psi_i - \psi_{i-1})n_i' - \frac{B(\psi_i - \psi_i' + 1) + B(\psi_i' - \psi_{i-1})}{2}]n_i' + B(\psi_{i+1} - \psi_i)n_i'] \tag{30} \]

Repeating this process for \(p\), we get
\[ \frac{dJ_p}{dx} = \frac{q\mu_p\mu_{max}V_iNC}{\Delta x^2}[B(\psi_i - \psi_{i-1})p_i' - \frac{B(\psi_i - \psi_i' + 1) + B(\psi_i' - \psi_{i-1})}{2}]p_i' + B(\psi_i - \psi_{i+1})p_i'] \tag{31} \]

Using this new arrangement, we finally arrive at a place where we can truly begin to solve the equations that we have now laid out, and obtain legitimate solutions for our system.

**FIG. 3:** Here we graph the voltages across the device (still using our scaled variables) at \(V_n = V_{OC}\) and \(V_n = V_{SC}\) on the same plot. One can easily see the effects of space charge manifested in the non-linear sections of the plots near both endpoints. The corresponding true differences from one electrode to the other are approximately 1.3 for \(V_{SC}\) and 0.5 for \(V_{OC}\).
IX. SOLVING METHOD

Once we have the equations in the form in which we currently have them, everything simplifies, essentially, into nothing more than an algebra problem, that we will solve again and again, iteratively closing in on the solution with each correction that we calculate. Starting with the Poisson Equation, we can begin to rewrite things in matrix form. Thus, Eq. (20) can be written equivalently as

\[
\begin{pmatrix}
-2 & 1 & 0 & \cdots & 0 \\
1 & -2 & 1 & \cdots & 0 \\
\vdots & \ddots & \ddots & \ddots & \vdots \\
0 & \cdots & 1 & -2 & 1 \\
0 & \cdots & 0 & 1 & -2 \\
\end{pmatrix}
\begin{pmatrix}
\psi'_1 \\
\psi'_2 \\
\vdots \\
\psi'_{N-1} \\
\psi'_N \\
\end{pmatrix} = \frac{\Delta x^2}{\Delta x^2} \begin{pmatrix}
(n'_1 - p'_1) - \psi'(0) \\
(n'_2 - p'_2) \\
\vdots \\
(n'_{N-1} - p'_{N-1}) \\
(n'_N - p'_N) - \psi'(L) \\
\end{pmatrix}.
\]

Once we have our first solution for \( \psi'_i \), obtained by using some starting guess for \( n' \) and \( p' \), we can start to zero in on actuals solutions for \( n' \) and \( p' \). First, we plug our new \( \psi' \) values into Eq. (25) and allow the sum to be carried out, now with no unknowns, to get a value for \( P \). Then, together with this value, we can plug our \( n' \) and \( p' \) guesses into Eq. (23) which gives us our product matrix for both \( n' \) and \( p' \) remembering with each to subtract away the respective bounds, of course. (the matrix for \( n' \) shown below)

\[
\begin{pmatrix}
\frac{\Delta x^2}{\mu_{n,p} x} & \frac{P}{G_{C,\text{max}}} - (1 - P)\gamma'(n'_1 p'_1 - n'_{\text{int}})N_C - (\psi'_1 - \psi'(0) + 1)n'(0) \\
\frac{\Delta x^2}{\mu_{n,p} x} & \frac{P}{G_{C,\text{max}}} - (1 - P)\gamma'(n'_2 p'_2 - n'_{\text{int}})N_C \\
\vdots \\
\frac{\Delta x^2}{\mu_{n,p} x} & \frac{P}{G_{C,\text{max}}} - (1 - P)\gamma'(n'_{N-1} p'_{N-1} - n'_{\text{int}})N_C \\
\frac{\Delta x^2}{\mu_{n,p} x} & \frac{P}{G_{C,\text{max}}} - (1 - P)\gamma'(n'_N p'_N - n'_{\text{int}})N_C - n'(L) \\
\end{pmatrix}
\]

Now, going back to our reworked continuity equations in order to complete the left hand side of these matrix equations, find that we will multiply the \( n' \) matrix by

\[
\begin{pmatrix}
[B(-\Delta \psi'_{i+1}) + B(-\Delta \psi'_i)] & B(\Delta \psi'_{i+1}) & 0 & \cdots & 0 \\
B(-\Delta \psi'_i) & [B(-\Delta \psi'_{i+1}) + B(-\Delta \psi'_i)] & B(\Delta \psi'_{i+1}) & \cdots & 0 \\
\vdots & \ddots & \ddots & \ddots & \vdots \\
0 & \cdots & B(-\Delta \psi'_i) & [B(-\Delta \psi'_{i+1}) + B(-\Delta \psi'_i)] & B(\Delta \psi'_{i+1}) \\
0 & \cdots & 0 & B(-\Delta \psi'_i) & [B(-\Delta \psi'_{i+1}) + B(-\Delta \psi'_i)]
\end{pmatrix}
\]

A similar equation holds for \( p' \) and the same solving method is used as was utilized for \( \psi' \).

Hence, with the new \( n' \) and \( p' \), we can go back and re-solve more accurately for \( \psi' \), which, in turn, allows us to find a better solution for \( n' \) and \( p' \) again.
to solve this problem, we introduce a mixing factor $M$ into the program that, instead of allowing each new guess to replace the former, compromises between the old and new guesses:

$$n_{i}^{j+1}(x) = n_{i}^{j}(x)M + n_{i}^{j+1}(x)(1 - M) \quad (35)$$

where $j$ is the iteration number.

If we set this mixing factor close to 1 (0.95 for example), an answer is approached more slowly, requiring many more iterations, but also more stably, which allows us to solve some systems for lengths up our desired length of 120 nm and for both open circuit and short circuit conditions (and everything in between).

Therefore, once we have determined a large enough mixing factor so that solutions converge for the full length of the device, we simply continue this process of correction until the differences between our old values and our new values for $\psi'$, $n'$, and $p'$ are less than some preset tolerance.

**X. RESULTS AND CONCLUSIONS**

Beginning with the device at short circuit, a few things become immediately apparent. Obviously, the electron density is much higher at the top contact, just as the hole density shoots upward towards the bottom contact due to the voltage distribution throughout the device. However, one notes that, as the concentrations linearize in middle of the device, the hole density remains about an order of magnitude larger than that of the electrons. This is simply due to the slower hole mobility [1], which causes the slower holes to pile up in the device while the faster electrons move towards the contact more easily.

Furthermore, comparing between short circuit and open circuit conditions, one notices that the carrier densities are an order of magnitude lower at short circuit. This is a result of the strong electric field within the device at short circuit, which guides the charges towards their respective ends of the cell effectively, thus extracting more. In fact, the efficiency of this extraction also causes a lower rate of carriers loss as a result of recombination, as the e-h pairs do not have time to recombine prior to exiting the device [1], and subsequently results in the maximum current that the device can reach.

Contrarily, at open circuit voltage, there exists no electric field to drive the charge carriers in the directions of their respective destinations, and so carrier extraction becomes remarkably inefficient. This results in more similar behavior between electrons and holes, as the lower hole mobility has no issues in keeping up with extraction, and a generally higher charge carrier concentration throughout the device. Additionally, a great majority of charge carriers are lost due to recombination and a zero current density results [1].
FIG. 5: The full-length device at short circuit. We see in (a) a voltage that runs roughly linearly from end to end of the device, climbing and diving only slightly at the electrodes. The current densities, meanwhile, show an excess of holes near the bottom contact and of electrons near the top contact as one would predict from the voltage characteristics.

FIG. 6: The full-length device at open circuit with $P = 1$. We see in (a) a voltage that levels out slightly over the middle of the device, but dives and climbs steeply near the lower and top contacts respectively. The current densities then mimic this behavior and show a linear dependence through the middle which alters near the ends as electrons gather near the higher-voltage electrode and holes gather oppositely.

Unfortunately, the right hand side of the continuity equations remains the cause of instability even after these adjustments have been made. Though the system can be solved to convergence for the short circuit and other low $V_a$ cases, higher $V_a$ situations diverge before any solution can be reached. Though it is most likely possible to still solve these problematic cases with a larger mesh size, and a $M$ value that approaches 1 even more closely, these procedures would require much computing power to see all the way through.

Luckily, after a bit of examination we note that this divergence issue is caused principally by the recombination term in the continuity equation, and so we find that if we set $P = 1$, thus taking only the generation term into account, we can solve the system for lengths up to 120 nm even with $V_a = .90$. Though this seems like a misrepresentation of the system, the results differ very minorly and still allow us to better understand the system from the general shapes of the voltage and charge carrier concentrations.

However, as we wish to ultimately determine the theoretical efficiency of our device, this approximation will not function. If we ignore the recombination term, the current density will read out as being larger than its true
value for many cases and the resulting J-V curve would give, for its fill factor, an over-sized box which would greatly overestimate the efficiency. Therefore, in an attempt to obtain a more legitimate J-V curve for our device, we shrink the cell length down to a more manageable length (the largest length at which convergence can be achieved through reasonable means while using the full continuity equation).

Using a smaller device length, we should eventually be able to attain an J-V curve for our device model, which though not perfectly true for full length should still prove to be significantly more useful than the curve provided at full length with $P = 1$. However, the sensitivity of the system has prevented this from coming fully into fruition at this point in time. Still, using other reports as reference points [6][3], we can predict our max power to occur near .65 volts, resulting in a fill factor around 50%.

In the future, we will use this model to test the effects of adjustments made to various parameters of the system. Different materials and arrangements can be tested theoretically in order to determine the potential worth of construction for experimental testing as well. Ideally, we will continue to fine-tune the system in an attempt to make our J-V curve more closely hug the ideal power rectangle created by $J_{SC}$ and $V_{OC}$. Additionally, material and environmental adjustments can be made in order to increase the band gap of our material, thus increasing $V_{OC}$, and also to increase both electron and hole mobilities for the system, which would result in a larger $J_{SC}$.

Furthermore, constructions are still being improved upon with more precise blending and increased surface area to further decrease the chances of exciton recombination and thus increase efficiency even more.

Essentially, this is a rather new field, which, due to the world’s increasing necessity to curb nonrenewable energy use, is growing rapidly and holds a truly promising future. Already, studies using tandem polymer cell construction report efficiencies of 6.2% [10] and this is only the beginning. Though organic cells may never reach the high efficiencies of tandem silicon devices or other costly approaches, the cost per watt ratio of organic devices should drop to lower values than we have ever seen for solar power, thus paving the way for cleaner, better energy production.

XI. ACKNOWLEDGMENTS

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