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Characterization of key performance parameters in dye sensitized solar cells using a designed experiment

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**CHARACTERIZATION OF KEY PERFORMANCE PARAMETERS IN DYE
SENSITIZED SOLAR CELLS USING A DESIGNED EXPERIMENT**

by

Todd Robert Hamrick

**Thesis submitted to
the College of Engineering and Mineral Resources
at West Virginia University
in partial fulfillment of the requirements
for the degree of**

**Master of Science
in
Mechanical Engineering**

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Abstract

CHARACTERIZATION OF KEY PERFORMANCE PARAMETERS IN DYE SENSITIZED SOLAR CELLS USING A DESIGNED EXPERIMENT

Todd Robert Hamrick

Inorganic photovoltaic cells have been in production for many years, but the silicon production process is expensive, so solar technology is cost prohibitive for all but niche markets. A more cost effective alternative would open usage of solar power production to more applications and make the cost to produce electricity more affordable. Inorganic solar cells could potentially be the lower cost alternative to conventional solar technology, but efficiency and durability are still not high enough for successful competition.

Other research has investigated how to improve individual aspects of dye sensitized solar cells. This work evaluated six primary factors of material and fabrication methods. Both the main factors and their two-level interactions were considered using designed experiments and regression analysis to evaluate which impacted maximum power production to the greatest extent. The experiment determined that three factors were of the greatest importance; use of catalyst, method of application of semi-conductive layer, and temperature. No two-level interactions were determined to be of statistical significance.

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1. Background and Introduction

Production of electricity using photovoltaic cells was initially developed in the early 20th century, and some commercially viable models using silicon technology were created in the 1950's. The energy crisis of the 1970's brought about a renewed interest in the technology, when research was dedicated to making the silicon based photovoltaic cells more robust, efficient and less expensive.² Silicon based solar cells utilize semiconductor technology similar to that for microchip production, and therefore is an expensive production process. Because of the high investment cost, today's solar cells occupy only niche markets for power production.¹

Organic photovoltaic cells are modeled after energy production found in nature, mimicking the way plants convert sunlight to energy. Such cells promise lower production costs because materials of lower purity can be utilized. Existing low cost production techniques such as gravure printing can also be used for manufacture. In 1991 Michael Grätzel developed a new class of organic photovoltaic cells by using organic dyes to sensitize comparatively inexpensive semiconductors. While researchers have made laboratory samples that are nearly as efficient as conventional cells, this class of photo electrochemical (PEC) cells is not yet commercially viability.^{1, 2}

Energy efficiency and durability of organic cells has been increasing in the lab, while the cost of silicon based cells has increased due to a worldwide increase in the consumption of hyper-pure silicon. Within a few years commercially viable organic cells are expected to begin replacing silicon based cells due to cost considerations.³

Grätzel cells are constructed by first coating conductive glass slides (Indium Tin Oxide ITO coated) with a semiconductor, usually titanium dioxide (TiO_2). The TiO_2 is sintered to affect its crystal structure. A porous structure is desirable because it maximizes the surface area of the semiconductor. The semiconductor layer is then treated with an organic dye.⁴

Finding an efficient organic dye has been the focus of much research. Dyes can be easily extracted from berries, leaves, chlorophyll, or nearly any plant material that contains flavoniods such as anthocyanin. Some highly efficient dyes have been developed and are commercially available. Most are ruthenium bipyridyl organic compounds. While they can be purchased, they are currently available only in laboratory quantities and are consequently too expensive for commercialization.⁵

Previous research has been conducted on each of the components of the photo electrochemical cell. Particular emphasis has been given to making more efficient organic dies, with some additional research conducted on improved application of semiconductors.² These studies intensively investigate specific characteristics independently. However, little is known about the interaction of the components. Few if any studies are available that investigate how materials interact with one another, or how production techniques work together with the materials to affect efficiency.

Research to evaluate relationships of the various components to ascertain how they interact with one another would be beneficial to understanding how best to improve overall efficiency of dye sensitized cells. This will increase understanding of how all of the components work together, and which contribute the most to overall efficiency.

This research evaluates these components and their interactions through the use of a designed experiment. Six factors were evaluated at two levels each, including two methods of applying the semi conducting layer at two thicknesses, temperature and time of firing, two different organic dyes, and the use of a catalyst. Thirty two cells were manufactured, each unique, according to a specific plan. Each was exposed to a uniform light source, and the maximum power was calculated based on voltage and resistance measured. Statistical analysis was used to determine which factors were the most significant and by how much.

2. Literature Review

Photovoltaic phenomena were first observed in the 19th century. Practical photovoltaic devices were developed in the 1950's using inorganic materials, and almost all production photovoltaics manufactured today are inorganic based silicon. Some organic materials were found to have photovoltaic properties as early as 1906, with polymers recognized as potential for PV cells in the 1950's. Following the energy crisis of the 1970's a great deal of research was pursued to find alternative energy sources, including "solar harvesting." While efficiencies and production costs for inorganic photovoltaics have improved to the point that they are commercially viable, they are still too costly for all but niche markets. Despite a great deal of research, organic photovoltaics have yet to become practical.²

Organic photovoltaics are attractive because they are potentially less expensive to manufacture on a large scale. Not only are the materials generally less expensive than silicon, they are more varied, more available, and high volume processing is very cheap. Organic photovoltaics have the potential to make solar harvesting a cost effective energy solution.

In Polymeric devices, perfect contact between metal electrodes and polymeric materials is not possible.⁶ A thin insulating layer often builds up, causing the device to lose efficiency quickly. A protective layer can be effective in improving the useful life of the device, but more work is required to make this technology viable.⁷

Most of the early research efforts regarding polymer photovoltaics centered on finding materials that were suitable for Photovoltaic processes. Many materials were studied including dyes and even chlorophyll.⁸ CW Tang of the Eastman Kodak Research Facilities in Rochester, NY carried out extensive tests on Photovoltaic devices using Chlorophyll extracted from green spinach.⁹

Tang made an important breakthrough while conducting additional research in 1979, which was published in 1986. He made use of a concept called heterojunction, where two different materials with different electron affinities and ionization potentials are used together. Devices using two materials are more efficient than those using one, and heterojunction has been the source of a great deal of research in the past two decades.¹⁰

Dye sensitized solar cells represent a separate class of photovoltaic devices, and are modeled after the way in which plants generate energy. The invention was the brainchild of Michael Grätzel of the Ecole polytechnique fédérale (Federal Polytechnic Institute) de Lausanne, Switzerland. In 1991 he found that sintered colloidal titanium dioxide particles could be dyed with organic chromophores, and the resulting construction constituted a device capable of producing electricity. He had created an artificial leaf.¹¹

While initial indications showed great promise, two problems, efficiency and durability, have yet to find effective solutions. Most research into dye sensitized solar cells since

their invention has focused on the various components of the cells independently. These include organic dyes, electrolytic carriers, counter electrodes, and semi-conductors. As early as 1992 Grätzel and others were searching for improvements in all of these.

Juices extracted from fruit were found to make good dyes for sensitizing the semi-conductive layer. Blackberries were soon found to be an excellent choice, as the anthocyanins bonded readily with crystalline titanium dioxide.¹² Other fruit juices were found to work well, as long as the anthocyanins chelate to the substrate. These include berry juice, pomegranate juice, and teas made from green citrus leaves, hibiscus leaves, or onion skins to name a few.^{13, 4} While cells made from these will produce electricity, efficiencies and durability are too low to be practical.

Ruthenium based organic complex dyes were developed by Grätzel and others as early as 1992.^{14, 15, 16} Collectively known as N-type dyes, these dyes have been the standard for this class of cells for many years, and some are commercially available for purchase. Additional research has improved the performance of N-type dyes by changing chemical structures to form a broader band response to incoming light.^{17, 18, 19} Some have also made use of the heterojunction principle by mixing dyes, and these have been found to be more efficient than single dyes.^{20, 21}

Research on electrolytic carrier solutions has been less intense since Grätzel used an iodide solution in his early research.^{22, 23} While other electrolyte solutions have been studied with varying success, use of any liquid poses problems.²³ A liquid sealed permanently inside the cell poses manufacturing issues, and outdoor exposure of liquid filled cells to low temperatures causes shortened life. A dry or “solid state” cell is therefore considered far more practical, and has been the greatest focus of research.

An efficient solid state electrolyte has yet to be developed. Work in this area focuses on elastomers, polymers, and mixtures.^{24, 25, 26, 27} Using gel polymers, a “quasi-solid state” solar cell has been created that shows great promise, and may be the key to making a practical dye sensitized solar cell.^{28, 29, 30}

Some counter electrode work has also been carried out, although this has been an area of secondary concern. Some of the research is dedicated to improving the original carbon coating electrode used by Grätzel.^{31, 32} More efficient, although probably not economically practical, have been counter electrodes produced by various applications of platinum.^{33, 34}

A great deal of research has been dedicated to the semi-conducting layer. Grätzel started with titanium dioxide, and this is still the standard for dye sensitized solar cells, although other metal oxides including zinc, tin, aluminum and others have been used with success. Many methods of deposition of metal oxides have also been studied including paste applications, dip coating, spin coating, electro-deposition, spray coating and sputtering.^{4, 41, 35} The method of application seems to matter less than the available surface area, so thin films are possible using some of these techniques. The most efficient dye sensitized cells achieve efficiencies over 10%, but have not yet been successfully scaled up for

production.³⁶ A recent Chinese design has sought to make a workable production design.³⁷

Some work has been conducted on the importance of the combination of factors in the construction of cells. Researchers in Japan found that dies properly linked to the titanium dioxide nanostructure produced improved open circuit voltage, thereby increasing power potential.³⁸ While some of these interactions are known, no major studies have investigated all of the factors and their interactions. No one has considered how the materials and methods of manufacture can work together to determine which is the optimum combination. A study of primary factors and interactions between them can be accomplished through the use of a designed experiment.

Designed experiments are superior to conventional one-factor-at-a-time experimentation, and have several advantages. They require fewer resources, requiring fewer data points for a complete study. Estimates of the effects are more precise because more data points are used to calculate effects, thereby reducing variability. Most importantly for this study, interactions between factors can be estimated more easily and precisely. This provides for improved estimates of optimum combinations.³⁹

A designed experiment is done in two related parts, selection of the experimental design and selection of the statistical analysis. The experimental design takes into account such issues as how many factors will be studied and at how many levels, what will be varied and what will be held constant, and what will be measured as the response variable. Many designs are possible depending on these factors among others.⁴²

Statistical analysis can be conducted in many ways, but a widely accepted method is the use of analysis of variance (ANOVA). This analysis defines the overall variability in the data and compares it with the variability in each set of treatments. By analyzing the difference in the variability, it is possible to determine which of the factors or combinations of factors are statistically significant.⁴²

Regression analysis is a powerful tool in statistical analysis. This method of analysis quantifies the results by equating the output response to the sum of all of the studied factors or combination of factors, each with a coefficient as seen in Equation 1. The coefficients are mathematically estimated based on the least squares fit of the data. The result is a model that equates the output response to the inputs. This allows for a quantified prediction of output responses from given inputs, and provides information about which inputs have the greatest response.⁴²

Equation 1

$$y = \beta_0 + \beta_1 x_1 + \dots + \beta_n x_n + \beta_{n+1} x_1 x_2 + \dots + \beta_z x_n x_m + \varepsilon$$

3. How Dye Sensitized Solar Cells Work

The basic layout of the dye sensitized solar cell can be seen in Figure 1. Two glass plates with conductive clear coating, usually Indium Tin Oxide (ITO) are used. Only one side of the glass is coated, so care must be taken to use the conductive side, which can easily be found by testing the resistivity with a multimeter. The coated side shows measurable resistance, while the uncoated side has infinite resistance.

A layer of semi-conductor is applied to one of the plates, making the cathode of the cell. Titanium dioxide (TiO_2) is used often, as this material is widely available and inexpensive. The application can be done in a number of ways and at thicknesses up to 0.5 mm. This layer is then fired or sintered in such a way as to cause the TiO_2 to form crystals. An organic dye is applied to the cooled semi-conducting layer and allowed to dry. To create the anode, a layer of graphite is applied to the other glass plate, which serves to improve conductivity of that plate and as a catalyst for the electrochemical process. The plates are then put face-to-face with a liquid electrolytic solution between them. This is often an iodine/iodide solution, which readily exchanges electrons.

The dye molecules are chemically attached to the semi-conductive material. They do this by linking a complex sugar group known as Cyanin to one of the oxygen molecules in the TiO_2 crystal structure, as can be seen in Figure 2.

Figure 2 Molecular Representation of Dye Attached to Titanium Dioxide Structure⁴

When a photon from the light source strikes the dye, electrons in the dye become excited and are released into the semiconductor. From there they are free to flow through the semiconductor to the glass plate and out to the circuit. Once completing the circuit, they flow back to the anode, where the conductive graphite allows free flow of the electrons back through the electrolyte solution to the original site of the lost electron in the dye.

⁴ , 40 , 41

4. Problem Statement

Using a designed experiment, analysis of variance and regression analysis, identify the primary factors and their interactions affecting power generation in dye sensitized solar cells and the degree to which they impact the output.

5. Methodology

5.1 Selection of Factors for Study

There are many different materials that can be used to make dye sensitized solar cells, and many different methods for manufacturing them. It is beyond the scope of this study to evaluate all of them. For this study, six factors were selected for evaluation; Application of Semi-conducting layer, thickness, sintering temperature, sintering time, dye type, and use of catalyst.

The semi-conducting layer is the focus of much research in the literature, and for that reason it was the primary focus of study in this work. Four of the six factors selected examine its application and treatment. Dye type and use of catalyst add extra dimensions to the study by evaluating how these factors affect power when combined with the four treatments of the semi-conducting layer. While it is impractical to study all possible combinations of materials and methods, this selection covers a wide range of the most common. This study evaluates six factors at two levels each, which provides an effective screening experiment to determine what the most important factors are to produce the greatest power.

5.2 Designed Experiment

The most thorough and organized approach to evaluating multiple factors and their interactions is through the use of a designed experiment. Six factors at two levels create a 2^6 factorial designed experiment. In order to reduce the number of cells that were to be created, the 2_{IV}^{6-1} half fraction factorial experimental design was followed, which requires the manufacture of 32 unique cells. Equation 2 represents the linear statistical model for this experiment.

$$Y_{ijklmn} = \mu + \alpha_i + \beta_j + \gamma_k + \tau_l + \nu_m + \omega_n + (\alpha\beta)_{ij} + (\alpha\gamma)_{ik} + \bullet\bullet\bullet + (\nu\omega)_{mn} + \varepsilon_{ijklmn} \quad \text{Equation 2}$$

where $i = 1,2 \quad j = 1,2 \quad k = 1,2 \quad l = 1,2 \quad m = 1,2 \quad n = 1,2$

The design layout for this experiment can be seen in Table 1. The run number was selected according to the standard method known as Yates' Order, and is the standard for designed experiments.⁴² Two levels of each factor were selected for evaluation. The + indicates the factor at a high level, and the – indicates the factor at a low level. The application method of the TiO₂ layer and the dye type were arbitrarily selected as + and – levels. The lower case letters in the “Level” column indicate that the factor will be at its high level for that run, and all others will be at their low level. The (1) indicates that all factors will be at their low levels for that run. The 32 runs were done in a random order, as is required by the assumption of the linear statistical model.

The purpose for the designed experiment is to provide information about all of the factors tested. The factors most significant to the desired outcome can be determined, as well those that are of less importance. It will also provide information about some interactions between the factors. If a particular set of factor settings work better in combination, the designed experiment will indicate them.

Some interaction information may be lost in the process unless all of the possible combinations of factors are produced. Since this is impractical, the organized method of designing the experiment manages the loss of interaction detail. This is done through specifying the “confounding” rules rather than leaving them to chance. Confounding means that the experiment will be unable to determine the cause of any statistically significant difference between the results. Because they may look the same, they are said to be “aliased.” By designing the experiment, the researcher assumes that individual factors will contribute the most to the final results, that two factor (second order) interactions will be of lesser import, and that impact to the results will be of lesser gravity as the order of interaction increases. For this experiment, only two factor interactions were considered, as higher order interactions are less likely to contribute significantly to the final results.⁴²

Table 1 Experimental Design Layout

Run	Level	A	B	C	D	E	F=ABCDE
1	(1)	-	-	-	-	-	-
2	a	+	-	-	-	-	+
3	b	-	+	-	-	-	+
4	ab	+	+	-	-	-	-
5	c	-	-	+	-	-	+
6	ac	+	-	+	-	-	-
7	bc	-	+	+	-	-	-
8	abc	+	+	+	-	-	+
9	d	-	-	-	+	-	+
10	ad	+	-	-	+	-	-
11	bd	-	+	-	+	-	-
12	abd	+	+	-	+	-	+
13	cd	-	-	+	+	-	-
14	acd	+	-	+	+	-	+
15	bcd	-	+	+	+	-	+
16	abcd	+	+	+	+	-	-
17	e	-	-	-	-	+	+
18	ae	+	-	-	-	+	-
19	be	-	+	-	-	+	-
20	abe	+	+	-	-	+	+
21	ce	-	-	+	-	+	-
22	ace	+	-	+	-	+	+
23	bce	-	+	+	-	+	+
24	abce	+	+	+	-	+	-
25	de	-	-	-	+	+	-
26	ade	+	-	-	+	+	+
27	bde	-	+	-	+	+	+
28	abde	+	+	-	+	+	-
29	cde	-	-	+	+	+	+
30	acde	+	-	+	+	+	-
31	bcde	-	+	+	+	+	-
32	abcde	+	+	+	+	+	+

Where the following chart indicates layout criteria

		+	-
		Dip	
A	TiO ₂ Layer	Coated	Paste
B	TiO ₂ Thickness	Thick	Thin
C	Heat Temp	High	Low
D	Heat Time	Long	Short
E	Dye Type	Blackberry	Pomegranate
F	Catalyst	Yes	No

5.3 Construction and Testing of the Solar Cells

5.3.1 Cell Construction

The cells were constructed by first cutting ITO coated glass into 64 pieces of 1 inch squares using a glass cutter. Half of the cells were segregated for use as anodes and set aside. The remaining plates were divided again, with 16 designated for dip coating and 16 for paste.

Paste was mixed by placing approximately 1cc of TiO_2 powder on a mixing plate. To this was added 0.5 cc of 10% acetic acid mixed with water. The mixture was kneaded until no lumps of dry powder remained, and a paste was achieved. The conductive side of the plates was found, and to all 16 of them adhesive tape was applied on three sides, making a frame around the edges. To eight of the slides, a second layer of tape was applied, creating a double thickness of tape. This procedure made the high and low thicknesses of the paste samples. The hollow center of each plate was then filled with paste. The paste was smoothed and the excess removed by using a straight edge as a doctor blade with the tape as a guide. The tape was then removed and the samples were ready for firing. Figure 3 is a photo of a cathode ready for paste and another after the paste has been applied and the tape removed.

Figure 3 Cathode on Right Ready for Application of Paste, On Left After Removal of Tape

Dip coating was mixed by adding 5.22 g Titanium Butoxide to 21.2 g Ethanol and 1.84 g of acetic acid. The mixture was allowed to mix for two hours at medium speed. At that point 21.2 g of Ethanol was added, along with 0.55 g of water added drop wise. This was allowed to stir for 16-20 hours, after which a white liquid was present. All 16 of the

plates were dipped at an extraction speed of 200 mm/sec, as seen in Figure 4. Eight of these represented the low thickness of the dip coated samples. All were allowed to air dry, and eight were dipped a second time at the same speed to make the high thickness level samples. These were then ready for firing.

Figure 4 Dip Coating of Anodes

Firing was done by pre-heating an oven to 300° C. Samples to be fired at that temperature were placed in the oven and allowed to soak for the appropriate time, ten or thirty minutes depending on the requirement from Table 1. The high temperature samples were prepared in the same way according to the table, but with the oven set at 450° C. At this point the samples were numbered so that they could be identified.

Dye was prepared by simply extracting juice from fruit. The berry juice was simply squeezed from California Blackberries, and 100% pomegranate juice from concentrate was purchased. Dyes were applied to the semi-conductor according to the table and allowed to dry. Just enough dye was applied to stain the semiconductor, usually three or four drops. Graphite was applied to the appropriate samples as seen in Figure 5 according to the schedule.

Figure 5 Application of Graphite Catalyst to Anode

Iodide solution was made by mixing 0.5 moles of potassium iodide with 0.05 moles of water-free ethylene glycol. Three drops were applied to one of the plates, and they were then put together. Once clamped the solar cells were ready for testing. This assembly process can be seen in Figure 6. Note that the binder clips serve as clamps, and are not used for electrical conduction.

Figure 6 Assembly of Cells

5.3.2 Power Curve Data Collection

Open Circuit Voltage and Power data were taken immediately upon construction of each sample cell. Samples were placed in a light box with direct exposure to a standard 70 watt electric light bulb at a distance of approximately four inches, as seen in Figure 7. The interior of the box was painted white so that all surfaces would reflect back to the cell. Leads with alligator clips were used to connect the solar cells, with one on the anode and another on the cathode.

Figure 7 Cell in Light Box with Leads to Circuit

In order to collect the appropriate data, the dual mode circuit in Figure 8 was created because two measurements must be taken for each data point. For each data point, both the resistance and voltage must be measured, where power is calculated according to Equation 3. A photo showing the set-up is provided in Figure 9.

Figure 8 Circuit Layout for Power Data Collection

$$P = \frac{V^2}{R},$$

where

$P = \text{Power}$ (Watts),

$V = \text{Voltage}$ (Volts),

$R = \text{Resistance}$ (Ohms).

Equation 3

The circuit was used by first closing the switch and setting the potentiometer to the lowest level that still produced a measurable voltage drop across the resistance. This voltage was measured by a multimeter, the value was recorded and the switch was opened. The resistance of the potentiometer was also measured by the multimeter. The switch was closed, the multimeter reset to measure voltage, and the potentiometer was moved until the voltage drop reading changed. This process was repeated until the power level no longer increased, at which point a maximum had been reached.

Samples must be made and tested in a random fashion to randomize error. The samples were randomized, and the order of testing was as follows: 23, 19, 27, 25, 31, 29, 17, 21, 18, 24, 30, 26, 20, 32, 22, 28, 13, 2, 8, 12, 3, 16, 14, 5, 6, 4, 10, 9, 11, 1, 7, and 15.

Figure 9 Data Collection

6. Results and Discussion

6.1 Thickness

Using these application methods, it was not possible to control the precise thickness of the TiO₂ layer at the time of application. In order to determine the thickness, it was measured after firing. Using a Profilometer (Veeco Dektak 150), thicknesses of representative samples were measured. The thicknesses are reported in Table 2.

Table 2 Measured Mean Thicknesses of Semi-conducting Layer

Cell Configuration	Thickness
Dip Coated, Thin Layer	140 nm
Dip Coated, Thick Layer	270 nm
Paste Applied, Thin Layer	55 μm
Paste Applied, Thick Layer	86 μm

The surface of the dip coated samples was quite rough, with particles making large peaks in the profile ranging from 2-500 nm for the single dipped samples, and 5-1000 nm on the double dipped samples. The surfaces of the paste applied samples were significantly smoother and more even than the dip coated samples. However, adhesion of the TiO₂ particles to the ITO glass was considerably higher on the dip coated samples, as observed on the samples.

6.2 Power Output

Power output of the cells was determined by measuring both the resistance of the potentiometer and the voltage drop across it at various increments. Using Equation 3, the power output at each point was calculated, and by systematically increasing resistance of the potentiometer, the maximum power was determined.

Maximum power is reached when the resistive load equals the internal resistance of the solar cell.⁴³ The internal resistance in this apparatus includes the contact resistance of the alligator clips to the glass slides. In order to ensure that the clips made a negligible difference to the apparent resistive load, resistivity of the connection was tested separately. Five samples were evaluated two ways, each at a distance of one inch between the connectors. First a 1/16 inch copper rod was inserted between the alligator clip and the conductive side of the glass, and resistance was measured. Next the clips were connected directly to the glass, and the resistance was measured again. The average difference between these was calculated to be 1.44 kOhms. Average difference was used

because the resistivity of the conductive coating is independent of attachment method. The average resistance of all cells at maximum power was 40.84 kOhms. The contact resistance was therefore an average of 3.5% of the apparent internal resistance of the cell, and can be neglected as insignificant.

The area of each cell was measured so that the output could be standardized to a per-square-meter basis. The maximum power output for each cell can be seen in Table 3. The raw data for each cell and its corresponding power curve is presented in Appendix A.

Table 3 Maximum Output of All Cells

Cell	Power (mW/m ²)		Cell	Power (mW/m ²)
1	0.05		17	0.91
2	0.00		18	0.00
3	5.13		19	0.46
4	0.00		20	0.32
5	5.75		21	3.93
6	0.75		22	3.21
7	0.19		23	1.85
8	0.09		24	1.25
9	4.72		25	0.87
10	0.00		26	0.05
11	0.01		27	4.41
12	0.08		28	0.01
13	1.63		29	4.48
14	0.13		30	0.54
15	5.39		31	0.56
16	0.16		32	7.42

6.3 Statistical Analysis

The data from Table 3 was input into a Statistical Analysis System (SAS) program capable of quickly and accurately performing the analysis. It was programmed to analyze the six main factors and all two factor interactions. The analysis of variance (ANOVA) is shown in Table 4.

Of particular interest is the statistical significance, which is determined by the F-test. The F-test compares the variance of two sets of data. The value is then compared to a risk value set by the experimenter. The risk value, commonly denoted as alpha (α), was selected to be 0.05, which is generally considered a reasonable rule of thumb. This means that there is a 5% chance that a significant difference will be found where none exists. Conversely, there is a 95% confidence that the statistical significance is real.

Table 4 ANOVA for the Designed Experiment

ANOVA for Response Y

Source	Master Model						Predictive Model				
	DF	SS	MS	F	Pr > F		DF	SS	MS	F	Pr > F
A	1	21.633	21.633	6.149	0.033		1	21.632	21.632	7.579	0.010
B	1	0.003	0.003	0.001	0.978						
C	1	12.909	12.909	3.669	0.084		1	12.909	12.909	4.523	0.042
D	1	1.352	1.352	0.384	0.549						
E	1	1.202	1.202	0.342	0.572						
F	1	35.083	35.083	9.972	0.010		1	35.083	35.083	12.291	0.0012
A*B	1	2.523	2.523	0.717	0.417						
A*C	1	1.075	1.075	0.305	0.593						
A*D	1	0.103	0.103	0.009	0.925						
A*E	1	9.012	9.012	2.561	0.141						
A*F	1	8.373	8.373	2.380	0.154						
B*C	1	1.688	1.688	0.480	0.504						
B*D	1	3.747	3.747	1.065	0.326						
B*E	1	0.570	0.570	0.162	0.696						
B*F	1	3.493	3.493	0.993	0.343						
C*D	1	1.50E-05	1.50E-05	4.60E-06	0.998						
C*E	1	4.578	4.578	1.301	0.281						
C*F	1	0.804	0.804	0.228	0.643						
D*E	1	1.224	1.224	0.347	0.568						
D*F	1	4.686	4.686	1.332	0.275						
E*F	1	0.376	0.376	0.106	0.751						
Model	21	114.361	5.446	1.548	0.241		3	69.624	23.28	8.131	4.75E-04
Error	10	35.181	3.518				28	79.918	2.854		
(Lack of Fit)							4	13.605	3.401	1.231	0.324
(Pure Error)							24	66.313	2.763		
Total	31	149.542					31	149.542			

The program determines the target F distribution, and calculates the F-value for the given data for comparison. If the F-value is greater than the calculated value, then it is outside of the distribution of where it would be expected to fall, and is therefore statistically significant.⁴² Statistical significance was found in three of the main factors and none of the two factor interactions. The F-Test Values from the ANOVA chart can be seen in Table 5.

Table 5 F-Test Values Extracted From ANOVA Table

Factor	Description	F-Master	F-Predictive
A	TiO ₂ Paste/Dip Coating	6.149	7.579
C	Heating Temperature	3.669	4.523
F	Catalyst	9.972	12.291

Regression analysis determines the degree to which these factors impact the final result (Y) and provides a predictive equation for the response. Using the least squares method for estimating the coefficients in Equation 1, the regression equation in Equation 4 was calculated in coded units.

$$Y = 1.699 - 0.8222 * A + 0.6351 * C + 1.047 * F \quad \text{Equation 4}$$

A more meaningful equation in terms of natural units is represented in Equation 5. Using this equation, it is possible to predict the estimated maximum power output of any cell from these three parameters.

$$E(Y) = -3.301 - 0.8222 * A + 0.0133 * T + 1.047 * F$$

Where

A = + 1 for Dip Coat, - 1 for Paste

F = + 1 for Catalyst, - 1 for No Catalyst

T = Temperature (Valid only between 300 °C and 450 °C)

Equation 5

From the constants in the equation it is possible to infer some information about the relative impact of each of these factors on the results. The catalyst (F) determines the greatest impact to the result, given that the constant associated with that factor has the largest absolute value. It is also important to note that the constant associated with TiO₂ layer (A) is negative. This indicates that if a negative value, meaning paste, were used, the resulting power would be higher than if a positive value were used, meaning that paste has a greater impact than dip coating. Higher temperature (C) is less of a factor, although still significant.

The regression analysis provides additional information about the predicted response. Equation 4 produces a value for expected response based solely on these three factors. They have such a significant impact that these three alone account for 46.6% of the total response. The other 29 factors and interactions contribute the remaining 53.4 % of the variance in the model.

7. Conclusions

The three most important factors contributing to the power output of the cells in this study are the use of catalyst, application method of the TiO_2 layer and achieving a high sintering temperature.

7.1 Catalyst

Catalyst was either present or absent. Its use provided the single highest contribution to the overall power output. This is apparent by comparing the mean power output of the 16 cells with catalyst at 2.746 mW/m^2 to the mean power output of the 16 cells without catalyst at 0.652 mW/m^2 . Finding a more efficient catalyst may provide the most significant improvement to dye sensitized solar cell design.

7.2 TiO_2 Layer

Two methods of application for the semi-conducting layer were employed, which imparted significantly different surface features and thicknesses. For this reason the thickness factor (B) is not meaningful when comparing between the different application methods. A comparison of mean power output of the eight cells of the separate type and thicknesses can be seen in Table 6.

Table 6 Power Output Comparison between TiO_2 Application Method and Thickness

	Thin	Thick	Difference	Power
Paste	2.792	2.249	-0.542	mV/m^2
Dip Coat	0.586	1.167	0.580	mV/m^2

The power output of the thick paste cells was lower than the thin paste cells. However the power output of the thick dip coated cells was higher than their thin counterparts. This is likely because the thickness of the paste cells was significantly higher than the dip coating method, and may have been so high that an insulating layer was created. On the other hand the thin dip coated cells were so thin that there was very little semi-conducting material available for reaction. The thicker dip coated cells had more semi-conductor than the thin ones, and could therefore process more electrons. A thickness between these two values may help to optimize the design.

7.3 Temperature

Sintering is required in order to change the crystal structure of TiO_2 , as un-sintered material chelates poorly with organic dyes. The higher temperature denoted as statistically significant indicates that a temperature near to 450°C is required to achieve improved chelation.

8. Recommendations

Three important factors in production of dye sensitized solar cells were identified through the use of a designed experiment and regression analysis. Additional work is required to completely optimize construction of such cells, including refining of values for these factors. Additional factors can also be studied such as different classes of dyes, different types of semi-conductors, and solid state (dry) electrolytes. Additional designed experiments and regression analysis should be used to improve knowledge about these factors. Experiments with more than two levels will be required in order to optimize the design.

Appendix A – Raw Data and Power Curves

The following charts show the raw data as collected from the circuit in Figure 8. The resistance and voltages are actual measurements, and the power calculations are based on

Equation 3. Maximum power is the highest level indicated. The length and width of each cell was measured so that all cells could be standardized to a square centimeter basis. The maximum power values were collected to make Table 3.

Cell #	Date	8-May-08		
5	Length (in)	0.774	Area (cm ²)	3.5753735
	Width (in)	0.716	OCV (Volts)	0.24
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	0.15	1.3	3.15E-05	
	0.85	9.5	2.97E-04	
	2.52	29.5	9.66E-04	
	3.2	44.4	1.72E-03	
	4.49	62.9	2.46E-03	
	6.44	87.9	3.36E-03	
	7.3	108.6	4.52E-03	
	8.3	130.4	5.73E-03	
	9.89	142.6	5.75E-03	
	11.45	151.6	5.61E-03	
			Max Power	5.75E-03

Cell #	Date	8-May-08		
6	Length (in)	0.959	Area (cm ²)	5.277583
	Width (in)	0.853	OCV (Volts)	0.18
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	0.32	2.2	2.87E-05	
	1.25	9.6	1.40E-04	
	2.58	19.9	2.91E-04	
	3.76	28.8	4.18E-04	
	5.96	41.8	5.55E-04	
	8.05	52.4	6.46E-04	
	9.84	60.4	7.02E-04	
	13.16	71.6	7.38E-04	
	15.96	79.7	7.54E-04	
	21.6	92.1	7.44E-04	
			Max Power	7.54E-04

Cell #	Date	8-May-08		
7	Length (in)	0.737	Area (cm ²)	3.3711739
	Width (in)	0.709	OCV (Volts)	0.08
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	2.63	2.2	5.46E-06	
	5.44	6.3	2.16E-05	
	11.05	15.0	6.04E-05	
	17.95	25.1	1.04E-04	
	36.6	43.9	1.56E-04	
	71.6	63.9	1.69E-04	
	80	71.8	1.91E-04	
	126.3	87.3	1.79E-04	
			Max Power	1.91E-04

Cell #	Date	7-May-08		
8	Length (in)	0.934	Area (cm ²)	4.4771652
	Width (in)	0.743	OCV (Volts)	0.17
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	0.36	2.2	3.00E-05	
	2.09	8	6.84E-05	
	3.46	11.3	8.24E-05	
	5.11	14.1	8.69E-05	
	6.38	15.2	8.09E-05	
	11.36	19.1	7.17E-05	
			Max Power	8.69E-05

Cell #	Date	8-May-08		
9	Length (in)	0.735	Area (cm ²)	3.3430578
	Width (in)	0.705	OCV (Volts)	0.2
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	0.22	2.4	7.83E-05	
	0.8	10.4	4.04E-04	
	3.07	40.8	1.62E-03	
	5.88	76.0	2.94E-03	
	7.72	97.7	3.70E-03	
	11.07	126.8	4.34E-03	
	14.21	149.7	4.72E-03	
	24.9	189.9	4.33E-03	
			Max Power	4.72E-03

Cell #	Date	8-May-08		
10	Length (in)	1.019	Area (cm ²)	5.4697181
	Width (in)	0.832	OCV (Volts)	0.01
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	0.63	0.4	4.64E-07	
	7.94	3.6	2.98E-06	
	15.66	6.2	4.49E-06	
	37.5	8.5	3.52E-06	
			Max Power	4.49E-06

Cell #	Date	8-May-08		
11	Length (in)	0.76	Area (cm ²)	4.1137982
	Width (in)	0.839	OCV (Volts)	0.06
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	0.64	1.0	3.80E-06	
	2.36	2.2	4.99E-06	
	6.68	4.4	7.05E-06	
	17.52	5.6	4.35E-06	
			Max Power	7.05E-06

Cell #	Date	7-May-08		
12	Length (in)	0.707	Area (cm ²)	4.8486419
	Width (in)	1.063	OCV (Volts)	0.12
	R (kOhms)	V (mV)	Power (W/m ²)	$= (V^2/R)/\text{area} * 1000$
	0.29	1.1	8.61E-06	
	0.73	2.9	2.38E-05	
	3.28	10.8	7.33E-05	
	5.28	14.2	7.88E-05	
			Max Power	7.88E-05

Cell #	Date	6-May-08		
13	Length (in)	0.89	Area (cm ²)	3.6461217
	Width (in)	0.635	OCV (Volts)	0.27
	R (kOhms)	V (mV)	Power (W/m ²)	$=(V^2/R)/\text{area} \times 1000$
	0.416	5	1.65E-04	
	2.3	26	8.06E-04	
	4.32	41.3	1.08E-03	
	5.38	50.8	1.32E-03	
	6.46	58.1	1.43E-03	
	9.66	75.3	1.61E-03	
	13.17	88.5	1.63E-03	
	16.76	99.5	1.62E-03	
			Max Power	1.63E-03

Cell #	Date	7-May-08		
14	Length (in)	0.887	Area (cm ²)	5.579505
	Width (in)	0.975	OCV (Volts)	0.1
	R (kOhms)	V (mV)	Power (W/m ²)	$=(V^2/R)/\text{area} \times 1000$
	0.34	1.9	1.90E-05	
	1.93	9.2	7.86E-05	
	4.9	17.6	1.13E-04	
	7.01	21.9	1.23E-04	
	9.37	26.1	1.30E-04	
	13.43	28.2	1.06E-04	
			Max Power	1.30E-04

Cell #	Date	8-May-08		
15	Length (in)	1.08	Area (cm ²)	6.0061815
	Width (in)	0.862	OCV (Volts)	0.29
	R (kOhms)	V (mV)	Power (W/m ²)	$=(V^2/R)/\text{area} \times 1000$
	0.18	5.4	2.70E-04	
	4.93	108.6	3.98E-03	
	5.57	120.6	4.35E-03	
	6.61	137.6	4.77E-03	
	7.68	152.6	5.05E-03	
	8.95	167.5	5.22E-03	
	10.78	186.8	5.39E-03	
	12.87	201.0	5.23E-03	
			Max Power	5.39E-03

Cell #	Date	7-May-08		
16	Length (in)	0.708	Area (cm ²)	4.1246627
	Width (in)	0.903	OCV (Volts)	0.11
	R (kOhms)	V (mV)	Power (W/m ²)	$=(V^2/R)/\text{area} \times 1000$
	0.3	1.9	2.92E-05	
	1.6	8.9	1.20E-04	
	4.2	16.1	1.50E-04	
	6.39	20.6	1.61E-04	
	9.02	24.7	1.64E-04	
	12.33	28.3	1.57E-04	
			Max Power	1.64E-04

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