Comprehensive Study of the Dye Sensitized Solar Cell

Gregory Lewis Vick

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COMPREHENSIVE STUDY OF THE DYE SENSITIZED SOLAR CELL

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Masters of Science in Mechanical Engineering

in

The Department of Mechanical Engineering

by
Gregory Lewis Vick, Jr.
B.S., Southeastern Louisiana University, 2008
August 2013
Dedicated

To

My Parents and Family
ACKNOWLEDGMENTS

First I would like to my advisor, Dr. Tryfon T. Charalampopoulos, for his guidance throughout my academic career. Dr. Charalampopoulos served as an outstanding advisor that I could turn to for any question or concerns that arisen throughout the completion of my studies. He was a crucial driving force that pushed me to do my best while in graduate school and completing my studies. This study could not have been possible without his direct supervision and encouragement.

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<td>D</td>
<td>diffusion constant (m$^2$/s)</td>
</tr>
<tr>
<td>E</td>
<td>macroscopic electric field Gradient (V/M)</td>
</tr>
<tr>
<td>E</td>
<td>energy (J)</td>
</tr>
<tr>
<td>G</td>
<td>generation rate of electrons (m$^{-3}$s$^{-1}$)</td>
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<tr>
<td>I</td>
<td>current (A)</td>
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<td>$I_d$</td>
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<td>V</td>
<td>voltage (V)</td>
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<tr>
<td>$e_o$</td>
<td>elementary charge (As)</td>
</tr>
<tr>
<td>h</td>
<td>Planck’s constant (Js)</td>
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<td>$j(e,i^-,i^+,e)$</td>
<td>current density (electrons, iodide, tri-iodide, catons) (A/m$^2$)</td>
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<tr>
<td>k</td>
<td>Boltzmann’s constant (J/Mole*K)</td>
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<td>k</td>
<td>chemical equilibrium constant</td>
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<tr>
<td>n</td>
<td>particle density (m$^{-3}$)</td>
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<td>n</td>
<td>ideality factor</td>
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<tr>
<td>$\bar{n}$</td>
<td>particle density without illumination (m$^{-3}$)</td>
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<tr>
<td>$\alpha$</td>
<td>absorptivity</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>dielectric constant</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
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<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>permittivity of free space ($\text{F} \cdot \text{m}^{-1}$)</td>
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<tr>
<td>$x$</td>
<td>coordinate</td>
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<td>$\mu$</td>
<td>mobility constant ($\text{m}^2/\text{Vs}$)</td>
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<tr>
<td>$\varphi$</td>
<td>photon flux density ($\text{m}^{-3} \text{s}^{-1}$)</td>
</tr>
<tr>
<td>Photon Flux ($\lambda$)</td>
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ABSTRACT

A complete electrical model of the dye-sensitized solar cell has been presented. This model relates the material parameters of the cell to the cell’s performance. The full model is reduced to an Idealized form and simulated to find an idealistic power curve or current (I) – voltage (V) curve. The operating parameters of reflectivity, temperature, reverse saturation current and ideality factor are investigated. A sensitivity analysis is completed to determine what parameters have a dominating influence on the overall cell performance. It was found, for the ideal case of the dye sensitized solar cell, that the factors of absorptivity, temperature, reverse saturation current, and ideality significantly influence the efficiency limits. Increasing the operating temperature and/or the ideality factor of the cell results in an increase in efficiency. Also the study shows an increase in efficiency resulting from a decrease in reverse saturation current and/or reflectivity. Comparison of the results was carried out with a previous study and it was found that an idealized dye sensitized cell has 9% more efficiency than an idealized p-n junction solid state device. The incorporation of nanotubes was studied in order to improve diffusion of free electrons within the active layer. The results are compared to the ideal study of the dye sensitized solar cell. Finally, an incorporation of a thin film anti-reflective coating was then investigated to show how reflectivity from the cell can be reduced. The results for this study are discussed and suggestions for improvement are provided.
CHAPTER 1. INTRODUCTION

1.1 Introduction
The dye sensitized solar cell is a relatively new photovoltaic device that offers an inexpensive affordable alternative to traditional solid state p-n junction photovoltaics. Due to the increasing demand for renewable energy this device has the potential to become one of the best solutions to clean energy. The vision first and foremost is to be able to produce these devices with low cost material and fabrication processes, thus sustaining low cost electricity production from solar radiation and secondly be able to maximize the efficiency of such devices.

The photovoltaic effect was first demonstrated by A. E. Becquerel in 1839 and the first solid state cell was built in 1853 by Charles Fritts by coating selenium with a thin layer of gold to form the junctions. This device had an efficiency of 1%. Following this discovery, in 1905 Albert Einstein explained the underlying mechanism of the photovoltaic effect for which he was awarded the Nobel Prize in physics in 1921. Several years later, in 1946 Russell Ohl patented the modern junction semiconductor solar cell which would lead to the development of the transistor [1]. The first practical device was developed in 1954 at Bell Laboratories by Daryl Chapin, Calvin Souther Fuller, and Gerald Pearson. This was a silicon based p-n junction device that achieved an efficiency of 6%. This device was suitable for minor uses since the cost of electricity it produced was about $250 per watt versus $2 to $3 per watt from a coal power plant. Soon after the production of the p-n junction there was a new demand for solar cells. It was suggested to add these cells to the Vanguard I satellite for power while in orbit instead of using batteries. The satellite was launched in 1958 and with the incorporation of photovoltaics had increased its self-sustainability for longer missions. Improvements slowed down over the next two decades until Exxon came into the picture looking for projects 30 years in the future. They developed the New Jersey Exxon lab, Solar Power Corporation. The first goal was to drive the price down for the
fabrication of these devices. They took the bulk silicon semiconductor and cut it into wafers and noticed that the rough-sawn wafers already had a suitable anti-reflective coating and that the electrodes could be printed directly on the wafer thus driving down manufacturing cost significantly. Along with other good practices, Exxon’s Solar Power Corporation began buying up “reject” silicon from existing manufactures at very low cost and by 1973 was producing panels at $10 per watt and selling them at $20 per watt, a fivefold decrease in price in two years [1]. While the big push for lowering cost production of the solid state devices was ongoing in the 1970s, a group at University of California Berkeley was working with organic dyes to understand and simulate the primary process in photosynthesis and in 1972 demonstrated electric power generation via the dye sensitized solar cell. It also had an efficiency of 1%. In the forty years following this demonstration the dye sensitized solar cells have been optimized to have efficiency around 11% [2].
2.1 Background-Previous Studies
The limitations of the parameters of the dye sensitized solar cell are material specific. The light absorbing dyes are completely organic and have different wavelength bands of absorption. Therefore for single layer dye sensitized cells the optimum dye would be one that has the absorption band that can absorb the most photons. At MIT there are currently experimenting with multiple layer dye sensitized cells with a different type of organic dye in each layer [3]. The idea is that as light passes through the layers, shorter wavelength photons will be absorbed in the top layers and the remaining longer wavelength photons will be absorbed in the lower layers as it passes through the cell.

The operating temperature of the cell has an upper limit justified by the boiling point of the liquid electrolyte. When approaching this limit the liquid begins to change phase to a gaseous state. The change in phase causes internal pressure and stresses which damage the cell. Researchers at Freiburg Materials Research Center in Freiburg Germany are working on the development of better liquid electrolytes for phase stability issue in extreme temperature environments. They have found that with the addition of MgI$_2$ to the electrolyte there is a reduction to the internal stresses of the cell thus prolonging the lifetime of the cell [4].

The reverse saturation current (Io) is also material dependent and is sensitive to the cross-sectional area of the cell [5]. In order to have very small values for the reverse saturation current, the cell needs to be small as possible. Therefore an interconnected array of smaller cells will have better performance than that of one large cell due to the decrease in the reverse saturation current. The ideality factor is introduced in the ideal diode equation (24) and is a measure of how closely the diode follows the ideal equation. In practice, there are second order effects so that the
diode does not follow the ideal equation and the ideality factor provides a way of describing them [6].

Diffusion and reflection are also limiting factors for the efficiency of the dye sensitized solar cell. Researchers at the National Renewable Energy Laboratory in Colorado have aimed to improve electron diffusion lifetime by 14% with the incorporation of nanotubes for the metal oxide [7]. The most up to date versions of solar cells are constructed with a glass shell often called a transparent conductive oxide layer (TCO). This layer is constructed of Fluorine doped Tin Oxide. The TCO layer has a reflectance of 10% of the incident light. Researchers at Honeywell have been applying silicon based anti-reflective coatings on solid state p-n junction solar cells to achieve a 3% increase in transmittance of light over a broad range of wavelengths (350nm -1000nm). This coating increased the cell’s performance by 3% [8]. Researchers at NREL (National Renewable Energy Laboratory) have also done work on antireflective coatings on silicon based solar cells. They used a coating of TiO₂ and seen similar results in reflectivity [9]. There are very few papers published on anti-reflective coating applications on dye sensitized solar cells. A study done by Linda yen-Chien Chen in 2010 showed a significant decrease in reflectance using an aluminum doped zinc oxide coating [10]. However, there hasn’t been (to my knowledge) any optimization conducted on the material used in the coating or the coating thickness to decrease reflectivity of light ranging in wavelengths from 200nm to 800nm.

2.2 History and Efficiency Evolution
The first p-n junction was created in 1883 by Charles Fritts and was around 1 percent efficient. Over the last 129 years this device has been optimized. Today a typical silicon p-n junction cell operates at around 14% efficiency but researchers have been able to reach up to 24% efficiency with these devices [11]. The DSSC is a relatively new technology that was developed in 1972 at University of California at Berkeley [2]. The first cell was also 1% efficient. Over the last 40
years these cells have been optimized to have peak efficiencies around 11% [2]. Figure 1 shows the evolution of efficiency over time.

![Figure 1: Timeline for efficiency limits for p-n junction cells (purple) and dye sensitized cells (red).](image)

(1) **1853** - Charles Fritts develops the first p-n junction cell by coating selenium with a thin layer of gold to form the junctions [12].

(2) **1954** - Bell Labs announces the development of the first modern silicon solar cell. It had an efficiency of 6% [12].

(3) **1957** - Hoffman Electronics creates an 8% efficient commercial p-n junction cell [12].
(4) **1958** - Hoffman Electronics creates a 9% efficient commercial p-n junction cell [12].

(5) **1959** - Hoffman Electronics creates a 10% efficient commercial p-n junction cell [12].

(6) **1960** - Hoffman Electronics creates a 14% efficient commercial p-n junction cell [12].

(7) **1985** - 20% efficient solar cells are created by Centre for Photovoltaic Engineering at the University of New South Wales [12].

(8) **1991** - The dye sensitized solar cell is invented. It had an efficiency of 1% [12].

(9) **1991** - Dye sensitized solar cell reaches an efficiency limit of 7.1% [13].

(10) **1995** - A new efficiency of 30% is reached by a p-n junction cell [12].

(11) **1996** - Dye sensitized solar cell reaches an efficiency limit of 11.2% [14].

(12) **2006** - New world record of an efficiency of 40% reached by p-n junction cell [12].

(13) **2006** - Dye sensitized solar cell reaches an efficiency limit of 11.5% [14].

(14) **2008** - New world record of and efficiency of 40.8% reached by p-n junction cell [12].

(15) **2011** - Dye sensitized solar cell reaches an efficiency limit of 12.3% [15].

### 2.3 Motivation for the Present Study

The ongoing development has reached a point where detailed numerical simulation can contribute to the optimization of these devices. For dye sensitization semiconductors, dye absorption, electron generation/recombination, kinetics, reflectivity and energy conservation all have an impact on the cell’s performance. There are two objectives of this work. The first objective is to explore the ideal performance characteristics of the DSSC to set a benchmark for the performance limitations. The other objective is to investigate the reflectivity effects of a cell and establish an optimum antireflective coating that results in the highest efficiency of a DSSC.
In order to better understand how the operating parameters influence the overall performance of the cell a complete parametric sensitivity analysis needs to be conducted. This will aid in the understanding of how each parameter influences the cell's performance and provide insight as to how the governing parameter can be modified to achieve higher overall efficiency of the cell.
CHAPTER 3. COMPOSITION OF SOLAR CELL

3.1 Composition of Dye Sensitized Cell
A dye-sensitized solar cell (figure 2) consists of a transparent conductive oxide glass (TCO) layer where a metal oxide is attached by a method of spin coating, dip coating, or (in the latest developments) grown by electronic deposition [16]. On the metal oxide layer there is a layer of Ruthenium dye complex that acts as a light harvester. These dye molecules are organic and have absorption properties that mimic chlorophyll [2]. The TCO, metal oxide, and dye make up the top plate. For the bottom plate there exists another TCO layer that platinum is deposited on for catalytic purposes (speeds up electron reinjection back into device after going through external circuit). Lastly an Iodine based liquid electrolyte is sandwiched between these two sides. The electrolyte acts as a charge acceptor/injector inside the cell.

Figure 2: Basic make up of DSSC [16].
3.2 Composition of the P-N Junction Cell
The traditional photovoltaic devices (p-n structures) are composed of two semiconducting wafers (usually silicon). One wafer being p-type or positively doped and the other layer n-type or negatively doped. These two doped wafers are sandwiched together to form the main body of the cell (figure 3) [17]. The doping is done by adding other elements (impurities) to the silicon [18].

For the n-type, the addition of group VI elements such as sulfur will create extra free electrons within the silicon wafer and thus give it a negative charge. Since sulfur has six electrons in its valence band and silicon has four electrons in its valence band, once sulfur is covalently bonded to silicon only eight electrons are used in the bond thus leaving two free electrons. The opposite happens for the p-type semiconductor where elements from group IV are introduced to the silicon material. Here an element such as boron which has three electrons in its valence band will covalently bond to silicon and thus will be lacking one electron (hole) in order to fill the bonded valence band [17]. This created p-n junction is then contained by a transparent conducting oxide layer (glass). During illumination the free electrons in the n-type semiconductor become excited and jump the bandgap to the p-type semiconductor where they pass through the external circuit and relax back to the n-type semiconductor (figure 4) [18].

In comparison to p-n junction solid state cells, the function of light absorption is separated from charge-carrier transport in dye sensitized solar cells. The complete process is outlined in figure 5. First the dye absorbs photons from the incident flux (step 1). The dye molecule’s energy is then raised to an excited state (1 to 2 electron volts or 1.62x10^{19} Joules) where a free electron is then injected into the conduction band in the metal oxide (step 2). Upon the releasing of the electron, the dye molecule is relaxed (step 3) and then a new electron is passed from the iodide to the hole in the dye molecule (step 4). Upon the releasing of the electron, the dye molecule is relaxed (step 3) and then a new electron is passed from the iodide to the hole in the dye molecule (step 4).
Electrons now in the conduction band of the metal oxide may diffuse or drift to the front electrode and be extracted as external current. The only loss reaction considered is that the free electrons in the conduction band may be captured by the oxidized species (triiodide) of the electrolyte. The possibility of the free electron being recaptured by the dye when it relaxed is ignored since this reaction rate is 100 times slower than that of the capturing of the electron by the electrolyte [20].

Figure 3: p-n junction photovoltaic [17].
Figure 4: Photovoltaic effect for p-n junction device [19].
CHAPTER 4. FULL MODEL OF DYE SENSITIZED CELL

The dye sensitized solar cell is modeled as a pseudo-homogeneous medium consisting of a transparent conductive oxide layer with nanoporous metal oxide layer and a light absorbing dye attached. Surrounding the metal oxide/dye composition is an iodine based electrolyte fluid. On the back side of the device is a Platinum layer that acts as a catalyst for electron injection. The cell is modeled as a 1 cm x 1 cm x 1 cm cube with a depth of the active layer 1x10^{-4} m (thickness of the metal oxide). The temperature, photon flux, and the motion of the charges and charge carriers are held constant. The mobile charge carriers involved in the cell are the electrons in the metal oxide conduction band, the iodide and the tri-iodide in the electrolyte solution, and the positively charge cations. The cations are used for charge neutrality. The inner electric field due to charge separation is calculated using Poisson’s equation [20].

Figure 5: Energy diagram for the modeled DSSC. Dye excitation (1), electron injection (2), dye relaxation (3), and relaxation (4) [21].
4.1 Derivation of the Continuity Equation

The continuity equation describes that the change in carrier density over time is due to the difference between incoming and outgoing flux carriers (in the differential element) plus the difference in the generation and recombination of electrons that take place within the differential element [22].

![Diagram of electron currents and possible generation and recombination processes](image)

Figure 6: Electron currents and possible generation and recombination processes [22].

This can be modeled as [22]:

$$\frac{dn(x,t)}{dt} Adx = \left( \frac{Jn(x)}{-e} - \frac{Jn(x + dx)}{-e} \right) A + \left( Gn(x,t) - Rn(x,t) \right) Adx \quad (1)$$
Where $e$ is the charge of an electron ($1.602 \times 10^{-19}$ coulombs), $J_n(x)$ is the current density, $n(x,t)$ is the carrier density, $A$ is the area, $G_n(x,t)$ is the generation rate and $R_n(x,t)$ is the recombination rate. Using Taylor series expansion:

$$J_n(x + dx) = J_n(x) + \frac{dJ_n(x)}{dx} dx$$  \hspace{1cm} (2)

Substituting (2) into (1) results in:

$$\frac{dn(x,t)}{dt} = \frac{1}{e} \frac{dJ_n(x,t)}{dx} + G_n(x,t) - R_n(x,t)$$  \hspace{1cm} (3)

For this analysis it is assumed steady state conditions prevail. As such, all the time dependent terms drop out and the equation reduces to:

$$\frac{1}{e} \frac{dJ}{dx} = G(x) - R(x)$$  \hspace{1cm} (4)

One of the main assumptions is that each absorbed photon generates one free electron in the metal oxide conduction band. Therefore the generation rate is obtained by summing up all the absorbed photons.

$$G(x) = \int_{200nm}^{800nm} \alpha(\lambda) \phi(\lambda) e^{-a(\lambda)x} d\lambda$$  \hspace{1cm} (5)

The incident photon flux density $\phi(\lambda)$ (photons/m$^3$) is given by the AM1.5 global solar spectrum [23]. The integration limits reflect the characteristics of the absorptivity of the dye. Since the dye only absorbs photons in the wavelength range from 200nm to 800nm these are the limits of integration (see figure 6).

4.2 Reduction/Oxidation Reactions

The complete reaction of iodide/triiodide redox electrolyte to replenish electrons to the holes in the dye molecules is a two-electron reaction [20].

$$3I^- \leftrightarrow I_3^- + 2e^-$$  \hspace{1cm} (6)
This total reaction is composed of a series of successive reactions [20]:

$$(I^- \leftrightarrow I + e^-) \times 2 \quad (7)$$

$$2I \leftrightarrow I_2 \quad (8)$$

$$I_2 + I^- \leftrightarrow I_3^- \quad (9)$$

Reactions (8) and (9) are fast chemical reactions in the order of picoseconds [20]. Now by applying the mass action law to (8) and (9) results in:

$$K_+I^2 = K_-I_2 \quad (10)$$

$$K_+I_2I^- = K_-I_3^- \quad (11)$$

Now substituting (10) into (11) and using an appropriate equilibrium constant $K_I$, the concentration of elementary iodine $n_I$ at any point $x$ in the effective medium is coupled with the concentrations of iodide ($n_{I^-}$) and triiodide ($n_{I_3^-}$) [20].

$$n_I(x) = K_I n_{I_3^-}(x) n_{I^-}^{-1}(x) \quad (12)$$

The charge transfer reaction between the metal oxide and the redox electrolyte is an elementary single-electron reaction [20].

$$I^- \leftrightarrow I + e^- \quad (13)$$

At equilibrium (no illumination), the forward reaction rate (rate constant $k_f$) is equal to the back reaction rate (rate constant $k_b$).

$$k_f \bar{n}_I^- = k_b \bar{n}_e \bar{n}_I \quad (14)$$

A deviation from equilibrium will be followed by a net electron flow through the metal oxide/redox electrolyte interface. Therefore the recombination rate can be the difference between backwards and forwards rates [20].

$$R_e = k_b n_e n_I - k_f n_I^- \quad (15)$$
Inserting \( k_f \) from (14) and using (12) the recombination rate of free electrons can be expressed as:

\[
R_e(x) = k_e \left\{ n_e \frac{\sqrt{n_{I_3}^-}}{n_{I^-}} - \frac{\sqrt{\bar{n}_{I_3}^-}}{\bar{n}_{I^-}^3 n_{I^-}} \right\} \tag{16}
\]

Where \( k \) is the relaxation constant, \( n \) is the particle densities (number of particles/m\(^3\)) for a given species and \( \bar{n} \) is the species density in the dark (no illumination).

Replacing (5) and (16) into (4) gives the continuity equation as:

\[
\frac{1}{e} \frac{dj}{dx} = \int_{200nm}^{800nm} \alpha(\lambda) \phi(\lambda) e^{-\alpha(\lambda)x} d\lambda - k_e \left\{ n_e \frac{\sqrt{n_{I_3}^-}}{n_{I^-}} - \frac{\sqrt{\bar{n}_{I_3}^-}}{\bar{n}_{I^-}^3 n_{I^-}} \right\} \tag{17}
\]

### 4.3 Kinetics and Electric Field

The transport equations are made up of a drift term (due to concentration gradients within the cell) and a mobility term (due to the electric field within the cell). For all four species involved (\( e, \Gamma, \Gamma_3, c \)) they are as follows:

\[
\frac{1}{e} j_e = D_e \frac{dn_e}{dx} + \mu_e n_e E \tag{18}
\]

\[
\frac{1}{e} j_{I^-} = D_{I^-} \frac{dn_{I^-}}{dx} + \mu_{I^-} n_{I^-} E \tag{19}
\]

\[
\frac{1}{e} j_{I_3^-} = D_{I_3^-} \frac{dn_{I_3^-}}{dx} + \mu_{I_3^-} n_{I_3^-} E \tag{20}
\]

\[
\frac{1}{e} j_c = D_c \frac{dn_c}{dx} + \mu_c n_c E \tag{21}
\]

Here \( D \) is the diffusion constant (m\(^2\)/s), \( \mu \) is the mobility constant (m\(^2\)/Vs), and \( E \) is the electric field (V/m). The diffusion constant (D) and mobilities are connected by Einstein’s relation [20]:

\[
D = \frac{kT}{e} \mu \tag{22}
\]
The electric field gradient is related to the charge-carrier densities by the Poisson equation:

\[
\frac{dE}{dx} = \frac{e}{\varepsilon_0 \varepsilon} \left[ n_c(x) - n_e(x) - n_{i-}(x) - n_{i3}^-(x) \right]
\]  \hspace{1cm} (23)

This equation is found by summing up the positive and negative charges within the cell. The dielectric constant \(\varepsilon\) describes the effective dielectric behavior of the pseudo-homogeneous medium. The permittivity of free space constant \(\varepsilon_0\) \((8.854 \ 187 \ 817... \times 10^{-12}\) farads per meter \((\text{F} \cdot \text{m}^{-1}))\) relates the units for electric charge to mechanical quantities such as length and force [20].
CHAPTER 5. IDEAL CASE

5.1 Derivation of Ideal Equation
For the ideal case it is assumed that there is no reflection of the solar flux by the TCO layer and ignore any of the reflection/transmission effects on the edges. It is also assumed that no relaxation (or recombination) takes place so the relaxation term is removed to express the ideal continuity equation:

$$\frac{1}{e} \frac{d j}{d x} = \int_{200nm}^{800nm} \alpha(\lambda) \phi(\lambda) e^{-\alpha(\lambda) x} d\lambda$$  \hspace{1cm} (24)

Now using ASTM G173-03 Reference Spectra (AM1.5) [23] spectral irradiance is used as a function of $\lambda$, where the irradiance is in watts per cm$^3$. Now using the photon energy equation:

$$E_{ph}(\lambda) = \frac{hc}{\lambda}$$  \hspace{1cm} (25)

The energy of the photons is a function of $\lambda$. The photon flux (number of photons/s/m$^2$) is found by dividing irradiance (W) by power.

$$\text{Photon flux } (\lambda) = \frac{\phi(\lambda)}{E_{ph}(\lambda)}$$  \hspace{1cm} (26)

Using the array of data for irradiance for each individual $\lambda$ the calculations were performed in Matlab to find the Photon Flux vs. Lambda relationship and a plot was made for 1 sun (Figure 7). One sun is the term used to define total radiation that reaches the earth’s surface from one sun. The dips and spikes are due to photon absorption by elements in the earth’s atmosphere. Different molecules absorb different wavelengths of light from the sun. O$_2$ and O$_3$ absorb wavelengths shorter than 300 nm and H$_2$O absorbs wavelengths above 700nm [24].
Now having the photon flux ($\phi(\lambda)$), absorptance coefficient ($\alpha$) as a function of $\lambda$ is derived. This data was taken from a plot in Chem. Mater. 2002, 14, 2527-2535 (Figure 8)[25]. A linear interpolation of the data was taken to derive the absorptance coefficient for a given $\lambda$.

A piece wise function was put into place for absorptivity ($\alpha(\lambda)$) to mimic the values in figure 8.

\[
\begin{align*}
\alpha(\lambda) &= 0 & 200 < \lambda < 350 & \quad (27.1) \\
\alpha(\lambda) &= .018\lambda & 350 < \lambda < 400 & \quad (27.2) \\
\alpha(\lambda) &= .00025\lambda + .8 & 400 < \lambda < 600 & \quad (27.3) \\
\alpha(\lambda) &= -.00475\lambda + 3.8 & 600 < \lambda < 800 & \quad (27.4)
\end{align*}
\]

Figure 7: Photon flux vs. wavelength for 1Sun.
Figure 8: Ratio of absorbed photons to incident photons. Dotted line indicates the absorbed photon ratio from back side illumination. Dashed line shows the ratio from forward side illumination. The solid line shows the total absorbed ratio [25].

Since the analysis is performed on the ideal case, it can be assumed that there is no reflectance throughout the cell. It is assumed that the incident flux vector is perpendicular to the face plate (figure 9). This assumption gives the highest possible view factor and therefore the highest possible photon flux through the cell. If the radiation was entering the cell at an angle then the view factor would decrease and there for the photon flux through the cell would decrease. Due to the fact that the active absorption region is only 10 micrometers reflections off the sides will have minimal effect on the net absorption of photons. Edge effects can be ignored throughout this study since the depth of the active region is only 10 micrometers [20].
Figure 9: Solar flux incoming perpendicular to TCO face plate (yellow). Purple is active metal oxide layer. Red is platinum layer.

Having the photon flux equation $\phi(\lambda)$ and the absorptivity equation $\alpha(\lambda)$ integration can now be performed over the active lambda domain ($300 < \lambda < 800$ nm) to find how many free charges are generated inside the cell. This data was put into Matlab in array form corresponding to each individual wavelength and integrated numerically using the trapz command which integrates the data using the trapezoidal rule. In the generation equation (24) there is an exponential $x$ dependence which models the decay of the photon flux as it passes deeper into the cell (outlined by red circle)[20]. This exponential decay follows the conservation of photons and represents the fact that once a photon is absorbed by an upper layer, it can no longer pass down to a sub layer of the cell. The photon flux will decrease exponentially as it travels deeper into the cell.
\[
\frac{1}{e} \frac{dj}{dx} = \int_{200nm}^{800nm} \alpha(\lambda) \phi(\lambda) e^{-\alpha(\lambda) x} d\lambda \quad (24)
\]

A plot for Photons Absorbed vs. Depth in Cell is obtained by inserting an x array (depth array) into the code varying x from 0 to $10^{-4}$ meter (which is a typical thickness of the active layer for these types of cells) and a step size (delta x) of $10^{-6}$ meter. Then by using the trapezoidal rule for every x value in the array, the plot is created (figure 10). Due to this small change in x it is hard to see the curve and the plot appears linear. The thickness of the absorption layer is small due to the diffusivity of the free electrons that are generated. This limit is 10 micrometers. If the active layer was longer than 10 micrometers then the free electrons would travel only their diffusion length (10 micrometers) and then relax. Upon relaxation the free electron will recombine with the electrolyte.

By integrating the curve from the depth of zero meters to 10 micrometers it is found that 1.2295x$10^{17}$ photons are absorbed by the cell. The incident incoming photon flux entering the cell is 1.7887x$10^{17}$. Therefore due to the absorptivity of the dye, there are only 68.74% of the photons absorbed by the cell. Therefore the limitations of the absorptance of the dye in the active layer reduce the performance of the cell by 31.26%. The results indicate that these cells are in need of a better performing dye that will have higher absorptivity for a wider range of wavelengths (limits of 200nm to 2500nm).
Figure 10: Photons absorbed as a function of depth in cell.
The photocurrent of the cell is found by first assuming that for every photon absorbed, a free electron is generated in the conduction band of the metal oxide. Now by multiplying the number of absorbed photons by the elementary charge (e) amperage is found. Since the number of absorbed photons has units of \( \text{m}^{-2} \cdot \text{s}^{-1} \) and the electric charge has units of (Coulombs) then by multiplying these together will result in amperes (Amps). Now by assuming that all these free electrons diffuse completely to the collection plate, the total current leaving the cell to the external circuit can be found. The total number of absorbed photons was found to be \( 1.22597 \times 10^{17} \). Multiplying the number of absorbed photons by the elementary charge, the current is found to be .01964 Amps. This is the photocurrent generated inside the cell.

The ideal continuity equation was used along with the following: photon flux reaching the surface from one sun, the absorptivity effects of the dye, reflection/transmission effects ignored, and the assumption that the photon flux was perpendicular to the surface of the cell. It was found that \( 1.22597 \times 10^{17} \) photons (68.74%) are absorbed by the cell resulting in 0.1964 Amps of electrical current that flows to the collection plate of the cell. The next section will address the flow electrons from the collection plate of the cell to the external circuit.

### 5.2 Equivalent Electrical Circuit

In order to determine the current voltage behavior of the cell under a load, an equivalent electrical circuit is presented (Figure 11) [26]. Notice in the figure the red circle around the internal diode. This internal diode effect is created by the electric field that is created by charge separation and it opposes and eventually balances out the diffusion of electrons within the cell [27]. The internal diode keeps the voltage across the cell from going to infinity as the charges separate and collect at the opposing plates. As the voltage increases due to charge collection, this diode allows more and more free electrons to recombine with holes. For the ideal case, the series
resistance (Rs) and shunt resistance (Rsh) are zero and the net current of the cell is the difference in the photocurrent (Iph) and the normal diode current (Id).

\[ I_{\text{ext}} = I_{\text{ph}} - I_d \quad (28) \]

The diode current is modeled using Shockley’s ideal diode equation.

\[ I_d = I_o \left( e^{\frac{e_0 V}{n k T}} - 1 \right) \quad (29) \]

Where \( I_o \) is the reverse saturation current for the diode, \( n \) is the ideality factor, \( k \) is the Boltzmann constant, \( V \) is the voltage across the diode, \( e_0 \) is the elementary charge, and \( T \) is absolute temperature. The reverse saturation current is material dependent for the diode and has typical values ranging from \( 10^{-12} \) to \( 10^{-15} \) amps. The ideality factor ranges from 1 to 2 depending on irregularities in the makeup of the diode [28]. The power curves (I-V curves) can now be modeled inserting equation (29) into (28) as:

\[ I_{\text{ext}} = I_{\text{ph}} - I_o \left( e^{\frac{e_0 V}{n k T}} - 1 \right) \quad (30) \]

In order to obtain the plots voltage is increased from zero (open voltage) to the point where the current is zero (short circuit).

The external current equation (equation 30) now can be utilized with the photocurrent \( I_{\text{ph}} \) that is found from section 5.1 to determine the power-voltage (P-V) and current-voltage (I-V) curves produced in the external circuit.

**5.3 Reverse Saturation Sensitivity Analysis (Io)**

The reverse saturation current for an ideal diode can be modeled by [29]:

\[ I_o = eA \left( \sqrt{\frac{D_p n_i^2}{t_p N_D}} + \sqrt{\frac{D_n n_i^2}{t_n N_A}} \right) \quad (31) \]
Figure 11: Simple equivalent circuit model for conventional pn-junction solar cells. This model consists of a constant current source ($I_{ph}$), a diode, series resistance ($R_s$), and shunt resistance ($R_{sh}$) [26].

Where $I_o$ is the reverse saturation current, $e$ is elementary charge, $A$ is the cross-sectional area, $D_{p,n}$ are the diffusion coefficients of holes and electrons, $N_{D,A}$ are the donor and acceptor concentrations at the n side and p side, $n_i$ is the intrinsic carrier concentration in the semiconductor material, and $t_{p,n}$ are the carrier lifetimes of holes and electrons [29]. The reverse saturation current is a parameter that keeps the voltage from going to infinity during open voltage conditions. It describes the reverse current or the recombination rate due to the diffusion of the minority carriers. All the parameters inside the parenthesis are material specific and depend on the fabrication and doping of the diode. It is also noted that the reverse saturation current ($I_o$) is dependent on the cross-sectional area of the diode ($A$). In order to minimize the reverse saturation current, the cross-sectional area of the diode has to be minimized. Dividing both sides of equation (31) by area will result in the reverse saturation current density. A plot (figure 12) was taken from Solar Energy Materials and Solar Cells [30] and it shows the reverse saturation current density function for a silicon based cell. There are reverse saturation current density values as low as $3.5 \times 10^{-13}$ (A/cm$^2$) and as high as $6.8 \times 10^{-12}$ (A/cm$^2$). If the cross-
sectional area of the cell can be reduced to 1mmx1mm, values for the reverse saturation current in the magnitude of $10^{-15}$ (Amp) can be achieved. Therefore depending on the fabrication limitations of the size of these devices, reverse saturation current values could be as low as $10^{-15}$ (Amp) or smaller [30].

![Figure 12: Reverse saturation current density as a function of polysilicon wafer thickness for different grain widths [30].](image)

For the first I-V curve (figure 13) the reverse saturation current is varied from $10^{-17}$ to $10^{-11}$. The other parameters are held constant; The ideality factor ($n$) is 1 and the temperature ($T$) is 300k. The output power is obtained by the product of voltage and current. Power curves are plotted in figure (14).

$$P = V \times I$$  \hspace{1cm} (32)

The maximum power for $I_0 = 10^{-11}$ (Amp) is 0.0089 watts and occurs where voltage is 0.48 volts and current is 0.0185 amps. When $I_0$ is lowered to $10^{-14}$, the max power is 0.0123 watts and
occurs where voltage is 0.65 volts and current is at 0.0189 amps. For the last case where Io is lowered to $10^{-17}$, max power is 0.0157 watts and occurs where voltage is 0.82 volts and current is 0.0191 amps. Therefore it can be concluded that for a lower reverse saturation current ($I_o$)($10^{-17}$ A), the cell will have a 76.4% increase in performance. Ideally, the best performance will come where $I_o$ approaches zero.

![Current vs Voltage](image)

Figure 13: Current-voltage curves for ideal DSSC. Ideality factor ($n$) = 1. Temperature ($T$) is 300k. Reverse saturation current ($I_o$) is 10-11, 10-14, and 10-17.
Figure 14: Current-voltage curves for ideal DSSC. Ideality factor \( n \) = 1. Temperature \( T \) is 300K. Reverse saturation current \( I_0 \) is \( 10^{-11}, 10^{-14}, \) and \( 10^{-17} \) Amperes.
5.4 Temperature Sensitivity Analysis
In this section the effects of temperature on the performance of the cell are assessed. As stated before, the diode prevents the voltage across the cell from going to infinity as more and more charges separate and collected at their respective plates. As temperature increases, the diode has less effect on recombining the free electrons and holes and thus promotes more collection of free electrons at the collection plate. Having more free electrons flowing from the collection plate to the external circuit will increase the external current and the overall performance of the cell. As shown in the ideal diode equation (29) when temperature increases the current through the diode decreases thus allowing a higher external current for a given voltage. Using equation (30) figures (15) and (16) are created to show the results for I-V and Power-Voltage curves for Temperatures of 275K, 300K, and 325K. For the temperature of 275K the max power of the cell is 0.0144 watts where voltage is 0.75 volts and current is 0.0191 amps. For the temperature of 325K, the performance of the cell increases by 17.4%. The max power increases to 0.0169 watts where voltage is 0.88 volts and current is 0.0193 amps. For the maximum temperature of 375K the performance increases 15.9% compared to the lowest temperature. The max power is 0.0196 watts where voltage is 1.02 volts and current is 0.0192 amps. These results show that as the temperature increases within the cell, the performance will also increase due to less recombining effect of the diode and more charges collecting at the collection plate and passing through the external circuit. The next section will address how Ideality factor plays a role in influencing the cells performance.
Figure 15: Current-voltage curves for ideal DSSC. Ideality factor (n) = 1. Temperature (T) is 275K, 325K, and 375K. Reverse saturation current (I_o) is 10^{-17}.
Figure 16: Power-voltage curves for ideal DSSC. Ideality factor (n)= 1. Temperature (T) is 275K, 325K, and 375K. Reverse saturation current (Io) is $10^{-17}$. 
5.5 Ideality Factor Sensitivity Analysis

As stated previously, there are second order effects so that the internal diode does not follow the ideal equation (equation 29). The ideality factor provides a way of addressing these effects [6].

The ideality factor (n) is a material dependent factor that ranges from 1 to 2 [27]. This factor represents the quality of the diode in fabrication [28]. In solid state p-n junction solar cells, the ideality factor can be influenced by the doping of the cell. In this analysis, the ideality factors of 1, 1.5 and 2 will be used (utilizing the upper limit, lower limit, and the median value). In practice, these values are used to curve fit a simulated result to an experimental result.

Figures (17) and (18) show that the performance of the cell increases when the ideality factor increases. The other parameters are held constant; The temperature (T) is 375k and the reverse saturation current (Io) is $10^{-17}$ (Amp). For the ideality factor of 1 (lower limit), the maximum power is .0196 watts where voltage is 1.03 volts and current is .0190 amps. When the ideality factor increases to 1.5, maximum power increases to .0294 watts where voltage is 1.54 volts and current is .0191 amps. The performance increases again when the ideality factor is raised to 2 (upper limit). The maximum power here is .0391 watts where voltage is 2.07 volts and current is .0189 amps.

Ideality factor clearly has a significant influence on the performance of the cell. The power increases from .0196 watts to .0391 watts when the ideality factor is increased to 2. Therefore by doubling the ideality factor, the performance of the cell doubles. It can be concluded that by manufacturing these cells to have a better ideality factor (no flaws in the crystal structures and high doping concentrations), the performance will be optimum.
Figure 17: Current-voltage curves for ideal DSSC. Ideality factor (n) = 1, 1.5, and 2. Temperature (T) is 375K. Reverse saturation current (Io) is $10^{-17}$ A.
Figure 18: Power-voltage curves for ideal DSSC. Ideality factor (n) = 1, 1.5, and 2. Temperature (T) is 375K. Reverse saturation current (Io) is $10^{-17}$ A.
5.6 Temperature Analysis on Ideal Cell
It was found that for best performance, the ideality factor (n) should be 2 (upper limit) and the reverse saturation current (Io) should be $10^{-17}$ amps and temperature should be at its upper limit. It is hard to determine this upper limit for temperature due to phase stability issues. The active light absorbing dye does not limit the functioning temperature since dyes have been found to maintain stability for 20 years of active illumination at temperatures as high as 550K [13]. However, due to the fact that the cell has a liquid electrolyte it is necessary to keep the temperature below the boiling point of the liquid. The temperature limit would have to be bound by the boiling point for Iodide/Triiodide solution which is around 375K [31]. If the temperature is too high (above 375K) the liquid will begin to change from a liquid phase to a gas phase. The change in phases causes internal pressure that will damage the seals in the cell. One alternative to correct the sealing problem at higher temperatures is the replacement of the redox electrolyte by a solid p-type semiconductor. The solid layer would penetrate the nanocrystalline metal oxide structure by a method of spin coating while in a liquid phase. This would permit the charge neutralization of dye molecules after electron injection by the hole transport properties of the p-type semiconductor [13]. Using a solid layer would fix the internal stresses caused by phase changes in the liquid electrolyte. The only downfall to this approach is that it is not immediately evident that an interpenetrating network of two conducting solids can so easily be established that an immobilized molecule at their interface can exchange charge carriers with both semiconductors but researchers are looking into this and results seem promising [13]. By changing the electrolyte from a liquid to solid phase this would boost the upper limit of the operating temperatures to the point in which the organic dyes become unstable (550K) [13].
Figures (19) and (20) show the performance curves for the “ideal” cell with optimum parameter values (n=2, Io = 10^{-17}) and temperature will change from 275K to the upper limit of 375K. For the lowest temperature (275K) the maximum power output is 0.0287 watts where voltage is 1.51 volts and current is 0.0190 amps. When the temperature is raised to its limit (375K) the maximum power raises to 0.0391 watts where voltage is 2.06 volts and current is 0.0190 amps. This is a 36.2% increase in performance from the low temperature limit to the high temperature limit. With the power curves established for an ideal cell, the efficiency analysis can now be conducted and the efficiency curves can be generated.

Figure 19: Current-voltage curves for ideal DSSC. Ideality factor (n) = 2. Temperature (T) is 275K, 325K, and 375K. Reverse saturation current (Io) is 10^{-17} A.
Figure 20: Power-voltage curves for ideal DSSC. Ideality factor (n) = 2. Temperature (T) is 275K, 325K, and 375K. Reverse saturation current (Io) is $10^{-17}$ A.
5.7 Efficiency Analysis of DSSC
The efficiency of the cell is the ratio between the maximum power and the incident light power.

\[ \eta = \frac{P_{\text{max}}}{P_{\text{in}}} = \frac{P_{\text{max}}}{A \cdot \phi} \]  

\( P_{\text{max}} \) (Watts) is the maximum power achieved by the P-V curves. The area of the cell (A) is 1 cm\(^2\) and the incident light power is .1 watts/cm\(^2\). Figure (21) shows how temperature influences the efficiency of the “ideal” cell with optimum parameters. Temperature again is varied from 275K to 375K. For the lower limit temperature of 275K the efficiency of this ideal cell is 27\%. When the temperature is raised to the upper limit of 375K the efficiency increases to 39\%. It can be concluded (figure 22.1) that the efficiency limit for an idealistic DSSC is 39\%.

William Shockley and Hans J. Queisser completed a study on the p-n junction solid state devices [32]. A detailed balance limit of efficiency was conducted where they found the ideal efficiency of the p-n junction to be 30\% (see figure 22.1) [32]. In comparison, the DSSC has a higher efficiency limit than that of the p-n junction (see figure 22.2). Now that maximum efficiency of the idealized dye sensitized solar cell has been established, the effects of reflectivity are investigated.
Figure 21: Efficiency-voltage curves for ideal DSSC. Ideality factor \( n \) = 2. Temperature \( T \) is 275K, 325K, and 375K. Reverse saturation current \( I_0 \) is \( 10^{-17} \) A.
Figure 22: Comparison of the “semi-empirical limit” of efficiency of p-n junction solar cell with “detailed balance limit” [32]. Figure 22.1 (Left) Represents the best experiment efficiency to date for p-n junction cells [32]. Figure 22.2 (Right) Efficiency limit of DSSC where temperature (T) = 375K, ideality factor (n) = 2, and reverse saturation current (Io) = 10^-17.
CHAPTER 6. REFLECTIVITY

Reflection is a phenomenon that occurs when incident light reaches an interface consisting of two homogeneous optical media [33]. Conservation of energy dictates that the incident light results in absorption, transmission, and/or reflection [34]. Figure (23) illustrates this phenomenon. Reflection is the portion of light that never passes through the surface of the second medium. It is the light that is now traveling away from the surface of the second medium. For any type of solar cell there is a need to reduce the total reflectance of light from the cell. This will allow the maximum amount of light to enter to the active region of the cell and thus increase the cell’s performance. The purpose of this section is to discuss the reflectivity effects and introduce a scheme to reduce the overall reflectivity of the dye sensitized solar cell.

![Diagram of light interaction](image)

Figure 23: Incident light resulting in absorption, reflection, and transmission.
6.1 Reflectivity Effects
For an optically smooth surface the law of reflection states: The reflected ray lies in the plane of incidence, and the angle of reflection (j) equals the angle of incidence (i) [33]. Reflectivity effects on the surface of the transparent conductive oxide (TCO glass) layer at the top of the cell are discussed in this section. Ideally the TCO layer transmits all the light to the active region of the cell.

A transparent medium is a medium which has the property of transmitting rays of light in such a way that the human eye may see through the medium distinctly [35]. When light travels from one transparent medium to another some of the light is reflected off of the surface and some of the light is transmitted through the surface (Figure 24) [36]. The angle measured from normal at which the incident path contacts the surface is known as the angle of incidence (i). The angles at which the light is reflected and transmitted are known as the angle of reflectance (j) and refraction (r) respectively [34]. Most transparent media that light passes through have a refractive index (n). The speed of light propagation (c) through the medium divided by the refractive index (n) is referred to as the phase velocity (V_{ph}) [37].

\[ V_{ph} = \frac{c}{n} \]  

(34)

Refractive index is also wavelength dependent. This study will review the refractive indices for different types of material such as MgF\(_2\), NaF, and CaF\(_2\). The first material studied is MgF\(_2\), and the refractive index can be modeled using the Lorentz-Lorenz formulae [38]:

\[ n_0 = 1.36957 + \frac{(3.5821)(10^{-3})}{(\lambda - 0.14947)} \]  

(35)

\[ n_e = 1.381 + \frac{(3.7415)(10^{-3})}{(\lambda - 0.14947)} \]  

(36)
Figure 24: Reflection and refraction of light between two adjoining media [36].
Where \( n_0 \) models the ordinary rays and \( n_e \) models the extraordinary rays. When a single ray of light enters a transparent medium it is split into two rays each traveling in a different direction. One ray (extraordinary) is bent, or refracted, at an angle as it travels through the medium. The other ray (ordinary) passes through the medium unchanged [39]. The refractive index for the amorphous phase is the average of these two indices [38]:

\[
n = n(\lambda) = \frac{1}{2}(n_0 + n_e)
\]  

(37)

Using equations (35), (36), and (37) and selecting a wavelength \( \lambda \) in the middle of the absorption spectrum (500nm) the refractive index for MgF\(_2\) is valued at 1.35 (figure 25). For comparison the refractive index vs. wavelength for sodium fluoride (NaF), calcium fluoride (CaF\(_2\)), and magnesium fluoride (MgF\(_2\)) are plotted (figure 26) [40]. For 200nm the index of refraction for MgF\(_2\) is 1.350768743 and for 800nm the index of refraction is 1.350768644. The equations show that there is only .0000073% change in the index of refraction for MgF\(_2\) from 200nm to 800nm. The refractive index for the TCO (zinc oxide) can be modeled as (figure 27) [41]:

\[
n_{TCO}(\lambda) = -6.555x10^{-11}\lambda^4 + 1.472x10^{-7}\lambda^3 - 1.173x10^{-4}\lambda^2 + .0381\lambda - 1.971
\]  

(38)

The refractive indexes of the two media and the angles of incidence and refraction are related by Snell’s law [34]:

\[
\frac{\sin r}{\sin i} = \frac{n_1}{n_2}
\]  

(39)

Here \( n_1 \) is the refraction index of medium 1, \( n_2 \) is the refraction index of medium 2, \( i \) is the angle of incidence, and \( r \) is the angle of refraction. With Snell’s law established, the reflectivity effects of an uncoated surface can be investigated.
Figure 25: Refractive index vs. wavelength for MgF$_2$
Figure 26: Refractive index vs. wavelength for MgF$_2$ (blue line), NaF (red line), and CaF$_2$ (green line).
Figure 27: Refractive index as a function of wavelength for TCO (glass) substrate.
6.2 Reflectivity of Uncoated Surface

The reflection of radiation by a transparent medium (such as the TCO layer) is modeled by the Fresnel’s equation \[34]:

\[
R = \frac{1}{2} \frac{\tan^2(i - r)}{1 + \tan^2(i + r)} + \frac{\sin^2(i - r)}{\sin^2(i + r)} \quad (40)
\]

Using equation (39), the index of refraction values for air (1.0), and the TCO layer, the angle of refraction as a function of the angle of incidence is plotted, see Figure 28. The angle of refraction is never equal to the angle of incidence with the exception of when the angles of incidence and refraction are zero. For normal incidence \(i = 0\) and medium 1 being air \(n_1 = 1\) and using equations (39) and (40), the reflectivity can be expressed as \[42]:

\[
R = \left(\frac{n_2 - 1}{n_2 + 1}\right)^2 \quad (41)
\]

Since the reflectivity changes with respect to wavelength it is necessary to define the average reflectivity to see how the reflectivity is valued as a function of all the wavelengths in the useful spectrum (200m-800nm):

\[
R_{avg} = \frac{\sum_{\lambda=200}^{800} R(\lambda)}{600} \quad (42)
\]

Using equation (42) the average reflectivity as a function of the angle of incidence is plotted (figure 29). Using equation (41) the reflectivity is found to be 12.53\% which is supportive of the value given in the introduction as 10\% reflectance by the TCO layer. This result is also seen in figure (7) where the angle of incidence \(i\) is zero. It may be seen from figure 7 that reflection is minimum when the angle of incidence of the incoming radiation is normal to the surface and reflection increases as the angle of incidence increases. Having established the governing equations and their resultant plots for reflectivity of an uncoated surface, the next topic to investigate is the reflectivity of coated surfaces.
Figure 28: Relationship between incident and refracted angles for a TCO (glass) substrate.
Figure 29: Average reflectivity as a function of incident angle for an uncoated TCO substrate.
6.3 Thin Film Coating

In order to significantly reduce the reflection of the TCO layer a thin coating is needed (figure 30). A thin film is defined as a film that involves deposition of individual molecules or atoms. The film has a thickness ranging from fractions of a nanometer to several micrometers. A Thick film involves deposition of particles. Therefore painting is a thick film technology and evaporation deposition is a thin film technology [43]. Then films are used widely in applications involving optics, chemistry, mechanics, magnetics, and electricity. This study will focus on the optical properties of thin films and how they are used to change the reflective properties of a substrate. The same principles apply to mirrors, compact disks, and antireflective lenses.

For a coated surface, the minimum reflectance where incident light angle is normal to the surface is given by [44]:

\[ R = \left( \frac{n_c^2 - n_1 n_2}{n_c^2 + n_1 n_2} \right)^2 \]  

(43)

Where \( n_c \) is the refractive index of the coating, \( n_1 \) is the refractive index of the medium (air), and \( n_2 \) is the refractive index of the substrate (TCO).

From equation (43) it can be seen that for the reflectance to be zero, using the refractive index of air \( n_1=1 \), the following must be true [44]:

\[ n_c = \sqrt{n_2} \]  

(44)

Knowing the refractive index of the TCO substrate, the average refractive index of the thin film metal oxide coating can be calculated. The average index of refraction for the TCO (200nm-800nm) is 1.97, and using equation (44) the index of refraction for the coating should be near 1.40 thus giving MgF2 the favorable of the three coatings investigated. Also MgF2 is the most common antireflective coating used today in optics. Another major benefit to using this coating is the low cost production of this coating by sol-gel techniques such as spin or dip coating [40].
Another important requirement is the film thickness (h). Notice in figure (30), there are reflections at both the air/film interface and the film/substrate interface. The reflective waves may cause interference with each other [42].

Figure (30): Reflection and transmission of light due to thin film coating.
6.3.1 Constructive/Destructive Interference
Interference results in the two waves combining into a wave that composed of the sum of their respective phases. There are two types of interference these waves can experience. The first is constructive interference, where the phases of the waves are similar and when the waves interfere the resultant wave has higher intensity than the original waves figure (31) [42]. This intensity is the sum of the intensities of the phases. The other type of interference is destructive interference where the phases of the waves when combined result in a wave with lower intensity [42].

The objective is to obtain an optical thickness of the coating such that the reflected waves are 180 degrees out of phase with each other. This will cause a resulting wave with no intensity. The conservation of energy then states that the energy lost by the combining of the two waves will appear as enhanced intensity by the transmitted wave [42]. The film thickness should be exactly ¼ the wavelength of the incident light in order to achieve no reflectance. By having a ¼ wavelength thickness, the phases of both reflected waves will be 180 degrees out of phase thus resulting in destructive interference figure(32) [38]. In order to establish which wavelength to use, constrained optimization will be performed to find which ¼ wavelength value gives the lowest reflectance. The other wavelengths will still benefit from this thickness since there reflective wave phases will still be out of phase and destructive interference will still take place. The only difference is that the reflected wave phases will not be out of phase by 180 degrees but will be out of phase enough to result in a lower intensity wave being reflected.
Figure 31: Constructive and destructive interference [42].
Figure 32: Destructive interference due to 1/4 wavelength thickness coating on a glass substrate [38].
Using Snell’s law (equation 39) resultant transmitted wave angle and the air/coating interface in terms of the refraction index of the air, refraction index of the coating, and the incident angle.

The same process is followed for solving for the transmitted wave angle at the coating/substrate interface.

\[ \theta_2 = \arcsin \left( \frac{n_1 \sin \theta_1}{n_2} \right) \]  \hspace{1cm} (45)

\[ \theta_3 = \arcsin \left( \frac{n_1 \sin \theta_1}{n_3} \right) \]  \hspace{1cm} (46)

Now Fresnel’s laws can be used to depict the reflection coefficients for both parallel (p) and perpendicular (s) components of the polarized radiation (defined in figure 33) [34] [45]:

\[ r_{12p} = \frac{n_2 \cos \theta_1 - n_1 \cos \theta_2}{n_2 \cos \theta_1 + n_1 \cos \theta_2} \]  \hspace{1cm} (47)

\[ r_{23p} = \frac{n_3 \cos \theta_2 - n_2 \cos \theta_3}{n_3 \cos \theta_2 + n_2 \cos \theta_3} \]  \hspace{1cm} (48)

\[ r_{12s} = \frac{n_1 \cos \theta_1 - n_2 \cos \theta_2}{n_1 \cos \theta_1 + n_2 \cos \theta_2} \]  \hspace{1cm} (49)

\[ r_{23s} = \frac{n_2 \cos \theta_2 - n_3 \cos \theta_3}{n_2 \cos \theta_2 + n_3 \cos \theta_3} \]  \hspace{1cm} (50)

The subscripts indicate the interface and the type of polarization. For example, \( r_{12p} \) gives the formula for the amplitude of reflectance for the parallel polarization at the air/coating interface.

The phase difference between the reflected waves from the air/coating interface and the coating/substrate interface can be modeled as [38]:

\[ \beta = \frac{2\pi}{\lambda} n_2 h \cos \theta_2 \]  \hspace{1cm} (51)
Figure 33: Parallel and perpendicular polarizations of incident light [45].
Where \((\beta)\) is the phase difference of the reflected waves, \((n_2)\) is the refractive index of the coating, \((h)\) is the thickness of the coating, and \((\theta_2)\) is the angle of transmission at the air/coating interface. Using an identity for reflection coefficient [46]:

\[
r_{13} = \frac{r_{12} + r_{23}}{1 + r_{12}r_{23}}
\]

(52)

Where \((r_{13})\) is the total reflection coefficient resulting from both interfaces. Thus, the net reflectance for the coated surface, accounting for both interfaces and the phase differences between the reflected waves, can be modeled as [38]:

\[
R_p = (r_{13p})^2 = \frac{r_{12p}^2 + r_{23p}^2 + 2r_{12p}r_{23p}\cos(2\beta)}{1 + r_{12p}r_{23p}^2 + 2r_{12p}r_{23p}\cos(2\beta)}
\]

(53)

\[
R_s = (r_{13s})^2 = \frac{r_{12s}^2 + r_{23s}^2 + 2r_{12s}r_{23s}\cos(2\beta)}{1 + r_{12s}r_{23s}^2 + 2r_{12s}r_{23s}\cos(2\beta)}
\]

(54)

Where \((R_p)\) and \((R_s)\) are the total reflectance of the parallel and perpendicular components of the radiation, and the net reflectance can be summarized as [38]:

\[
R = \frac{1}{2} \left( R_p + R_s \right)
\]

(55)

Using equations (45)-(55) reflectivity \((R)\) as a function of incident angle \((i)\), wavelength of light \((\lambda)\), and thickness of coating \((h)\) can be plotted (figures 34 and 35). In order to establish how the thickness affects the total incoming light flux into the solar cell, the next section will establish an average reflectivity for wavelengths in our active region.

**6.3.2 Film Thickness Sensitivity Analysis**

This section investigates how the film thickness \((h)\) of a coating influenced the average reflectivity of the TCO substrate. In order to find the optimum coating thickness \((h)\), the average reflectance for the total spectrum of light that is used by the dye sensitized solar cell (200nm-
800nm) is established. This was possible by summing up all the curves for wavelengths of 200nm to 800nm and dividing by 600.

\[ R_{\text{avg}}(h) = \frac{\sum_{\lambda=200}^{800} R(\lambda, h)}{600} \]  

This would give the average reflectivity over all wavelengths for a specific coating thickness (h).

Using equation 56, curves are plotted for coating thicknesses ranging from 50nm to 200nm. These limits correspond to the quarter wavelength limits of our cell (200nm to 800nm). For the purpose of clarity figure 36 only shows the average reflectivity for 50nm, 87nm, 125nm, 162nm, and 200nm. I found the lowest average reflectance curve was produced when the thickness was 87nm (blue curve in figure 36). This curve shows at a zero angle of incidence the average reflectivity is 0.05 which is 100% lower than the reflectance value of 0.1 that was used in the ideal study. To further establish an optimum film thickness that results in an absolute minimum average reflectance, optimization will have to be conducted.

6.3.3 Optimization Analysis
In this section the film thickness coating (h) will be optimized by using numerical schemes for unconstrained optimization. For the dye sensitized solar cell there is a flux of useable light ranging from 200 nm to 800nm coming into the cell. Therefore it is necessary to optimize the average reflectance ranging for the wavelengths (200 nm – 800 nm). The reflectivity given by equation 55 is a function of wavelength (\(\lambda\)), angle of incidence (i), and film thickness (h):

\[ R = \frac{1}{2} \left( R_p + R_s \right) \]  

(55)
Figure 34: Reflectivity as a function of wavelength. The incident angle (i) is zero. The film thickness of the coating (h) is valued as: 50nm (red), 87nm (blue), 125nm (black), 162nm (green), and 200nm (purple).
Figure 35: Reflectivity as a function of wavelength. The incident angle (i) is 45 degrees. The values of film thickness (h) are: 50nm (red), 87nm (blue), 125nm (black), 162nm (green), and 200nm (purple).
Figure 36: Average reflectivity as a function of incident angle. The film thickness (h) is 50nm (red), 87nm (blue), 125nm (black), 162nm (green), and 200nm (purple).
Typically in optimization schemes, the total differential would be utilized with the reflectivity function. The solution would provide a single wavelength and coating thickness value that results in the absolute minimum reflectance. In this study we have a constant flux of usable light ranging from 200nm to 800nm. Optimizing the coating thickness to one specific wavelength is not favorable in this study. Therefore it is necessary to use an average reflectivity equation that expresses how the film thickness affects the total incoming light flux. Using optimization schemes on this equation will optimize the film thickness for the complete light flux rather than for just a single wavelength of light. We will constrain the angle of incoming angle of incidence (i) to zero and use the average reflectivity function:

\[
R_{\text{avg}}(h) = \frac{\sum_{\lambda=200}^{\lambda=800} R(\lambda, h)}{600}
\]  

(56)

The average reflectivity with respect to film thickness (figure 37) is plotted for thicknesses ranging from 10 nm to 1750 nm. It can be seen that the curve is oscillating and that there are multiple minimums that exist. The absolute minimum is found numerically by setting the derivative (with respect to film thickness) of average reflectivity to zero.

\[
\frac{d(R_{\text{avg}}(h))}{d(h)} = 0
\]  

(57)

The absolute minimum can be seen to exist between 10 nm and 200 nm. Figure 38 reduces the range to see the absolute minimum more clearly. It can be seen that there is an absolute minimum average reflectivity that exists between the film thicknesses of 10 nm and 100 nm. Now by using the Matlab differentiation command (diff) I plotted the derivative of the average reflectivity and found the absolute minimum to be where the derivative equals zero (71 nm) (figure 39). Therefore it can be concluded that a 71 nm thick coating on a TCO substrate will promote the lowest amount of reflectivity for the dye sensitized solar cell.
Figure 37: Average reflectivity as a function of the film thickness of the coating ranging from 10 nm to 1750 nm.
Figure 38: Average reflectivity as a function of film thickness of the coating ranging from 10 nm to 500 nm.
Figure 39: Derivative of average reflectivity as a function of film thickness (h). Film thickness ranges from 50 nm to 150 nm (shows absolute minimum).
Now the reflectivity of the uncoated TCO substrate can be compared to the reflectivity of the 71nm coated TCO substrate. By setting the incident angle to zero and the film thickness to 71nm it can be seen how the reflectance changes with respect to wavelength for the uncoated and coated surfaces (figure 40). The coated surface (red) has lower reflectivity than the uncoated surface on the interval of 200nm-800nm. More importantly the reflectivity is significantly lower on the ranges of 400nm-600nm. In this region the absorptivity of the incident light by the dye is highest (90%). Comparing the average reflectivity as a function of incident angle (figure 41), it is seen that an average of 10% decrease in reflectivity throughout the incident angles on the span of zero degrees to fifty degrees. It is also seen a decrease in reflectivity throughout the remaining span of fifty to ninety degrees. Thus it can be concluded that for a coating of MgF2 of thickness of 71 nm on a TCO substrate will result in a 10% decrease in reflectivity where the incident angle is zero degrees. The next thing to consider is how this decrease in reflectivity influences the overall performance of the dye sensitized solar cell.

In order to see how the dye sensitized solar cell’s performance is influenced by the decrease in reflectivity the incoming light flux into the cell has to be adjusted. This is possible by adjusting the original photon flux vector that is a function of reflectivity and wavelength. With the original photon flux values (uncoated surface) and the new photon flux values (coated surface) a plot is created to show current as a function of voltage for both an uncoated and coated cell (figure 42). A plot is also created of power and efficiency as a function of voltage for both uncoated and coated cells (figures 43 & 44). These plots use average parameter values of a 1 cm x 1 cm cell to show typical results instead of idealized results.
Figure 40: Reflectivity as a function of wavelength. Incident angle (i) is zero degrees. The uncoated TCO substrate (blue) and the 71nm coated TCO substrate (red).
Figure 41: Average reflectivity as a function of the incident angle (i). The uncoated TCO substrate (blue) and the 71 nm thick coated TCO substrate (red).
Figure 42: Current as a function of voltage for uncoated TCO substrate (blue) and coated TCO substrate (red) where film thickness (h) is 71nm.
Figure 43: Power as a function of voltage for uncoated TCO substrate (blue) and coated TCO substrate (red) where film thickness (h) is 71nm
Figure 44: Efficiency as a function of voltage for uncoated TCO substrate (blue) and coated TCO substrate (red) where film thickness (h) is 71nm.
CHAPTER 7. FULL MODEL ANALYSIS OF DYE SENSITIZED CELL

This section will investigate the full electrical model of the dye sensitized solar cell and the results will be compared to the ideal results along with other experimental results. There are two papers that have solved the full model in detail. The first paper was completed by Jorg Ferber, Rolf Stangl, and Joachim Luther in Freiburg Germany in 1997 [20] and the second paper by Li Sin Lai at the University of Hong Kong in 2009 [47]. Results from both papers will be used for comparing the ideal results and other experimental results.

In order for the full model to be solved, there needs to be boundary conditions that coincide with the six differential equations (17),(18),(19),(20),(21), and (23). The dye sensitized solar cell model assumes particle conservation of cations and of the iodine nuclei. Denoting initial concentrations by an upper index “0”, this yields two integral boundary conditions [20]:

\[
\int_0^d n_c \, dx = \int_0^d n_{c0} \, dx = n_{c0} d \quad (58)
\]

\[
\int_0^d (n_{i_3^+} + \frac{1}{3} n_{i^-}) \, dx = \left( n_{i_3^+0} + \frac{1}{3} n_{i^-0} \right) d \quad (59)
\]

In equation (58) \(d\) is the thickness of the active region, \(c\) represents cations, and \(0\) represents initial concentration before illumination. This equation represents that at any time during illumination, the total number of cations within the active region is equal to the total number of cations before illumination hence particle conservation. In equation (59) \(i_3^-\) is triiodide and \(i^-\) is iodide. This equation represents that the total number of iodide and triiodide particles at any given time during illumination is equal to the total number of iodide and triiodide particles before illumination [20].

From the reaction scheme of equation (6), it follows that the generation of two electrons in the \(\text{TiO}_2\) conduction band is always coupled with the annihilation of three iodide ions [20]:
\[ \int_0^d \left( \frac{1}{2} n_e + \frac{1}{3} n_i^- \right) \, dx = \left( \frac{1}{2} n_e^0 + \frac{1}{3} n_i^0^- \right) d \]  \quad (60)

It is assumed that the macroscopic electric field only exist in the region of charge separation therefore at the boundaries \((x=0, x=d)\) is negligible \([20]\).

\[ E(d) = E(0) = 0 \]  \quad (61)

It is also assumed that there is no electrical contact between the TiO\(_2\) and the Platonized TCO, therefore the current density of the electrons in the TiO\(_2\) conduction band at \(x = d\) is equal to zero \([20]\).

\[ j_e(d) = 0 \]  \quad (62)

The final boundary condition is a function that relates the particle concentrations and the boundaries to the external resistance of the external circuit. The derivation is quite cumbersome and exists in reference \([20]\).

\[ f(n_i^-(d), n_i^0^-(d), n_e(0), J_e(0); R_{ext}) = 0 \]  \quad (63)

The method for solving the six coupled differential boundary conditions (17),(18),(19),(20),(21), and (23) with the appropriate boundary conditions is described in detail in appendix A.

In Jorge Ferber’s paper the structure of the cell is exactly the same as the structure used in the previous ideal study. For the full model the following assumptions are made \([20]\):

1. The only optical loss is due to reflection of irradiation from the TCO plate at the top surface of the cell. The amount of irradiation reflected from this plate is 11\%.

2. The model represents the functionality of the cell at steady state.

3. Conservation of particles is applied

4. Photon-to-electron conversion efficiency is 100\%.

The base case parameters used in this first study are listed in table 1 \([20]\).
Table 1: Base parameters used for modeling the DSC. AM1.5 radiation is incident from the front and corrected for 11% loss by reflection and absorption of the conducting glass substrate [20].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Base case numerical value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron relaxation rate constant</td>
<td>$k_e$</td>
<td>$10^4 \text{s}^{-1}$</td>
</tr>
<tr>
<td>Electron mobility</td>
<td>$\mu_e$</td>
<td>0.3 cm$^2$/Vs</td>
</tr>
<tr>
<td>Iodide diffusion constant</td>
<td>$D_{\text{Red}}$</td>
<td>$8.5 \times 10^{-6} \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Triiodide diffusion constant</td>
<td>$D_{\text{Ox}}$</td>
<td>$8.5 \times 10^{-6} \text{ cm}^2/\text{s}$</td>
</tr>
<tr>
<td>Initial concentration of iodide</td>
<td>$C_{\text{Red}}^0$</td>
<td>0.45 M</td>
</tr>
<tr>
<td>Initial concentration of triiodide</td>
<td>$C_{\text{Ox}}^0$</td>
<td>0.05 M</td>
</tr>
<tr>
<td>Effective mass of electron</td>
<td>$m_e^e$</td>
<td>5.6 $m_e$</td>
</tr>
<tr>
<td>Exchange current density of the platinum electrode</td>
<td>$j_0$</td>
<td>0.1 A/cm$^2$</td>
</tr>
<tr>
<td>Symmetry parameter</td>
<td>$\beta$</td>
<td>0.78</td>
</tr>
<tr>
<td>Effective relative dielectric constant</td>
<td>$\varepsilon$</td>
<td>50</td>
</tr>
<tr>
<td>Difference of conduction band and standard</td>
<td>$E_{\text{CB}} - E_{\text{Redox}}^\alpha$</td>
<td>0.93 eV</td>
</tr>
<tr>
<td>Electrolyte redox energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sheet resistance of coated glass substrate</td>
<td>$R_{\text{TCO}}$</td>
<td>6 $\Omega/\square$</td>
</tr>
<tr>
<td>Shunt resistance</td>
<td>$R_p$</td>
<td>10 k$\Omega$</td>
</tr>
<tr>
<td>Incident spectral photon flux density</td>
<td>$\Phi(\lambda)$</td>
<td>$\pm$ AM1.5 global solar spectrum, 89 mW/cm$^2$</td>
</tr>
<tr>
<td>Thickness of inner cell</td>
<td>$d$</td>
<td>10 $\mu$m</td>
</tr>
<tr>
<td>Cell area</td>
<td>$A$</td>
<td>1 cm$^2$</td>
</tr>
<tr>
<td>Porosity</td>
<td>$p$</td>
<td>0.5</td>
</tr>
<tr>
<td>Roughness factor</td>
<td>$R_f$</td>
<td>1000</td>
</tr>
</tbody>
</table>

Using the parameters of Table 1 the current-voltage curve was made (figure 45.1) and is compared to the ideal case (figure 45.2). The only optical loss considered in the full model evaluation is the 11% loss due to reflection by the TCO layer at the top surface of the cell [20].

The results obtained by Ferber were stated to be a little high compared to typical experimental results due to the following aspects [20]:

1. Optical loss mechanisms as absorption by triiodide have not been taken into account.
2. The real photon-to electron conversion efficiency is not equal to 100%, as assumed in this model.
3. The electron motilities used may be too high as indicated by reference [48]. Despite this, higher current densities than the calculated 15mA/cm$^2$ have already been observed in experiments [49].
In comparison to the ideal case, the full model has a maximum power value of .00775 watts where current is .0155 amp and voltage is .5 volts for a module of area 1 cm$^2$. The ideal case shows a maximum power value of .0199 watts where current is .0199 amp and voltage is 1 volt for a module of the same area. This shows that the ideal cell is 257% more power output compared to the real performance of a dye sensitized solar cell. Obviously 11% of this power loss is due to the 11% of the incoming solar flux that is reflected by the TCO layer. The other major contribution to the loss of power is the diffusivity of the free electrons and the relaxation rate constant. In the ideal case it was assumed that all the free electrons diffused completely to the collection plate and recombination was neglected. In the full model, diffusivity and relaxation rates apply. The active region in both cases was compromised of a nanoparticulate film of thickness 10 micrometers. This film was made up of TiO$_2$ nanoparticles connected in a three dimensional network [20]. Slow electron transport is the main limiting factor in the performance of nanoparticle based dye sensitized cells, incorporating highly-ordered TiO$_2$ nanotube arrays is a promising approach to improve the cell’s performance [47].

7.1 Incorporating Nanotubes
The nanotube arrays, aligning in perpendicular orientation to the collection plate, possess a high surface-to-volume ratio that facilitates rapid charge percolation pathway and high absorption of the ruthenium based dye [47]. The charge-collection efficiency is improved by promoting faster transport and slower recombination [47]. The dye molecules are absorbed on the interior and exterior walls of the nanotubes [47]. In the second paper the full model was evaluated for a TiO$_2$ nanotube based cell. Figure (46) [50] and figure (47) [51] show the differences in makeup between nanoparticle and nanotubular based cells.
Figure 45.1: (Left) Current-Voltage curve of the full modeled DSSC, calculated with the “base case” parameters of Table 1. Cell area 1 cm$^2$ [20].

Figure 45.2: (Right) Current-voltage curve for ideal DSSC. Temperature is 375K. Ideality factor is 1. Reverse saturation current is $10^{-17}$ amp.
In order to compare the results from this paper to the ideal case, the ideal results for a cell of area .785 cm² needs to be adjusted to have the same area as this nanotube based dye sensitized solar cell. The current-voltage curve for the nanotube based dye sensitized solar cell (using table 2 parameters) is displayed in figure (48.1) [47][52]. The new ideal current-voltage curve for the .785 cm² dye sensitized solar cell is displayed in figure (48.2). In comparison, the ideal dye sensitized solar cell has higher current and voltage values throughout its curve. The maximum power of the ideal dye sensitized solar cell is 0.015 watts. The maximum power of the nanotubular cell is 0.0008 watts. Therefore the ideal dye sensitized solar cell generates 87.5% more power than the nanotubular solar cell.

Figure 46: Nanoparticle based DSSC [50].
Figure 47: Nanotube based DSSC [51].
In Li Sin Lai’s paper the following parameter values were used:

Table 2: Parameters used in nanotube based DSSC [47].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Notation</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron relaxation rate constant</td>
<td>$k_e$</td>
<td>$10^3$ s$^{-1}$</td>
</tr>
<tr>
<td>Electron diffusion in nanotubes</td>
<td>$D_{e,2}$</td>
<td>$1.7 \times 10^{-5}$ cm$^2$/s</td>
</tr>
<tr>
<td>Triiodide diffusion constant in photoelectrode</td>
<td>$D_{i,2}$</td>
<td>$8.5 \times 10^{-5}$ cm$^2$/s</td>
</tr>
<tr>
<td>Iodide diffusion constant in photoelectrode</td>
<td>$D_{r,2}$</td>
<td>$1.2 \times 8.5 \times 10^{-6}$ cm$^2$/s</td>
</tr>
<tr>
<td>Initial concentration of triiodide</td>
<td>$C_{i,c}^+$</td>
<td>50 mM</td>
</tr>
<tr>
<td>Initial concentration of iodide</td>
<td>$C_{r,c}^+$</td>
<td>450 mM</td>
</tr>
<tr>
<td>Effective mass of conduction electron</td>
<td>$m_e^+$</td>
<td>$5.6 \times$ mass of electron</td>
</tr>
<tr>
<td>Exchange current density of platinum electrode</td>
<td>$j_0$</td>
<td>0.1 mA/cm$^2$</td>
</tr>
<tr>
<td>Symmetry parameter</td>
<td>$\beta$</td>
<td>0.78</td>
</tr>
<tr>
<td>Difference of TiO$_2$ conduction band and</td>
<td>$E_{cs} - E_{cm}^{oc}$</td>
<td>0.93 eV</td>
</tr>
<tr>
<td>standard electrolyte redox energy levels</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Series resistance</td>
<td>$R_T$</td>
<td>15 ohms</td>
</tr>
<tr>
<td>Shunt resistance</td>
<td>$R_p$</td>
<td>100k ohms</td>
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<td>Pore size</td>
<td>$d_p$</td>
<td>110 nm</td>
</tr>
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<td>Wall thickness</td>
<td>$w$</td>
<td>20 nm</td>
</tr>
<tr>
<td>TiO$_2$ barrier thickness</td>
<td>$b = l - d$</td>
<td>55 nm</td>
</tr>
<tr>
<td>TiO$_2$ nanotube length</td>
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<td>2$\mu$m</td>
</tr>
<tr>
<td>Spacer thickness</td>
<td>$l$</td>
<td>25$\mu$m</td>
</tr>
<tr>
<td>Cell area</td>
<td>$A$</td>
<td>0.785 cm$^2$</td>
</tr>
<tr>
<td>Porosity of TiO$_2$ nanotubes</td>
<td>$\phi$</td>
<td>0.5808</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>298 K</td>
</tr>
<tr>
<td>Incident photon flux density under AM1.5 (=1000W/m$^2$)</td>
<td>$\phi$</td>
<td>$1 \times 10^3$/cm$^2$/s</td>
</tr>
<tr>
<td>Dye concentration</td>
<td>$C_{dp}$</td>
<td>$5 \times 10^{-4}$ mol/cm$^3$</td>
</tr>
</tbody>
</table>
Clearly there is an overall efficiency limit primarily by the photocurrent generated inside the cell. It is seen that the max current for the nanotube based cell is only about 2.3 mA/cm² compared to the nanoparticle based cell that has a max current of 15.5 mA/cm². The relatively low photocurrent is a result of several factors including a small absorptivity factor, photoanode reflectivity, and low injection/charge collection efficiency [53]. It is reasoned that the reduced dimensionality of the nanotube array electrodes, relative to nanoparticulate electrodes would allow for efficient charge collection over long distances (7-10 µm) due to more rapid electron transport [53]. It was found that the absorptivity of nanotube bases cells (α = .14) were much smaller that of the nanoparticle based cells (α = .40) [54]. In order to increase the light absorptance, longer nanotubes are needed as seen in figure (49.1) [54]. For a comparison of nanoparticle based cell to the ideal dye sensitized solar cell, the thickness of the ideal case solution was changed to a film thickness of 7.3 µm (figure 49.2).
It may be seen that from figure (49.1) that nanotube based cells offer better performance that nanoparticle based if the lengths of the tubes are comparable to the thickness of the nanoparticle film. The reasoning can be justified by the one dimensionality of the nanotubes giving the free electrons a straight shot to the collection plate vs. migrating thought the particulate grid offered by the nanoparticle film based cells.

Figure 49.1: (Left) J-V characteristics of dye-sensitized (a) NT and (b) NP solar cells as a Function of film thickness under simulated AM1.5 light[54].

Figure 49.2: (Right) Ideal J-V characteristics of dye-sensitized NP solar cells as a function of film thickness under simulated AM1.5 light.
CHAPTER 8. SUMMARY

8.1 Summary
The results of this work may be summarized as follows:

a. A full model of the DSSC was presented which included the continuity equation (17), four transport equations (18),(19),(20), and (21), and the electric field (Poisson’s) equation (23). The continuity equation was idealized to find the current densities in the cell and the photocurrent produced during open circuit voltage. A linear interpolation method was used to develop the absorptivity equation \( \alpha(\lambda) \). Once the ideal photocurrent was found, the ideal I-V curves were calculated.

b. A sensitivity analysis was performed on all the parameters to determine the highest power production from the cell. Then with the optimized parameters, an efficiency curve was product for the ideal DSSC. The theoretical limit of the DSSC was then compared to a study by Shockley. It was found that the DSSC has a theoretical limit that is 5% higher than that of the ideal p-n junction. This theoretical limit was also compared to results of the full model and experimental results taken for both nanoparticle and nanotubular based cells. It was found that the DSSC has a theoretical power production limit that is 5 times higher than that of the nanoparticle and nanotubular based cells.

c. The factors that reduce the theoretical limit of the DSSC are the absorptivity of the dye, reverse saturation current \( (I_o) \), temperature \( (T) \), the ideality factor \( (n) \), and the reflectivity of the TCO layer. The absorptivity of the dye is the highest contribution to losses (38.2%) due to low absorbance near the inferred range (200nm to 400nm). These findings indicate that there exists a need for a better light harvester that can achieve a high absorptance over a wider range of wavelengths. The reverse saturation current needs to be kept to a minimum and the ideality
factor maximized to obtain the best performance. These two factors are material based and synthesizing routines could be optimized to benefit these.

c. The reflectivity at the TCO layer was fully addressed. The results indicate that applying a 71nm thin film coating of MgF2 will decrease the reflectivity from 12% to 4%. This is a 66.6% decrease in reflectivity. This decrease in reflectivity will result directly in a significant 2% increase in performance. Studies have shown that it is feasible to produce a 71nm coating on a substrate [56]. These thin film coatings have been produced since 1935 where since it has developed into a useful technology for lenses, windows, and other transparent media. Thin film antireflective coatings have evolved to where the deposition of the coatings have become very inexpensive [56][57]. The above results suggest that the DSSC technology has much room for improvement in several areas in order to move the efficiency towards the limit and become a preferred, affordable means for light energy conversion.
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Appendix A Numerical Aspects

The solution method to the set of the six coupled first-order ordinary differential equations was taken from J. Ferber’s paper [20]. In a standard two point boundary problem, every boundary condition is given at one of the points $x = 0$ or $x = d$. Both integral boundary conditions (58), (59), and boundary conditions like (60), combining values of variables at both the points $x = 0$ and $x = d$, are numerically unfavorable. However, the equations can be transformed:

a. Integral boundaries
The integral boundaries are transformed to further differential equations $N + I$ ($I = 1, 2, \ldots$) which are added to the set of $N = 6$ equations. The principle is sketched by the following equivalence:

$$\int_0^d n_c(x) \, dx = \text{const} \iff y'_{N+1}(x) = n_c(x), \quad y_{N+1}(0) = 0, \quad y_{N+1}(d) = \text{const.} \quad (A.1)$$

Thus, one additional differential equation with two local boundary conditions is generated, one of them replacing the former integral boundary condition.

b. Boundary conditions given at two points
This problem can be solved by an additional trivial differential equation $N + j$ with appropriate local boundary conditions

$$y'_{N+j} = 0, \quad y_{N+j}(0) = y_{N+j}(d) = n_e(0) \quad (A.2)$$

Thus, the value of $n_e(0)$ can be replaced by $y_{N+j}(d)$ in (39), and the extra boundary condition for the additional differential equation is

$$y_{N+j}(0) - n_e(0) = 0 \quad (A.3)$$

With these transformations, a standard two-point boundary problem is obtained. All variables are scaled by typical values of the variables in order to obtain a dimensionless form.

The set of differential equations is extremely stiff, due to Poisson’s equation. However, a relaxation method works well, using routines from [55]. The set of differential equations is replaced by finite-difference equations on an appropriate mesh of points that span the interval $[0, d]$. To begin the calculations, a trial solution, consisting of values for the dependent variables at each mesh point, has to be substituted into the finite-difference equations. The iteration, now called relaxation, is a kind of Newton method and consists of simultaneously adjusting all the values on the mesh so as to bring them into successively closer agreement with the finite-difference equations and the boundary conditions.

To calculate a complete I-V curve, the program is started in the open-circuit condition with the equilibrium values as an initial estimate. Then the external resistance is varied, as in real experiments, using the previous solution each time as the initial estimate.
Appendix B Code

This code is used for finding the I-V, P-V, and Efficiency – Voltage curves for an uncoated TCO substrate.

%A Comprehensive Study of Dye Sensitized Solar Cells
%Gregory Vick
%Thesis Research
%Aug 10, 2012

clc;
clear all;

%import excel data for AMG 1.5 solar irradiation
D = xlsread('C:\Users\michelle\Documents\MATLAB\dsscdatacm.xlsx');

%initiate the wavelength vector for all wavelengths from 200nm to 800 nm
lambna=D(:,1);

%initiate photon flux vector for the photon flux for given wavelength
phi=D(:,5);

%initiate absorptivity vector for the absorptance for a given wavelength
absorb=D(:,6);

%define elementary charge
e=1.60217646*10^-19;

%define delta x or increment throughout the active region of TiO2
dx=.000001;

%define cell depth
depth = .0001;

%define nodes
nodes=(depth/dx)+1;

%define x
x(1)=0;

%define boltzman constant
k = 1.38e-23;

%define Temp
T=375;
%create x array
for i=2:nodes
    x(i)=x(i-1)+dx;
end
x=x';

%Program to find the photon flux for a given depth (x position)
for i=1:nodes
    intg=absorb.*phi.*exp(-absorb.*x(i));
    integral(i)=sum(intg);
end

%Program to find the current at a given depth (x position)
integral2=fliplr(integral);
j(1)=0;
for i=2:nodes
    j(i)=j(i-1)+e*integral2(i-1)*dx;
end
intcurrent=e*integral(1)

%Program to find the current-voltage relationship
for j=17
    vmax=2.5
    deltat=.01
    v=0:.01:vmax;
    length=(vmax/deltat)+1
    Io=1*10^-j;
    poww=zeros(size(v));
    lext=zeros(size(v));
    power=zeros(size(v));
    efficiency=zeros(size(v));
    for i=1:length
        lext(i)=intcurrent-Io*(exp(e*v(i)/(2*k*T))-1);
        power(i)=lext(i)*v(i);
        efficiency(i)=power(i)*100/.1;
        poww=lext(i)*v(i)
        countt=i
    end

%plot for voltage vs. current curve
figure(12)
plot(v,lext)
axis([0 vmax 0 .02])
% program for finding total internal current generated
j=fliplr(j);
current2=trapz(j);

% plot for current vs. depth in cell
amps=e.*integral;
figure(8)
plot(x,amps)
title('Photocurrent vs. Surface Depth')
xlabel('depth (m)')
ylabel('Photocurrent (Amps)')

%plot for photons absorbed for a given depth
figure(2)
plot(x,integral)
title('Photons Absorbed vs. Surface Depth')
xlabel('depth (m)')
ylabel('Photon flux (photon/sec cm^2)')

%plot for wavelength vs. photon flux
figure (3)
plot(lambna,phi);
title('Photon flux vs. Wavelength')
xlabel('Wavelength (nm)')
ylabel('Photon flux (photon/sec cm^2)')
Appendix C Code

This code is used to find the reflectance of an coated surface for a given wavelength

% Gregory Vick
% code to determine the reflectance of surfaces

clc;
clear all;

%initialize the refraction index of air
n1=1;

%initialize the refraction index of TCO glass substrate
n2=1.9;

%initialize the chosen wavelength
lambda=.0000005;

%initialize the refraction index of magnesium coating
no=1.36957+(.0035821)/(lambda-.14947);
ne=1.381+(.0037415)/(lambda-.14947);
n3=.5*(no+ne);

%initialize parameters
theta1=0;
theta2=0;
theta3=0;
f=0;
s=0;
R=0;
B=0;
h=.0000008/4;
Rf=0;
Rptob=0;
Rpbottom=0;
Rp=0;
Rstop=0;
Rsbottom=0;
Rs=0;
Rtot=0;

%this section solves for reflectivity as a function of incident angle
for i=1:90
theta1(i)=i;
theta2(i)=asind((n1/n2)*(sind(theta1(i))));
theta3(i)=asind((n1/n3)*(sind(theta1(i))));

r12p(i)=(n2*cosd(theta1(i))-n1*cosd(theta2(i)))/(n2*cosd(theta1(i))+n1*cosd(theta2(i)));

r23p(i)=(n3*cosd(theta2(i))-n2*cosd(theta3(i)))/(n3*cosd(theta2(i))+n2*cosd(theta3(i)));

r12s(i)=(n1*cosd(theta1(i))-n2*cosd(theta2(i)))/(n1*cosd(theta1(i))+n2*cosd(theta2(i)));

r23s(i)=(n2*cosd(theta2(i))-n3*cosd(theta3(i)))/(n2*cosd(theta2(i))+n3*cosd(theta3(i)));

B(i)=((360/lambda)*n2*h*cosd(theta2(i)));

Rptop(i)=(r12p(i))^2+(r23p(i))^2+2*r12p(i)*r23p(i)*cosd(2*B(i));

Rpbottom(i)=1+(r12p(i))^2*(r23p(i))^2+2*r12p(i)*r23p(i)*cosd(2*B(i));

Rp(i)=Rptop(i)/Rpbottom(i);

Rtop(i)=(r12s(i))^2+(r23s(i))^2+2*r12s(i)*r23s(i)*cosd(2*B(i));

Rsbottom(i)=1+(r12s(i))^2*(r23s(i))^2+2*r12s(i)*r23s(i)*cosd(2*B(i));

Rs(i)=Rtop(i)/Rsbottom(i);

Rtot(i)=.5*(Rp(i)+Rs(i));

f(i)=((tand(theta1(i)-theta2(i)))^2)/((tand(theta1(i)+theta2(i)))^2);

s(i)=((sind(theta1(i)-theta2(i)))^2)/((sind(theta1(i)+theta2(i)))^2);

R(i)=.5*(f(i)+s(i));

end

R(1)

%plot(theta1,theta2)

%Creation of reflection vs. incident angle plot

plot(theta1,R)

hold on

plot(theta1,Rtot,'color','black')

% title('Reflectivity vs. Incident Angle')

% xlabel('Incident angle [theta]')

% ylabel('Reflectivity')

%This section solves for refractive index of coating

labnna=0;

no=0;

ne=0;

n=0;

ncaf=0;

for i=1:600;

labnna(i)=200+i;

lambda(i)=.0000002+(i/1000000000);

no(i)=1.36957 + .0035821/(lambda(i)-.14947);

ne(i)=1.381 + .0037415/(lambda(i)-.14947);

nmgf(i)=.5*(no(i)+ne(i));

nnaff(i)=.32785*lambda(i)*lambda(i)/(lambda(i)*labda(i)-.013689);

nnafs(i)=3.18248*labda(i)*labda(i)/(labda(i)*labda(i)-1645.9249);

nnaf(i)=sqrt(1.41572+nnaff(i)+nnafs(i));

ncaf(i)=1.45757-.000492*i;

end
% plot(labnna, nmgf)
% hold on
% plot(labnna,nnaf,'color','red')
% plot(labnna,ncaf,'color','green')
Appendix D Code

This code is to find the reflectance of a coated surface for all wavelengths (200nm-800nm)

% Gregory Vick
% code to determine the reflectance of surfaces for all lambda

clc;
clear all;

%initialize the refraction index of air
n1=1;

%initialize parameters
theta1=0;
theta2=0;
theta3=0;
f=0;
s=0;
R=0;
B=0;
h=.000000350/4;
Rf=0;
Rptob=0;
Rpbottom=0;
Rp=0;
Rstop=0;
Rsbottom=0;
Rs=0;
Rtot=0;
lambda=0;
labnna=0;
labnna=0;
n2=0;

for i=1:300

%initialize the chosen wavelentgh
lambda(i)=.0000002+(i/500000000);
labnna(i)=200+2*i;
%initialize the refraction index of magnesium coating
no(i)=1.36957+(.0035821)/(lambda(i)-.14947);
ne(i)=1.381+(.0037415)/(lambda(i)-.14947);
n2(i)=.5*(no(i)+ne(i));
%n3(i)=1.38;
%initialize the refraction index of TCO glass substrate
n3(i)=-6.555760687e-11*labnna(i)^4+1.4716792498e-7*labnna(i)^3-1.173064740e-4*labnna(i)^2+3.8108550369e-2*labnna(i)-1.9707079;
%n2(i)=1.9

%this section solves for reflectivity as a function of incident angle for j=1:90
theta1(i,j)=j;
theta2(i,j)=asind((n1/n2(i))*(sind(theta1(i,j))));
theta3(i,j)=asind((n1/n3(i))*(sind(theta1(i,j))));
r12p(i,j)=(n2(i)*cosd(theta1(i,j))-n1*cosd(theta2(i,j)))/(n2(i)*cosd(theta1(i,j))+n1*cosd(theta2(i,j)));
r23p(i,j)=(n3(i)*cosd(theta2(i,j))-n2(i)*cosd(theta3(i,j)))/(n3(i)*cosd(theta2(i,j))+n2(i)*cosd(theta3(i,j)));
r12s(i,j)=(n1*cosd(theta1(i,j))-n2(i)*cosd(theta2(i,j)))/(n1*cosd(theta1(i,j))+n2(i)*cosd(theta2(i,j)));
r23s(i,j)=(n2(i)*cosd(theta2(i,j))-n3(i)*cosd(theta3(i,j)))/(n2(i)*cosd(theta2(i,j))+n3(i)*cosd(theta3(i,j)));
B(i,j)=((360/lambda(i))*n2(i)*h*cosd(theta2(i,j)));
Rptop(i,j)=(r12p(i,j))^2+(r23p(i,j))^2+2*r12p(i,j)*r23p(i,j)*cosd(2*B(i,j));
Rpbottom(i,j)=1+(r12p(i,j))^2*(r23p(i,j))^2+2*r12p(i,j)*r23p(i,j)*cosd(2*B(i,j));
Rt(i,j)=Rptop(i,j)/Rpbottom(i,j);
Rstop(i,j)=(r12s(i,j))^2+(r23s(i,j))^2+2*r12s(i,j)*r23s(i,j)*cosd(2*B(i,j));
Rsbottom(i,j)=1+(r12s(i,j))^2*(r23s(i,j))^2+2*r12s(i,j)*r23s(i,j)*cosd(2*B(i,j));
Rs(i,j)=Rstop(i,j)/Rsbottom(i,j);
Rt(i,j)=.5*(Rt(i,j)+Rs(i,j));
f(i,j)=((tan(theta1(i,j))-theta3(i,j))^2)/((tan(theta1(i,j))+theta3(i,j))^2);
s(i,j)=((sind(theta1(i,j))-theta3(i,j))^2)/((sind(theta1(i,j))+theta3(i,j))^2);
R(i,j)=.5*(f(i,j)+s(i,j));
end
end

%This section solves for the Transmission array through the cell
Transmittanceunc=1-R(:,1)
Transmittancecot=1-Rtot(:,1)
Rt=sum(Rtot);
Rp=Rt/300;
% Rp
Rg=sum(R);
Ru=Rg/300;
Appendix E Code

This code is used for optimization of film coating thickness

% Gregory Vick
% code for optimization
clc;
clear all;

%initialize the refraction index of air
n1=1;

%initialize parameters
theta1=0;
theta2=0;
theta3=0;
f=0;
s=0;
R=0;
B=0;
h=0;
Rf=0;
Rptob=0;
Rpbottom=0;
Rp=0;
Rstop=0;
Rsbottom=0;
Rs=0;
Rtot=0;
lambda=0;
labnna=0;
labnna=0;
n2=0;
hmm=0;

%This section is for creating film thickness (h)
for k=1:100
    count=k
    h(k)=(.0000002+.000000004*k)/4;
    H(k)=h(k)*1000000000;
end

%This section creates a wavelength array
for i=1:300
    %initialize the chosen wavelength
    lambda(i)=.0000002+(i/500000000);
    labnna(i)=200+2*i;
    %initialize the refraction index of magnesium coating

\[ \text{no}(i) = 1.36957 + \frac{0.0035821}{(\lambda(i) - 0.14947)}; \]
\[ \text{ne}(i) = 1.381 + \frac{0.0037415}{(\lambda(i) - 0.14947)}; \]
\[ \text{n2}(i) = 0.5(\text{no}(i) + \text{ne}(i)); \]
\[ \% \text{n3}(i) = 1.38; \]
\[ \% \text{initialize the refraction index of TCO glass substrate} \]
\[ \text{n3}(i) = -6.555760687e-11 * \text{labnna}(i)^4 + 1.4716792498e-7 * \text{labnna}(i)^3 - 1.173064740e-4 * \text{labnna}(i)^2 + 3.8108550369e-2 * \text{labnna}(i) - 1.9707079; \]
\[ \% \text{n2}(i) = 1.9 \]

\[ \% \text{this section solves for reflectivity as a function of incident angle} \]
\[ \text{for } j = 1 \]
\[ \theta_1(i,j) = j; \]
\[ \theta_2(i,j) = \sin^{-1}(\frac{n_1}{n_2(i)} \sin(\theta_1(i,j))); \]
\[ \theta_3(i,j) = \sin^{-1}(\frac{n_1}{n_3(i)} \sin(\theta_1(i,j))); \]
\[ \text{r12p}(i,j) = (n_2(i) \cos(\theta_1(i,j)) - n_1 \cos(\theta_2(i,j))) / (n_2(i) \cos(\theta_1(i,j)) + n_1 \cos(\theta_2(i,j))); \]
\[ \text{r23p}(i,j) = (n_3(i) \cos(\theta_2(i,j)) - n_2(i) \cos(\theta_3(i,j))) / (n_3(i) \cos(\theta_2(i,j)) + n_2(i) \cos(\theta_3(i,j))); \]
\[ \text{r12s}(i,j) = (n_1 \cos(\theta_1(i,j)) - n_2(i) \cos(\theta_2(i,j))) / (n_1 \cos(\theta_1(i,j)) + n_2(i) \cos(\theta_2(i,j))); \]
\[ \text{r23s}(i,j) = (n_2(i) \cos(\theta_2(i,j)) - n_3(i) \cos(\theta_3(i,j))) / (n_2(i) \cos(\theta_2(i,j)) + n_3(i) \cos(\theta_3(i,j))); \]
\[ \text{B}(i,j,k) = \left( \frac{360}{\lambda(i)} \right) n_2(i) h(k) \cos(\theta_2(i,j)); \]
\[ \text{Rptop}(i,j,k) = r_12p(i,j)^2 + r_23p(i,j)^2 + 2 * r_12p(i,j) * r_23p(i,j) \cos(2 * B(i,j,k)); \]
\[ \text{Rpbottom}(i,j,k) = 1 + r_12p(i,j)^2 * r_23p(i,j)^2 + 2 * r_12p(i,j) * r_23p(i,j) \cos(2 * B(i,j,k)); \]
\[ \text{Rp}(i,j,k) = \text{Rptop}(i,j,k) / \text{Rpbottom}(i,j,k); \]
\[ \text{Rstop}(i,j,k) = r_12s(i,j)^2 + r_23s(i,j)^2 + 2 * r_12s(i,j) * r_23s(i,j) \cos(2 * B(i,j,k)); \]
\[ \text{Rsbottom}(i,j,k) = 1 + r_12s(i,j)^2 * r_23s(i,j)^2 + 2 * r_12s(i,j) * r_23s(i,j) \cos(2 * B(i,j,k)); \]
\[ \text{Rs}(i,j,k) = \text{Rstop}(i,j,k) / \text{Rsbottom}(i,j,k); \]
\[ \text{Rtot}(i,j,k) = 0.5 * (\text{Rp}(i,j,k) + \text{Rs}(i,j,k)); \]
\[ \text{hmm}(i,j,k) = \cos(2 * B(i,j,k)); \]
\[ \% \text{This section creates the derivative of the Reflectivity vector} \]
\[ \text{derref} = \text{diff}(\text{Ruse}); \]
Vita

Gregory Lewis Vick, Jr. was born in Jacksonville, FL, USA to Gregory and Michelle Vick on August 29, 1988. He graduated high school from Pearl River High School in Pearl River, La. Immediately following graduation, he enrolled at Southeastern Louisiana University, where he graduated with a Bachelor of Mathematics degree in December 2009. He enrolled at Louisiana State University in August 2010 to pursue a Master of Science in Mechanical Engineering degree under Dr. Tryfon T. Charampopoulos. He is a candidate for graduation in the Summer Commencement of 2013 for his research, Comprehensive Study of the Dye Sensitized Solar Cell.