The Fabrication and Characterization of Organic Solar Cells

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Abstract

Organic solar cells hold promise for low cost energy production, but only if further developments in their design and manufacture make them practical for real-world applications. This thesis looked at one combination of materials (P3CT and MEA stabilized ZnO nanoparticles) that advance solar technology by being moderately stable under atmospheric conditions. While a fully functional and characterized cell was not achieved, progress was made toward that goal. The material processing and performance characterization steps were generally successful, leaving material preparation/selection as the main area needing improvement. One multi-celled slide with partial functionality was fabricated and had open circuit voltages up to 26 mV. A full I-V curve was measured for a silicon reference cell.
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5 Characterization</td>
<td>29</td>
</tr>
<tr>
<td>3.5.1 Circuit</td>
<td>29</td>
</tr>
<tr>
<td>3.5.2 Illumination</td>
<td>30</td>
</tr>
<tr>
<td>4 Results and Analysis</td>
<td>34</td>
</tr>
<tr>
<td>4.1 Silicon Reference Cell</td>
<td>34</td>
</tr>
<tr>
<td>4.2 Literature Results</td>
<td>35</td>
</tr>
<tr>
<td>4.3 My Results</td>
<td>36</td>
</tr>
<tr>
<td>4.4 Analysis</td>
<td>39</td>
</tr>
<tr>
<td>5 Conclusions</td>
<td>40</td>
</tr>
<tr>
<td>6 Acknowledgements</td>
<td>42</td>
</tr>
<tr>
<td>Bibliography</td>
<td>43</td>
</tr>
<tr>
<td>List of Figures</td>
<td>46</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 The Role of Energy in Society

When one thinks of all the technological advances over the past century, space travel, plastics, supercomputers, and genetic engineering to name a few, it is a bit odd to think that the energy used to do or make those things essentially comes from burning stuff. While we are a few levels above cavemen burning wood for warmth, that is essentially what we are doing. Eighty-five percent of US energy consumption comes from burning fossil fuels: coal, petroleum, and natural gas.[1] A breakdown of total US energy consumption by source is shown in Figure 1.1, while US electricity production is shown in Figure 1.2. The attraction of fossil fuels lies in their familiarity and their availability. Because we have been using them since the start of the Industrial Revolution, fossil fuels are a very mature technology. And while petroleum can be a bit of a problem, the US has over two hundred years worth of coal reserves (based on current consumption) and it can be had for dirt cheap.[2]

The average efficiency of American coal power plants is around 37%, though new plants that use the latest technology can approach 50% efficiency.[3] Ultimately these sources will be limited by the second law of thermodynamics to below 70% efficiency, though combined cycle plants that produce...
Figure 1.1: A bar chart of US energy usage. From [1].

Figure 1.2: A bar chart of US electricity production. From [1].
electricity and heat can get up to 80% and beyond. Relying on fossil fuels has served us reasonably well up until this point, but that era has now come to an end because of global climate change. It turns out that by burning all those carbon containing compounds that were trapped under the Earth’s surface for millennia we are releasing CO$_2$ into the atmosphere, thereby strengthening the natural greenhouse effect that the atmosphere provides. The changes to the climate that are occurring due to this process are probably best avoided, which means that new sources of energy will have to be found that do not rely on burning carbon compounds.

1.2 Solar Energy

Fortunately there exist many alternative forms of energy production that are both clean and renewable. They are "clean" in the sense that they don’t emit CO$_2$ or any other pollutant and "renewable" in the sense that they are not dependent on substances that take thousands or millions of years to form through natural processes. Such renewable energy sources include solar (both photovoltaics and solar thermal), wind, hydro, geothermal, tidal, and biofuels. Here we will just be focusing on solar energy in the form of photovoltaics. Light’s ability to generate electric current was first observed in 1839 by A. E. Becquerel when he discovered the photoelectrochemical process.[4] Then in 1906 anthracene became the first organic compound in which photoconductivity was observed. Photoconductivity of organic materials was studied in the 1950s with the aim of using them as photoreceptors. At about that same time inorganic materials entered the field when Bell Laboratories developed the first inorganic solar cell in 1954. The photovoltaic effect was first observed in an organic material in the 1960s after it was discovered that some common dyes had semiconducting properties. A major breakthrough in the field came in 1986 when Tang discovered that the output power could be greatly increased if two materials were used instead of just one.[5] This
concept, known as a heterojunction, is now the fundamental idea behind the theory and design of organic photovoltaics (see chapter 2). One of the largest breakthroughs since that point was the creation of the first dye-sensitized solar cell by Michael Grätzel in 1991. Grätzel later improved his cell to be over 11% efficient, a huge jump over previous cells that had efficiencies of just 1% or less. The Grätzel cell is still the most efficient organic solar cell in the world. For comparison, silicon solar cells have efficiencies up to 20%, while the most advanced (and expensive) GaAs cells have gotten above 40%.

1.3 Basic Theory of Inorganic Photovoltaics

A photovoltaic (PV) device converts light directly into electric current and voltage. Traditionally this is done by forming a diode from the junction of two regions in an inorganic semiconductor, one doped to be n-type and the other p-type. An n-type semiconductor has a small fraction of its atoms substituted with atoms one space over to the right on the periodic table. Similarly p-type has some atoms replaced by those one space to the left. The dopants in the n-type have one more electron than all their neighbors and readily give it up, while the p-type dopants have one fewer electron and will accept electrons. When the electrons donated from the n-type region are accepted in the p-type region they form what’s called the depletion region. Due to the net build up of charge there is a net electric field in this region as shown in Figure 1.3. Semiconductors have “bands” of allowed energies. The highest band that would be filled at 0 K is called the valence band, while the next highest, seperated by some bandgap of forbidden energies, is called the conduction band. Because the conduction band is mostly empty, the electrons that are in it can move relatively easily. When a photon with enough energy strikes an electron in a semiconducting material it is excited into the conduction band. At the junction of p- and n-type semiconductors the electron and resulting positive hole would then accelerated apart due to
the electric field. The result is an electric potential and current that output power.

Almost all solar cells currently in commercial production can be understood with this p-n junction model. Silicon, the same material that is used to make transistors in our microprocessors, is the material of choice for commercial solar cells. Solar cells can now be made from single crystal, multi crystal, amorphous, and ribbon silicon. Other materials that have been widely studied but do not have large market shares include CdTe, GaAs, Ge, and copper indium gallium (di)selenide (CIGS). These other materials have mostly failed to be widely commercialized (outside of niche markets like space) because of their high cost. CdTe is an exception that has recently emerged as a competitive technology.[7] But even silicon based solar cells, currently the most cost efficient that can be produced on a commercial scale, still have a rather poor power to price ratio. Figure 1.4 shows that the price of solar
energy is currently much higher than competing sources of energy. Solar will never be competitive for large scale energy production until the price per kWh is brought in line with those other sources.

![Cost of Electricity by Energy Source](image)

**Figure 1.4:** A bar chart of the cost of electricity by production source. Note that solar energy bar reflects the fact that such energy can cost between 25¢ and 50¢ per kWh, depending on the technology used and the estimated lifetimes of the cells. Figure adapted from [8].

### 1.4 Economics of Solar Energy

The economics of solar energy are different than those of coal, gas, or oil. In the latter cases the cost is primarily driven by the (market determined) price of the fuel. The cost of solar energy is instead driven by the cost of the initial capital investment. The "fuel" in this case is free. The cost then is determined by the manufacturing cost of making the panels, the
installation cost, maintenance costs, and the lifetime over which those costs can be amortized. Organic photovoltaics are one strategy for bringing down the cost of solar energy. By replacing the crystalline semiconductor with some sort of organic molecule the manufacturing cost of solar cells might be brought down to the same level as for making sheets of plastic, because that is what they would be. Currently organic solar cells are significantly less efficient than most inorganic solar cells (1-11% vs. 15-40%), but it might still make sense to use them even at half the efficiency if they could be produced at one-tenth the price.

1.5 Organic Solar Cells

While the external behavior of organic photovoltaics is the same as that of inorganic PVs, the mechanism by which the voltage and current are generated is quite different. The organic PV material is not crystalline, so there are not nice bands for the electrons, nor is there an electric field to drive them. Because of that, when an excited electron is created by incident light it will quickly recombine with its hole unless something causes them to separate before recombination can happen. For that reason OPVs consist of two materials, one that electrons prefer and another that holes prefer. Once the electron and hole are separated into distinct materials, they can just diffuse apart due to their respective concentration gradients. For more information on this process see chapter 2. Thus there are three roles that will need to be filled by the materials: absorption of light in the visible spectrum (if this is to be used in the sun), a semiconducting material that will take the electrons when excitons separate (the acceptor), and a semiconducting material that will take the holes (the donor). Usually the first role and one of the others is shared by one material. The conducting materials must be semiconductors so that the cell can maintain an output voltage and not just produce photoconductivity. If the charge carriers are generated far from the
Figure 1.5: Some organic molecules commonly applied in evaporated organic solar cells: ZnPc (zinc-phthalocyanine), Me-Ptcdi (N,N’-dimethylperylene-3,4,9,10-dicarboximide), and the buckminster fullerene C60. Figure and caption from [9].

electrodes, the materials will also need to be efficient charge conductors (long carrier lifetimes) so that the charges are not lost before collection. Many material combinations have been tried that fit these requirements. They can be classified into three primary categories: molecular, polymer, and hybrid. Figure 1.5 shows a few examples of small organic molecules while Figure 1.6 shows some polymers that have been used in OPVs. The materials used in this thesis are an example of a hybrid OPV because they include an organic polymer as well as inorganic ZnO nanoparticles.

Now that the basic electronic roles of the donor and acceptor materials has been established, consider their physical interaction. Because excitons will only separate into charge carriers at the interface of the two materials, it is desirable to maximize the interface surface area to volume ratio. This can be done by making very thin films of one material on top of the other, by mixing the two materials and forming what is known as a bulk heterojunction, or by making some more complicated structure that will maximize the junction surface area while maintaining a path for the charge carriers to get to the
Figure 1.6: Several solution processible conjugated polymers and a fullerene derivative used in organic solar cells. Upper row: the p-type hole conducting donor polymers MDMO-PPV (poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene), P3HT (poly(3-hexylthiophene-2,5-diy) and PFB (poly(9,9’-dioctylfluorene-co-bis-N,N’-(4-butylphenyl)-bis-N,N’-phenyl-1,4-phenylenediamine). Lower row: the electron conducting acceptor polymers CN-MEH-PPV (poly-[2-methoxy-5-(2’-ethylhexyloxy) -1,4-(1-cyanovinylene)-phenylene) and F8TB (poly(9,9’-dioctylfluoreneco -benzothiadiazole) and a soluble derivative of C60, PCBM (1-(3-methoxycarbonyl) propyl-1-phenyl[6,6]C61). Figure and caption from [9].
Figure 1.7: An illustration of various types of heterojunctions. In three dimensions there is a continuous path in both materials from the interface of the materials to the electrodes. Adapted from [4].

electrodes. See Figure 1.7 for an illustration of heterojunctions of varying levels of complexity.

In the construction of a working solar cell the organic layer is just one of the necessary components. The device must also be designed to efficiently get light in and charge out. Figure 1.8 shows a basic schematic. On the side where light will come from there is a transparent conducting electrode. Indium tin oxide (ITO) is very commonly used for this purpose. There is also often a glass substrate that provides mechanical support. Anti-reflection coatings can help minimize losses due to non-absorption. On the other, dark side the electrode usually consists of a thin film of metal (such as Au or Al) that has been evaporated onto the device. Care must be taken with the attachment of the electrodes to the organic material, lest an insulating layer form. Strategies have been developed for certain materials, such as adding
buffer layers, to solve this problem.

1.6 The Challenges of Organic Solar Cells

Despite all the research that has been done on OPVs they still face a number of obstacles that are preventing them from moving beyond the laboratory. The first is sensitivity to oxygen. Many of the cells being produced in labs today are fabricated and tested without ever being exposed to air (and the natural humidity it contains). While encapsulation techniques do exist, these would add to production costs. This thesis deals with materials that are air stable and have met this challenge. Even if cells are not destroyed by exposure to air, many have short usable lifetimes because they degrade quickly with exposure to light. Another challenge is the size of cells being produced. Currently most cells are being made with areas on the order of 1 mm². To actually be usable cell areas will have to be increased to the order of 10s or 100s of cm² and those cells will have to be able to be assembled into
larger panels with areas on the order of m$^2$. Further challenges lay in how to actually utilize the electricity generated. For example, if periodic sources such as solar and wind become a large fraction of total production, electricity storage will have to be created on a scale never before seen. Clearly switching away from fossil fuels will require large investments in infrastructure and even changes to the way society views energy.

1.7 Summary

We have seen that organic photovoltaics have the potential to be part of the world’s solution to the future of energy, but still face many challenges. They have the promise of being a cheaper alternative to inorganic solar cells, but must increase in efficiency and improve operating stability before they will become widely used. The fundamental mechanism behind the photovoltaic effect in organic heterojunctions is now understood. The key to future improvements in this field lies in better understanding the materials involved and their structures.

This thesis will examine a particular combination of materials that hold promise to address the challenge of air stability. By preparing and operating the cell in ambient conditions with no extra protection, overall cost could be kept low. After a reliable process for fabricating these cells is developed, the material structure and dependence of performance on process parameters could be studied to further improve the design.
Chapter 2

Theory

2.1 Organic Photovoltaics

One of the keys to developing higher performance organic solar cells has been the development of an accurate theory of how they work. It is important to understand that though OPVs share superficial similarities with inorganic photovoltaics, they operate by different mechanisms. Broadly, a built-in electric field drives apart charge carriers in different energy bands in inorganic PVs, while in OPVs charge carriers diffuse apart after being dissociated at interfaces. The basic theory of inorganic PVs was discussed in the introduction, so we shall only consider the mechanism of OPVs here.

Perhaps the defining feature of OPVs is that for them carrier generation and separation are one and the same process. An incident photon creates an exciton (that is an excited electron-hole pair) in the photosensitive material, but generally the excitons are so closely bound that they are better thought of as mobile excited states than two separate particles bound together.[10] Excitons generated more than about a diffusion length away from the material heterojunction ($\sim10^{-6}$-$10^{-9}$ m) will contribute nothing because they will recombine before they have a chance to dissociate. Those that are generated close enough to the interface will either be quenched (dissociated) or reflected
at the surface. A fast quenching rate will ensure that most of the excitons generate charge carriers rather than get reflected and recombine.

In order to get excitons to form charge carriers at the heterojunction interface the offset of the energy bands of the two materials must be greater than the binding energy of the exciton, as shown in figure 2.1. The optical band gap (the energy needed to create an exciton) is less than the electrical band gap (the energy needed to create a free electron hole pair) because of the low dielectric constant and weak intermolecular forces in organic semiconductors relative to those of a silicon type semiconductor.[10] Therefore, the exciton will not have sufficient energy to break apart into the component charge carriers except at the interface where there is an offset to the band energies. This explains why carrier generation and separation are the same process and why carriers can only form at the heterojunction interface.

Once charge carriers are generated and transported from the heterojunction to the electrodes, they must be extracted. This again comes down to choosing the right materials such that the charge carriers have an energetically favorable path to the electrodes, while still retaining some voltage at the output. This is illustrated in figure 2.2.

### 2.2 Characterization

A solar cell is characterized on a basic level by the graph of its current as a function of voltage, known as its I-V curve. An example of such a graph is shown in figure 2.3. From this graph a few important performance parameters can be extracted, mainly the open circuit voltage, short circuit current, fill factor, and maximum power. Open circuit voltage is the voltage the cell produces when it is sourcing no current and represents the maximum voltage of the cell. The short circuit current is the current the cell can produce when the two electrodes are shorted together (i.e. $V = 0$).

Because power is the product of voltage and current, the point on the
Figure 2.1: Band offset makes exciton dissociation energetically favorable at the interface. From [10].
Figure 2.2: An example of the energy levels that allow for charge extraction. From [4].

Figure 2.3: An example of a current-voltage graph. From [4].
Figure 2.4: An illustration of the maximum power point and fill factor. From [11].

The graph that forms the largest rectangle with the two axes represents the point of maximum power output. Fill factor is just the ratio of the actual maximum power to the ideal maximum power, that is

$$\frac{P_{MAX}}{P_T} = \frac{V_{MP}I_{MP}}{V_{OC}I_{SC}}$$ \hspace{1cm} (2.1)

The source of the name should be apparent from the visual representation shown in figure 2.4. From this point it is straightforward to get the power conversion efficiency, just divide the maximum power output by the power of the incident light:

$$e = \frac{P_{MAX}}{P_{IN}}$$ \hspace{1cm} (2.2)

A few more characterization parameters can be found by modeling a solar cell as a current source in parallel with a diode with two resistive elements, as shown in figure 2.5. $R_S$ is the series resistance while $R_{SH}$ is the shunt
resistance. The effects of these two non-idealities are shown in figure 2.6. So the current delivered to the load becomes that of the current source (from the photovoltaic effect) minus the losses from the diode and the resistors,

\[ I = I_l - I_0 \left( e^{\frac{q(V+IR_S)}{nkT}} - 1 \right) - \frac{V + IR_S}{R_{SH}} \]  \hspace{1cm} (2.3)

where \( I_0 \) is the reverse bias saturation current, \( q \) is the charge of the electron, \( n \) is the ideality factor of the diode, \( k \) is Boltzmann’s constant, and \( T \) is temperature.
Chapter 3

Experimental Procedures

3.1 Materials

One of the principle difficulties that presents itself when trying to fabricate a organic solar cell is the instability of most cell materials in ambient conditions. Most of the cells presented in the literature are fabricated and characterized without ever being exposed to air. To follow this approach would require a glovebox, something not easily accessible to me. Furthermore such materials fail to live up to one of the claimed benefits of using organic materials, cheap and easy processing. They also have very short lifetimes, making them useless in any real application without some type of encapsulation that would also add to the cost and difficulty of manufacture. Long lifetime also helps spread out fixed manufacturing and installation costs over time, lowering the price per watt. Due to these advantages we decided to use the materials described by Krebs, et. al. in their article “A simple nanostructured polymer/ZnO hybrid solar cell-preparation and operation in air.”[12] The appeal of this approach was enhanced by the willingness of Krebs to provide us with samples of the key materials. A diagram of the various layers of material is shown in Figure 3.1.
3.1.1 Active Layers

The two active materials were ZnO nanoparticles and the polymer poly-(3-(2-methylhex-2-yl)-oxy-carbonyl-dithiophene) (P3MHOCT) which becomes poly(3-carboxy-dithiophene) (P3CT) upon the application of heat. The polymer absorbs the incident photons (with energies somewhere in the red and above) and acts as the electron donor. The ZnO nanoparticles serve as the acceptor material as well as semiconducting charge pathway to the front electrode. The ZnO nanoparticles are about 5 nm in diameter and have methoxyethoxygenic acid (MEA) attached on their surfaces as ligands. These MEA stabilized ZnO nanoparticles have the advantage over other candidate materials that they are stable in humidity and are solution processable.[12]

3.1.2 Electrodes

For the transparent front electrode Indium Tin Oxide (ITO) on a glass substrate was used. ITO is one of the most commonly used materials for this purpose. It was supplied by Kintec Co. as well as included in the materials sent by Krebs. The ITO slides from Kintec were patterned to have a center stripe and six fingers approaching from the sides following the design used by the Malliaras group at Cornell University. This shape can be made out in Figure 3.3(a) and (d). For the back electrode a layer of PEDOT:PSS was included to help the charge extraction process, again a common practice. For the electrode itself a few materials were tried. One was a silver based paste (Dupont 5007) that could just be brushed on using a cotton swab. Evaporated metals were also tried, namely Al on top of a thin CsF layer (cell 1). This was found to have mismatched energy levels to those of the other materials. Gold should have the correct energy level and was also tried. To match the back electrodes to the ITO pattern a shadow mask (as seen in figure 3.2) was custom milled out of a thin sheet of brass using a 1/32” bit.
Figure 3.1: The layers of the organic solar cell built in this thesis. Note that the thicknesses are not to scale. The top layer in the diagram, that is the back electrode, is about 100 nm for the evaporated metals or in the 100s of µm for the Ag paste. The PEDOT:PSS layer also has a thickness on the order of 100s of µm. The P3CT/ZnO and ZnO layers are roughly on the order of nm, while the ITO (the front electrode) is on the order of µm. The glass is 1.1 mm thick.
3.2 Cell Geometries

Three cell geometries were tried. The first was done on the Kintec ITO slides with the evaporated metals. This pattern allows 6 independent cells to be made on the same slide. The last two were done with the ITO slides provided by Krebs and using the Ag paste. Figure 3.3 has both diagrams and photographs of the configurations. For geometries 1 and 2 where there is more than one cell per slide, the ITO serves as a common contact for each of the cells.

3.3 Fabrication Process

I will describe the idealized fabrication procedure here then afterwards discuss the practical difficulties faced during my attempts. The ZnO was received in solution with chlorobenzene at a concentration of 175 mg/ml, so
Figure 3.3: Various cell geometries. (a),(d) Geometry 1. (b),(e) Geometry 2. (c),(f) Geometry 3. White is glass, pink is ITO, and grey is the active PV areas.

chlorobenzene was added to dilute it to a concentration of 50 mg/ml. Then the polymer, which was received in powdered form, was mixed with the ZnO solution and chlorobenzene to achieve concentrations of 50 mg/ml with respect to ZnO and 25 mg/ml with respect to P3MHOCT. This was subsequently stirred by a magnetic stir bar in a closed bottle for 6 hours then filtered through a Teflon syringe filter with .45 um pores.

3.3.1 Spin Coating

With these two solutions prepared the layers of the cell (see Figure 3.1) can be spun. After first wiping the slide with chlorobenzene or spinning on a little IPA to clean it, a layer of the ZnO is spun on at 1000 RPM. Next a cotton swap wetted with chlorobenzene is used to wipe away the ZnO from everywhere except where the cell area is being defined. Then it is placed on a 310°C hotplate for 5 minutes to make the film insoluble. Following that, the polymer solution is spun on at 1000 RPM and wiped away in a similar pattern. The slide is again placed on the hotplate, this time at 210°C for 5
minutes. Next comes a layer of PEDOT spun on at 2800 RPM, wiped, and dried at 120°C on the hotplate for 10 minutes.

### 3.3.2 Back Electrode

Finally the back electrode is added one of two ways, by brushing on Ag paste or evaporating a metallic thin film (Au or Ag). If the Ag paste is used the slide is again dried at 140°C on the hotplate for 5 minutes after first having the desired pattern of electrodes painted on the slide using a cotton swab. For the metallic thin films thermal evaporation is done at high vacuum ($10^{-6}$ torr). For the gold electrodes 267 amps of current caused evaporation at 3.3 Å/sec to form a 93 nm thick film. At this point the cell is ready for characterization.

### 3.4 Difficulties

A number of difficulties arose during this project related to unfamiliarity with the use of chlorobenzene. Chlorobenzene has a high vapor pressure and will evaporate rather quickly if left exposed to the atmosphere. The mistake was also made of storing these solutions containing an organic solvent in plastic (polymer) bottles. The combination of these two forces led to the polymer mix and stock of ZnO drying out over time. This made keeping concentrations of the components at the desired levels impossible and may have caused an undesirable chemical or physical change in the materials.

I also had a few problems with the spincoating step. The ZnO layer never came out uniform. It was always splotchy white spots concentric to the axis of rotation. The polymer layer generally came out as a nice uniform red film as long as the slide was kept clean. The PEDOT layer often came out poorly for unknown reasons. It would stick to a few spots to create thick layers, but not spread out and adhere to the rest of the surface. When tested on clean ITO/glass slides good films were produced, making it likely
that interactions with the other layers caused the poor PEDOT films. I also had to learn to approach wiping differently for the PEDOT as it was not soluble in chlorobenzene and had to be mechanically scraped away. After cells 2 and 3 I thought I had problems with electrical shorts between layers, though this hypothesis seems less likely to me after the problem persisted despite taking measures to eliminate shorts. The resistances of the cells were also inconsistent with the resistance that would have resulted from traveling through PEDOT to the edge of the layers, meaning it would have had to have been a through hole if it was indeed a short. Given the uniform coverage of the polymer layer, through holes also seemed unlikely.

3.5 Characterization

3.5.1 Circuit

The electrical circuit used to measure I-V curves is shown in diagram form in figure 3.5.1. By varying the resistance of the potentiometer the voltage across the cell can be set. In this case the voltage is the independent variable, while the current is the dependent variable. The advantage of this circuit as opposed to just measuring the output to a variable load is that the curve can be extended passed the axis and the exact minimum and maximum resistances of the potentiometer are not important. The intersection with the voltage axis \( (I = 0) \) is the open circuit voltage while the intersection with the current axis \( (V = 0) \) is the short circuit current. This measurement also gives us the maximum power, fill factor (see equation 2.1), and, if the illumination intensity is known, power conversion efficiency (equation 2.2). Voltages and currents were written down by hand from the multimeters. In the case of the silicon reference cell, electrical contact was made using two small, gold clips, as seen in Figure 3.7. A small piece of transparent plastic is inserted between the cell and the clip so that each clip only contacts one electrode. For the organic solar cells, probes were pressed against the metal
contacts on the cell.

An improved method of characterization would be to automate the generation of an I-V curve using a combination of software and hardware. An example of such a system is the National Instruments PXI-4130 Power Source Measurement Unit and accompanying software. Unfortunately such hardware has a very large price tag relative to the budget of this thesis. The software[11], however, is provided free of charge for LabView users and might be implemented in the future to analyze data collected manually.

3.5.2 Illumination

The sun’s spectrum is to first order that of a 5800 K blackbody. Passing through the atmosphere complicates the spectrum considerably as some wavelengths are absorbed or scattered much more strongly than others. Other factors that determine the spectrum that actually ends up hitting the surface include latitude, time of day, season, level of pollution, humid-
ity/clouds, and more. In order to be able to make meaningful comparisons between systems tested with different light sources, standard reference spectra were defined, such as the one shown in Figure 3.5. Solar cells meant for terrestrial use are generally tested at 1000 W/m² and air mass (AM) 1.5, meaning the sun has a zenith angle of 48°. In order to meaningfully compare the performance of this system to that of other published results a solar simulator with this spectrum and intensity would have to be used as the illuminating source. A light that meets these requirements for wavelengths shorter than the infrared exists in the lab of Hal Van Ryswyk at Harvey Mudd College and might be used in the future.

For the data presented here the cells were illuminated using a FOSTEC bright white light source. The spectrum of this light was measured using an Ocean Optics spectrometer as shown in figure 3.6. While not ideal, it is not too much of a problem that this spectrum lacks light in the infrared and ultraviolet because the former would have energies less than the optical band gap, while the latter will thermalize down to that level and give up any extra energy they had. The light and circuit setup was tested by measuring the I-V curve of a Si solar cell. Those cells were manufactured for JPL and are left over from one of their Mars orbiters. They are 2 cm by 4 cm and have nominal efficiencies of 13-14%. A photo of the cell is shown in figure 3.7.
Figure 3.5: The spectrum of the sun in space and on the Earth’s surface. From [14].
Figure 3.6: The spectrum of the FOSTEC white light source

Figure 3.7: The silicon solar cell used as a reference to characterize the light source and I-V curve measurement process.
Chapter 4

Results and Analysis

4.1 Silicon Reference Cell

The Si reference solar cell was illuminated by the FOSTEC light source at about 50 and 23,000 lux. Illuminance was measured using a CircuitSpecialists.com MS8209 multimeter. Full sunlight was out of the range of the multimeter, with illuminance greater than 40,000 lux. The 50 lux I-V curve is shown in figure 4.1. The open circuit voltage was 367 ± 3 mV while its short circuit current was 1.05 ± 0.05 mA. The maximum power output was about 0.18 mW. At an assumed efficiency of 13% this indicates an illumination intensity of 1.7 W/m², which is reasonable given the low illumination. The cell was tested again under illumination closer to that of the sun. The I-V curve in figure 4.2 shows an open circuit voltage of 530 mV, a short circuit current of 106 mA, and maximum power of 14.1 mW. The linearity of this curve is evidence of a large series resistance (see Figure 2.6). At 13% efficiency this would mean the incident light had an intensity of about 140 W/m², the right order of magnitude given that it is still operating at less than full sunlight. Under the actual sun at 2:30 pm, blocked slightly by a thin cloud, this cell had $V_{OC} = 550$ mV, $I_{SC} = 180$ mA, and $P_{MAX} = 39$ mW. Due to light fluctuations caused by the cloud a full I-V curve could not be
measured, so the maximum power value is the highest from a limited number of measurements. That power output at 13\% would mean an intensity of 390 W/m$^2$, still a bit low, but possibly reasonable given the presence of clouds.

4.2 Literature Results

Cells made from the same materials as those used in this thesis had the performance shown in Figure 4.3. The open circuit voltage was around 500 mV and the short circuit current density was about .28 mA/cm$^2$. Figure 4.4 shows that the performance initially is a modest 0.05\% and that it falls to about half that value after 140 hours of operation.

![Figure 4.1: The I-V curve of the Si reference cell under 50 lux illumination.](image)
4.3 My Results

A total of 5 P3CT/ZnO cells were fabricated and tested. Unfortunately the performance of these cells left much to be desired, with only the first producing any output voltage whatsoever. Cell 1 (shown in Figure 3.3(a)) consisted of the layers described in chapter 3 as well as an evaporated back electrode. That layer was 15 Å CsF below 150 Å of Al. Unfortunately, the circuit for producing the I-V curve was not set up, nor was there a picoammeter available for measuring the low short circuit currents. All short circuit currents were less than .1 mA. The open circuit voltages are given in table 4.1. All voltages are given in millivolts. The third row has the same illumination as the second, but with the cell rotated 90 degrees to measure the effect of non-uniform intensity of the source. After two days of dark storage the areas on the cell were measured again and all of there voltages had fallen to below 1.3 mV. The resistance of the areas at that time ranged from 190 to 890 kOhms.
Figure 4.3: The I-V curve of a P3CT/ZnO cell by Krebs et al. in [12].
Figure 4.4: The performance over time of a P3CT/ZnO cell by Krebs et. al. in [12].

<table>
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<th>lux</th>
<th>area 1</th>
<th>area 2</th>
<th>area 3</th>
<th>area 4</th>
<th>area 5</th>
<th>area 6</th>
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<td>80</td>
<td>2.6</td>
<td>5.1</td>
<td>5.2</td>
<td>11.8</td>
<td>17.0</td>
<td>16.0</td>
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<tr>
<td>1,200</td>
<td>4.8</td>
<td>6.9</td>
<td>5.6</td>
<td>19.0</td>
<td>25.9</td>
<td>23.4</td>
</tr>
<tr>
<td>1,200</td>
<td>4.2</td>
<td>5.8</td>
<td>5.3</td>
<td>18.1</td>
<td>24.6</td>
<td>21.5</td>
</tr>
</tbody>
</table>

Table 4.1: $V_{OC}$ of cell #1 in mV

Cell 2 used the Ag paste but produced no output. Its illuminated I-V curve is that of an ohmic resistor with resistance of 11 ohms. Cell 3 was similar with $V_{OC}$ of 0.0 mV and a dark resistance of 18 ohms. Cell 4 was made with special attention to terracing the layers to avoid any chance of a short occurring on the outside edges. Figure 3.3(b) shows a photograph of this cell. Each of the three active areas on this cell had open circuit voltages of 0.1 mV, while their dark resistances were 29, 31, and 40 ohms. Cell 5 was again an evaporated metal, this time 93 nm of gold. Again there was no
output. Dark resistances were in the 1.5 to 2.5 kohms range.

4.4 Analysis

Do to the lack of performance in all but one cell it is impossible to say which variables were or were not limiting performance. It is thought that cell 1 had a reduced $V_{OC}$ because of a mismatch in the energy levels of the polymer and the CsF. The total lack of performance in the other cells remains a mystery. It was initially thought to be a short either through or at the edges of the material. This now seems less likely because of the persistence of the problem in spite of efforts to reduce the chance of such a short. One possible explanation for the performance failures offered by Frederik Krebs is that the ZnO particles either clumped together due to exposure to too much water (humidity) or that they failed to re-suspend after the chlorobenzene dried up. It was not possible to test this hypothesis due to the limited supply of polymer.
Chapter 5

Conclusions

Solar energy will be an important part of a sustainable energy future, but only if current challenges can be overcome. This thesis looked at one combination of materials that advance solar technology by being moderately stable under atmospheric conditions. While a fully functional and characterized cell was not achieved, progress was made toward that goal. The processes of spin-coating the various layers and evaporating a custom pattern of electrodes and an apparatus for basic characterization were successfully developed, so functioning materials seem to be the only missing step in creating a working cell. One cell with partial functionality was fabricated and had open circuit voltages up to 26 mV. A full I-V curve was measured for a silicon reference cell.

Obviously much remains to be done. The next steps are to get a cell working then try to optimize its performance to at least some acceptable level. This can be done by sticking more closely to the published fabrication process, in particular avoiding allowing the solutions to dry out, and continued troubleshooting. To help speed the characterization process a mechanical support could be machined that would create electrical connections by simply placing the slide in the holder. The data could be analyzed in more detail (getting $R_S$ and $R_{SH}$ for example) by using LabView analysis.
software. It would also be desirable to get an I-V curve when the cell is illuminated by an AM1.5 source so that the results will be comparable to the reported values. Another measurement of interest would be cell lifetimes under various operating conditions.
Chapter 6

Acknowledgements

First and foremost let me thank David Tanenbaum for his four years of advising and guidance and his supervision of this thesis. He has been the single biggest influence in my education and development as a scientist. He has helped steer me straight each of the many times I have run into difficulties that were beyond me.

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Bibliography


List of Figures

1.1 A bar chart of US energy usage. From [1]. .................. 6
1.2 A bar chart of US electricity production. From [1]. ........ 6
1.3 An illustration of a p-n junction. From [6]. ................. 9
1.4 A bar chart of the cost of electricity by production source. 
   Note that solar energy bar reflects the fact that such energy 
   can cost between 25¢ and 50¢ per kWh, depending on the 
   technology used and the estimated lifetimes of the cells. Figure 
   adapted from [8]. ........................................ 10
1.5 Common organic molecules used in opvs .................... 12
1.6 Common polymers used in opvs ............................... 13
1.7 An illustration of various types of heterojunctions ........ 14
1.8 An illustration of the basic structure of a solar cell. Adapted 
   from [4]. ............................................... 15

2.1 Band offset makes exciton dissociation energetically favorable 
   at the interface. From [10]. .............................. 19
2.2 An example of the energy levels that allow for charge extrac- 
   tion. From [4]. ........................................ 20
2.3 An example of a current-voltage graph. From [4]. ........... 20
2.4 An illustration of the maximum power point and fill factor. 
   From [11]. ............................................. 21
2.5 This circuit is a model for a solar cell. From [11]. .......... 22
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>The layers of the organic solar cell built in this thesis</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>The custom machined shadow mask used to define the evaporated electrodes</td>
<td>26</td>
</tr>
<tr>
<td>3.3</td>
<td>Various cell geometries. (a),(d) Geometry 1. (b),(e) Geometry 2. (c),(f) Geometry 3. White is glass, pink is ITO, and grey is the active PV areas.</td>
<td>27</td>
</tr>
<tr>
<td>3.4</td>
<td>The circuit used to take measurements for the I-V curve</td>
<td>30</td>
</tr>
<tr>
<td>3.5</td>
<td>The spectrum of the sun in space and on the Earth’s surface.</td>
<td>32</td>
</tr>
<tr>
<td>3.6</td>
<td>The spectrum of the FOSTEC white light source</td>
<td>33</td>
</tr>
<tr>
<td>3.7</td>
<td>The silicon solar cell used as a reference to characterize the light source and I-V curve measurement process.</td>
<td>33</td>
</tr>
<tr>
<td>4.1</td>
<td>The I-V curve of the Si reference cell under 50 lux illumination.</td>
<td>35</td>
</tr>
<tr>
<td>4.2</td>
<td>The I-V curve of the Si reference cell under 23,000 lux illumination.</td>
<td>36</td>
</tr>
<tr>
<td>4.3</td>
<td>The I-V curve of a P3CT/ZnO cell by Krebs et. al. in [12].</td>
<td>37</td>
</tr>
<tr>
<td>4.4</td>
<td>The performance over time of a P3CT/ZnO cell by Krebs et. al. in [12].</td>
<td>38</td>
</tr>
</tbody>
</table>