



Characterizing Variability in Smestad and Grätzel's Nanocrystalline Solar Cells: A Collaborative Learning Experience in Experimental Design

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Key Words: Variance Component, Staggered Nested Design, Complex Aliasing, Plackett-Burman Design

Abstract

This article describes a collaborative learning experience in experimental design that closely approximates what practicing statisticians and researchers in applied science experience during consulting. Statistics majors worked with a teaching assistant from the chemistry department to conduct a series of experiments characterizing the variation in measured voltage output of Smestad and Grätzel's nanocrystalline titanium dioxide (TiO₂) solar cells.

These solar cells can be constructed easily in a laboratory, and they are reported to produce an open circuit voltage in direct sunlight of 0.3 to 0.5V. Statistics students planned a series of experiments as part of an experimental design class, and the chemistry TA performed the experiments in the lab where the statistics students could observe. The students wrote a description of what they did and the results. From the students' comments about what they learned from this experience, it appears that this type of exercise could be very beneficial in training future consulting statisticians and scientists or technologists who will use experimentation in their work.

1. Introduction

Since the article by [Hunter \(1977\)](#) on teaching design of experiments, much has been written about the value of hands-on experience for students in experimental design classes, including recent articles by [Richardson et al. \(2005\)](#) and [Steiner et al. \(2008\)](#). Recent textbooks ([Dean and Voss 1990](#), and [Lawson 2010](#)) also show many examples of experiments conducted by students. [Mackisack \(1994\)](#) stated that successful student projects usually involve experiments aimed to quantify some simple obvious effects that are strongly suspected to be present and that are based on activities already familiar to students, such as sports. Conversely, [Easterling \(2004\)](#) advocated using examples that are credible in a scientific or business context in order to convince students of the value of experimental design and analysis in their subsequent careers. Demonstration experiments from disciplines that use laboratories, such as biology, chemistry, and engineering, provide an ample source of credible problems that can be used for hands-on practice with experimental designs.

Laboratory demonstration experiments from other disciplines traditionally use the vary-one-factor-at-a-time approach to illustrate simple cause-and-effect relationships. However, [Fisher \(1971\)](#) explained that this approach is not very helpful in genuine research intended to advance the state of knowledge. These demonstrations could be easily modified to incorporate modern DOE techniques. In some demonstration experiments there is more than one potential independent variable; thus the opportunity exists to use experimental design techniques that are very efficient for multifactor plans. Doing so would have double benefits. Students from disciplines that use laboratory experiments usually learn a less-than-optimal way to approach research problems. By incorporating DOE techniques in their laboratory experience, students would be exposed to more effective research techniques. Statistics majors could also benefit by helping to design laboratory experiments and by analyzing the data. Most statistics majors have never been inside a laboratory and have never experienced the realities of performing physical experiments and collecting data. Having this experience will make them more effective consultants.

This article describes a trial case of involving statistics students to design and analyze experiments for a lab demonstration project normally used by chemistry departments. The project described here was not part of a normal chemistry lab class, but was performed one time to specifically involve students in an experimental design class. Since the experimental design class was small, all the students participated together to plan the experiments and analyze the data, rather than doing individual projects themselves. They collaborated with a teaching assistant who was hired from the chemistry department to actually perform the experiments in a lab where the statistics students could observe and record the results. The project ended up involving a series of experiments aimed at answering a specific research question.

The specific demonstration experiment considered was Smestad and Grätzel's dye-sensitized nanocrystalline titanium dioxide (TiO_2) solar cells (Smestad and Grätzel 1998). Much has been written about the possibilities of producing inexpensive solar energy using TiO_2 nanocrystals to demonstrate the relevance of TiO_2 solar energy research (see Lewis 2007, for example). Smestad and Grätzel developed a simple chemistry lab demonstration experiment to create TiO_2 solar cells. These cells, called *Grätzel cells*, can be made by sintering a film of TiO_2 paste onto a conductive, tin-coated microscope slide in an oven, staining the film with berry juice, clipping a carbon coated conductive microscope slide on top as a counter electrode, and allowing an electrolyte solution to seep between the slides by capillary action. Several step-by-step descriptions of this procedure, with illustrations, can be found online with sources for all materials (Johnsen and Chasteen 2006, <http://www.sciencegeekgirl.com/activities/Blackberry%20solar%20cell.pdf>).

To create TiO_2 solar cells in the lab, there are multiple process steps that must be completed and there are several potential factors that could be varied at each step. The response is the voltage produced by the solar cell in a constant light source. This response is both objective and quantitatively measured. The published information about the experiment indicates that voltage resulting from the Grätzel cells should be in the range of 0.3V to 0.5V, but it does not explain what causes the variability. Consequently, the research question the students focused on was identifying which factors affect voltage, and what conditions or factor settings would result in consistently high voltage readings.

2. The Collaborative Learning Experience

Table 1 presents a timeline showing the topics that were taught in the experimental design class week by week along with a short description of project activities completed at the same time. The first week of class, the instructor described Grätzel cells and introduced the idea of determining which factors influenced variability. Students were shown diagrams of

how the solar cells work and photographs of steps in the laboratory process followed to create these cells.

Materials to conduct the laboratory experiments were ordered before the first week of class. However, due to problems with one of the suppliers, and the fact that the wrong TiO_2 powder was initially ordered, it wasn't until the tenth week of class that all materials were available to conduct experiments.

In the meantime the project was in the back of the students' minds as they learned experimental design techniques that might help them solve the problem. In the first week, when definitions of factors, experimental units, responses, lurking variables, etc. were presented in class, students were asked to apply these definitions in class discussions to the aspects of the demonstration experiment they would eventually be working on. Having a concrete example that the students would become involved with helped them become more engaged in the discussions and ideas.

As the first 10 weeks of the semester progressed, part of the class discussions explored how each of the experimental design techniques being studied could be applied to the lab project that would begin when the materials arrived.

Table 1. Project Timeline and Class Topics

Week	Class Topics	Project Activities
1	Introduction, Definitions, Cause and Effect Relations, Checklist for Planning Expts., and CRD for one factor.	Introduced problem of optimizing Grätzel cells. Discussed definitions in relation to the problem.
2	Factorial Designs, two-factor, multifactor, 2^k	Discussed potential factors for studying Grätzel cells.
3	RCB Designs, factorials in RCB, generalized block designs	Discussed potential blocking factors in lab experiments.
4	Latin Square, Sampling Experiments, Variance Component Estimation	TA prepared oven for experiments. Discussed sources of variance in experiments.
5	Nested and staggered nested designs, designs with fixed and random factors	Discussed applicability of nested designs to determine sources of variability in Grätzel cells.

Table 1. Project Timeline and Class Topics, continued

Week	Class Topics	Project Activities
6	2^{k-p} designs, augmenting fractional factorial designs, Plackett-Burman designs	Discussed possible use of screening designs in <i>Grätzel cell</i> expts.
7	Mixed-level FF designs using Orthogonal Arrays(OA), BIB PBIB and Youden Square designs	Discussed applicability to <i>Grätzel cell</i> expts.
8	Confounded Block designs Blocking OA designs	
9	Split-Plot Designs, fractional factorial split plot designs	Discussed value of split-plot for studying multistep processes.
10	Sample size estimation for split-plot designs Crossover designs	All materials are ready for lab experiments.
11	Design and analysis of repeated measure experiments	TA performs pilot experiment for students to observe.
12	Response Surface designs Non-standard RS designs Analysis of RS designs	Discussed where to start; students plan sampling experiment.
13	RS designs in split plots, mixture experiments, analysis of mixture experiments	TA performs sampling experiments for students to observe.
14	Constrained mixture experiments, mixture experiments with process variables	Students analyzed data, proposed factors for screening experiment, and planned PB design.
15	Split-plot mixture experiments	TA performed screening experiment, students analyzed data and proposed confirmation experiment.
16		TA performed confirmation experiment.

Since the demonstration experiment was so rich in possibilities, virtually all design techniques studied in the first nine weeks of class seemed applicable. When the instructor asked the students in class to consider how a particular method might be used for the lab project, students had plenty of ideas and were willing to share them in class discussions.

When all materials for conducting the experiments were finally available, the instructor suggested that the chemistry TA conduct a pilot experiment (see [appendix](#) for details) to see if the steps of Smestad and Grätzel's procedure could actually be repeated in our lab.

This suggestion was based on the recommendation for a pilot experiment in the checklist for planning experiments given by Bisgaard (1999). By observing the pilot experiment conducted in the lab, students could see how long it took to construct and test a *Grätzel cell*, and the physical realities of what factors could be varied in future experiments. They also realized there are basically seven steps to creating a TiO_2 solar cell in the lab, as shown in Figure 1.

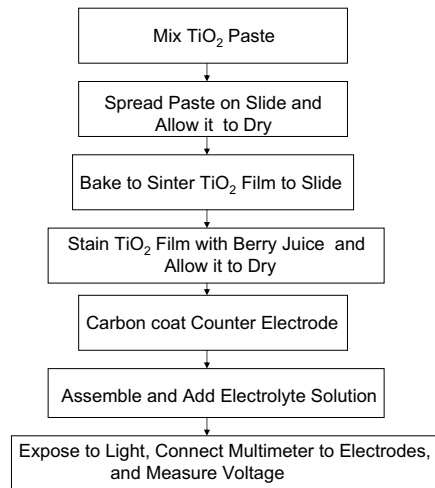


Figure 1. Steps in the creation of a TiO_2 solar cell

At this point, the instructor challenged the students to plan experiments to determine which factors caused the voltage variability in the solar cells and, if possible, to determine conditions that would consistently produce voltages near the maximum possible output voltage (0.5 V). This created an atmosphere similar to that of an initial consultation between a client and a statistical consultant. Since students had recently studied split-plot experiments in the experimental design class, and they were shown to be efficient for studying multistep processes, the students initially considered some type of split-plot experiment. However, it was late in the semester and there were only 23 conductive microscope slides remaining to be used in experimentation. Since there were several factors that could be varied at each process step, the problem seemed daunting.

When there are multiple process steps and little knowledge about which factors may be influential at each step, the textbook used in the class (Lawson, 2010) recommends starting with a variance component study (illustrated in Figure 2) so that resources are not wasted studying factors that may contribute little to variability. This topic was studied the fourth and fifth weeks of class. Since there seemed to be too many potential factors to study, the students decided to start with a variance component study to see if they could focus further

experiments on the process steps that contributed the most variability to voltage readings. They reached this decision by consensus in a class discussion.

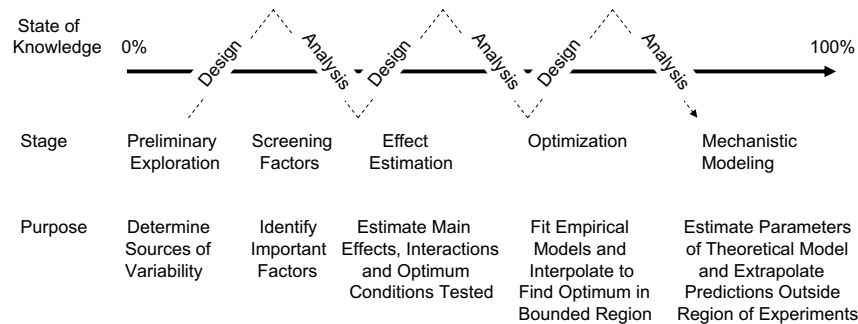


Figure 2. Experimentation and the state of knowledge

Outside of class, students planned a staggered nested design as described in the textbook. They prepared a list of experiments for the TA to perform, and again observed the experiments being conducted in the lab. Again outside of class, they analyzed the data and summarized their findings. They found that most of the variability in the voltage readings resulted from inconsistencies in one process step.

Based on observations in the lab, a brainstorming session was held in class during which the students and instructor considered what procedures in the critical process step may have been inconsistent in the variance component study. Based on the ideas generated, some potential factors for a screening experiment were suggested. The TA was consulted to see if the suggested factors could be varied in further experiments. After getting a positive response from the TA, the students planned a screening experiment to see if they could identify significant factors in the process step where the most variability in voltage readings had been observed. Again, this was done outside of class and reviewed by the instructor in the next session. Next, the students prepared a list of experiments for the TA to perform.

After observing the screening experiments being conducted in the lab, they analyzed the resulting data with guidance from the instructor and reference to an example in the textbook. They determined the factors and interactions that had significant effects on voltage. Based on a model incorporating the significant effects, they predicted conditions that would result in the maximum voltage, and recommended one confirmation experiment to be conducted with the one remaining microscope slide.

3. Details of the Statistical Work Performed by Students

3.1 Sampling Experiment

In the variance component study, all of the Grätzel cells were constructed and tested in the same way, but organized so that the variability in voltage readings could be attributed to different process steps. These experiments investigated four specific process steps:

- Preparing the TiO_2 paste
- Baking the slides in the oven
- Making two slides for each oven run
- Putting the slide together and measuring the voltage

The resulting data allowed the estimate of the total variance, σ_T^2 , to be partitioned into the following variance components: $\sigma_B^2 + \sigma_O^2 + \sigma_S^2 + \sigma_A^2 = \sigma_T^2$. Component σ_B^2 represents the variance from one paste batch to another, and it would be caused by any differences in the way the paste batches were prepared. Component σ_O^2 represents the variance from one oven run to another within the same paste batch, and it would be caused by differences in the oven conditions from run to run. Component σ_S^2 represents the variance from slide to slide within an oven run, and it would be caused by any differences in the way slides were prepared from the same paste batch. Finally, component σ_A^2 is the variance in re-tests of the same slide.

A staggered nested design was used, as described by [Lawson \(2010\)](#) and illustrated in [Figure 3](#). This type of design allows estimation of variance components with fewer experiments than would be required by a fully nested design. In accordance with this design, the TA prepared three batches of TiO_2 paste. From each batch of paste, three slides were coated with TiO_2 . Two of the three slides from each batch were baked together in one oven run, and the third slide was baked alone in a second oven run. One of the two slides baked together in the same oven run was selected for repeat testing, and the other two slides from each batch were tested only once.

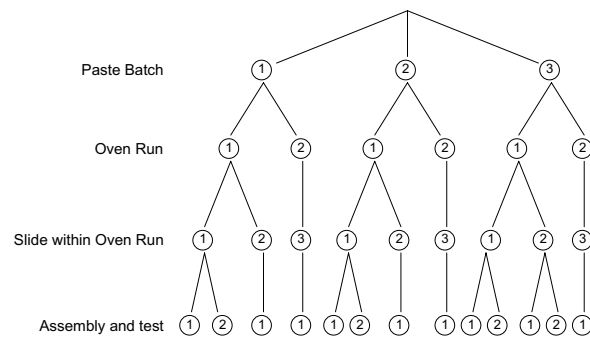


Figure 3. Staggered nested design

This process resulted in the use of a total of nine slides. One additional slide was used for the carbon-coated electrode on all of the nine slides. Three slides were planned to be re-tested, and it was decided to re-test one additional slide later. The results are shown in Table 2, where the re-test of observation 11 was observation 13. This experiment resulted in a total of 13 tests made using only 10 slides. The level indicators for Batch, Oven Run, etc. in the table correspond to the nodes shown in Figure 3. The voltages ranged from .34-.46, consistent with what had been reported in the literature for Grätzel cells.

Table 2. Staggered Nested Design

Observation	Batch	Oven Run	Slide	Assembly	Voltage
1	1	1	1	1	.41
2	1	1	1	2	.46
3	1	1	2	1	.435
4	1	2	3	1	.37
5	2	1	1	1	.405
6	2	1	1	2	.44
7	2	1	2	1	.34
8	2	2	3	1	.405
9	3	1	1	1	.45
10	3	1	1	2	.455
11	3	1	2	1	.38
12	3	2	3	1	.45
13	3	1	2	2	.44

To obtain estimates of the variance components, the restricted maximum likelihood (REML) approach was used. The results are shown in Table 3. This table shows that the majority of the variation comes from retesting the same slide. It was also noticed that the voltage was higher for every slide retested than on the initial test of that slide. This observation led to

some ideas about what might have been different in initial and repeat tests.

Table 3. Variance Component REML Estimates

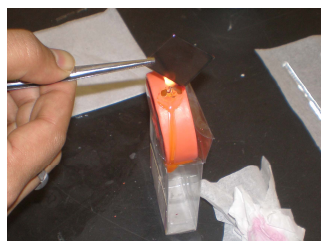
Variance Component	Estimate	Percent of Total
Batch	0.00006469	4.6%
Oven Run	0	0.0%
Slide	0.0001299	9.1%
Re-test	0.0012249	86.3%

3.2 Screening experiment

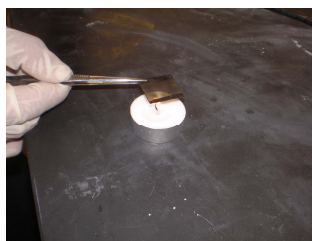
The next step was to run a screening experiment to try and identify the important factors causing increased voltage on retest cells. The primary focus was to purposely vary factors that were believed to have changed from the first test to the re-test on re-tested slides. The factors first thought of in a brainstorming session were the following:

1. Amount of carbon on the cover slide
2. Concentration of the electrolyte solution
3. Time in light before testing

The first candle used to deposit carbon was expended in the course of experiments. The second candle used was different, and it was felt that it may have deposited more or less carbon on the counter electrode. The amount of carbon on the cover slide could be controlled by the time the slide was held over a burning candle. Thus, this was included as a factor in the design. The high and low levels of the amount of carbon are illustrated in Figure 4.



(a) heavy carbon



(b) light carbon

Figure 4. Carbon coating counter electrode

The iodide electrolyte solution was allowed to seep between the slides of the solar cell as illustrated in [Figure 5](#). The left picture in this figure shows the electrolyte solution being applied to the bottom offset slide that has the baked-on TiO_2 layer. The right picture in this figure shows the electrolyte solution seeping between the slides by capillary action. After a solar cell was tested, the cover slide was removed, cleaned, and reused on the next cell tested. The iodide electrolyte solution on the TiO_2 layer of a cell that had been disassembled was allowed to dry overnight. When that cell was reassembled for retesting, the iodide solution was reapplied, leading to the hypothesis that the iodide concentration was higher on cells that were retested. In the screening experiment, the high concentration of electrolyte was created in the same way by disassembling a slide, allowing the electrolyte to dry, and then reassembling and reapplying the electrolyte before testing.



Figure 5. Adding iodide electrolyte solution

The time in the light prior to connecting the electrodes was not timed in the variance component study, and it was felt that the time could have differed between initial tests and retests of the same slide. Therefore, this was also included as a factor in the design.

It would require eight slides to study three factors at two-levels each in a full factorial without replicates. However, it would be easy to test more than three factors in a fractional factorial design. Therefore, additional factors were sought that were easy to vary and could have affected voltage in the variance component study.

Although neither the type of berry juice nor amount of berry juice used to stain the slides had been changed in the variance component study, they were easy to vary. It was decided to include them as factors in the screening design to see whether they had a significant influence on voltage. Blackberry juice was chosen as an alternative to pomegranate, and it was decided to vary the amount of juice used to stain the TiO_2 film by doubling the number of drops of juice applied on half the tests. The thickness of the TiO_2 layer was not purposely varied in the variance component study, but it was easy to vary and was included as the sixth factor in the screening design. A complete list of all the factors included in the screening experiment and a description of their levels is shown in [Table 4](#).

Table 4. List of Screening Factors and Factor-Level Descriptions

Factor	Factor Level Description
A = Thickness of TiO ₂	“–,” or thin, means one layer of tape was used to create the TiO ₂ reservoir. “+,” or thick, means two layers of tape were used.
B = Time in Light	“–” means test right away. “+” means let the slide sit in the light for three minutes prior to connecting electrodes.
C = Electrolyte Conc.	“–” means one application of electrolyte solution. “+” means apply once, wait until dry, apply again.
D = Amount of Carbon	“–” means the plate was covered with carbon, but not opaque. “+” means the slide was opaque with carbon.
E = Amount of Juice	“–” means two drops of juice. “+” means two drops, wait until dry, then two more drops.
F = Type of Juice	“–” means blackberry juice was used. “+” means pomegranate juice was used.

Since there were 13 conductive slides remaining, it was decided to use a resolution III Plackett-Burman (PB) screening experiment to analyze these factors. [Plackett and Burman \(1946\)](#) developed a screening experiment design that allows more flexibility than a factorial or fractional factorial design by only partially confounding all of the effects. PB experiments are available in run sizes that are multiples of four and allow two levels for each factor. The design used for this study is shown in [Table 5](#). The unassigned columns (u7-u11) are orthogonal to the assigned main effects and represent confounded strings of interactions. By using a screening design with complex aliasing, both factor screening and response optimization could be accomplished in one step (see [Cheng and Wu 2001](#), [Lawson 2003](#)).

A 2^{6-3} 8-run fractional factorial design could have been used, but such a design would only be resolution III and would leave each main effect fully confounded with 2 two-factor interactions. This would leave little ability to identify any potentially important two-factor interactions without follow-up experiments. A 2^{6-4} fractional factorial design could have

been used if there were 16 slides, but there were only 13 slides remaining after the pilot experiment and variance component study. The students decided to use a 12-run PB because it met the resource constraint and only partially confounded main effects with two-factor interactions. The partial confounding allowed a best-subsets regression approach to compare different models consisting of subsets of the main effects and two-factor interactions, thereby making inferences about which factors and interactions were significant. Since it was thought that a two-factor interaction could be significant, the PB design was a better choice than a resolution III 2^{6-3} .

Table 5. 12-run Plackett-Burman design

run	A	B	C	D	E	F	u7	u8	u9	u10	u11	Voltage
1	+	-	+	-	-	-	+	+	+	-	+	0.50
2	+	+	-	+	-	-	-	+	+	+	-	0.45
3	-	+	+	-	+	-	-	-	+	+	+	0.52
4	+	-	+	+	-	+	-	-	-	+	+	0.49
5	+	+	-	+	+	-	+	-	-	-	+	0.50
6	+	+	+	-	+	+	-	+	-	-	-	0.50
7	-	+	+	+	-	+	+	-	+	-	-	0.52
8	-	-	+	+	+	-	+	+	-	+	-	0.50
9	-	-	-	+	+	+	-	+	+	-	+	0.45
10	+	-	-	-	+	+	+	-	+	+	-	0.48
11	-	+	-	-	-	+	+	+	-	+	+	0.50
12	-	-	-	-	-	-	-	-	-	-	-	0.48

The half-normal plot of effects in the left panel of [Figure 6](#) showed only one possibly significant effect (C). Fitting a model that included only main effect C revealed that Factor C was significant at the $\alpha = 0.05$ level, but the model only had $R^2 = 0.42$. The second largest effect in [Figure 6 \(a\)](#) was unassigned column (u7) in the design matrix that was partially confounded with many two-factor interactions. [Lin and Draper \(1992\)](#) and [Wang and Wu \(1995\)](#) showed that since PB designs involve complex aliasing, some interactions are estimable when only a subset of the factors are significant even though the design has resolution III.

Therefore, a best-subsets regression was used to see if there was a reasonable model for predicting voltage well, that included a subset of the main effects and interactions. The results of the best-subsets regression showed that C (concentration of electrolyte) and D (amount of carbon) were important main effects, no matter how many terms were in the model. The improvements in R^2 started leveling off once the model had four terms (as shown in right panel [b] of [Figure 6](#)). Consequently, the model that had the highest R^2 of all four-variable models was chosen to represent the data. This model included two main

effects — C=Electrolyte Conc., and D=Amount of Carbon; — and two interactions — AE (Thickness of $\text{TiO}_2 \times$ Amount of Juice), and EF (Amount of Juice $\times$ Type of Juice). This model was simple, yet had a high $R^2 = 0.93$. Adding more terms to the model seemed to have little marginal benefit. When this model, including these four terms, was fit to the data, all terms were significant at the $\alpha = 0.05$ level and diagnostic residual plots revealed no abnormalities.

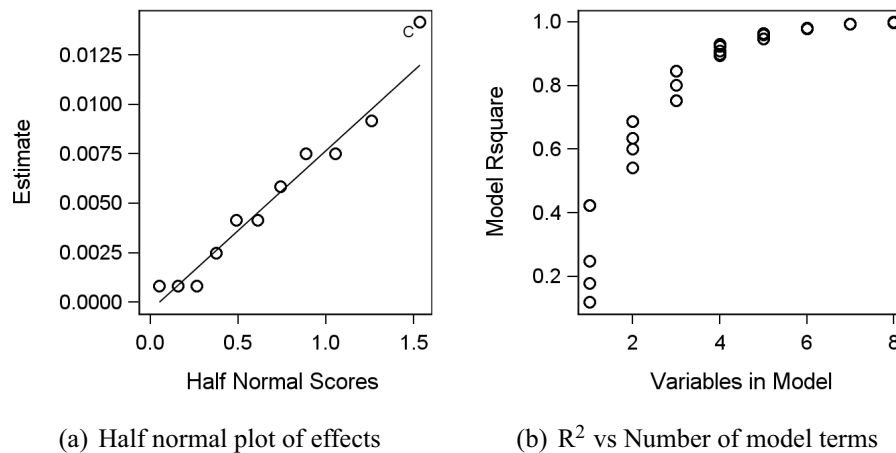


Figure 6. Model selection

The significant main effects revealed that increasing the electrolyte concentration caused an increase of 0.025 volts, and increasing the amount of carbon on the cover slide reduces voltage by 0.15 volts, no matter what the levels of the other factors are.

The interaction plots are shown in Figure 7. The AE interaction (thickness of the $\text{TiO}_2 \times$ amount of juice) shows that the effect of TiO_2 Thickness upon voltage depends on the amount of juice, and that the highest voltage is achieved with a thin TiO_2 layer and the low amount of juice. The EF interaction (Amount of Juice $\times$ Type of Juice) means that the effect of the amount of juice on voltage depends on the type of juice used, and that the highest voltage can be achieved with a low amount of pomegranate juice or a high amount of blackberry juice.

Using the information from the significant main effects and interactions, the maximum voltage was predicted to occur when there is a high concentration of electrolytes, a low amount of carbon, a thin layer of TiO_2 , and a low amount of pomegranate juice. Using the fitted equation for the model involving main effects C and D and the AE plus EF interactions, the expected voltage at the optimal predicted conditions was calculated to be 0.5308, with a 95% prediction interval for an individual value of (0.51 - 0.55). Therefore, it was predicted that Grätzel cells made at the optimal conditions should fall within these limits and would more consistently produce voltage near the maximum of the 0.3 to 0.5

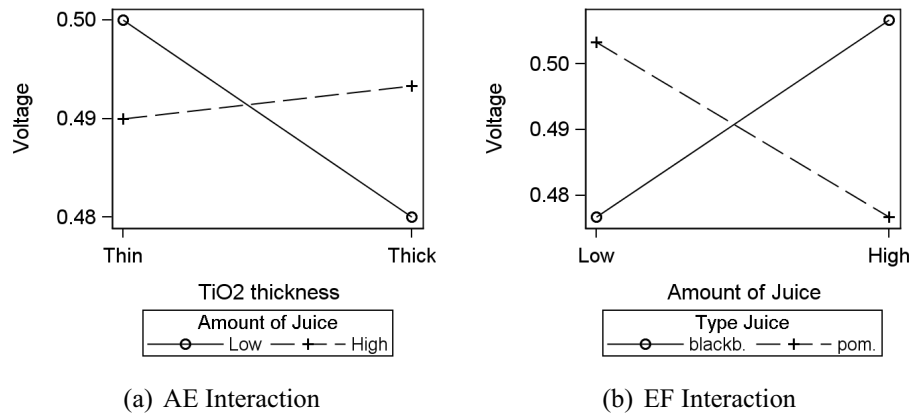


Figure 7. Interaction plots

range reported in the literature.

3.3 Confirmation Experiment

The next step was to conduct additional experiments to justify the model predictions. However, only one tin dioxide-coated conductive slide remained after the screening experiment. Therefore, it was decided to use that slide in a simple confirmation experiment as described by [Montgomery \(2005, p. 295\)](#).

The confirmation experiment was conducted to see if the optimal conditions identified with the model that was fit to the screening-optimization experiment were repeatable. The remaining slide was prepared with a thin layer of TiO₂ and stained with the low amount of pomegranate juice. Next, the counter electrode was coated with a thin layer of carbon, the slide was assembled, and the electrolyte solution was applied. Then the slide was disassembled and the electrolyte solution was allowed to dry overnight. The next day the slide was reassembled and the electrolyte solution was applied again. This duplicated the high concentration of electrolyte that was used in the screening experiment. Finally, the assembled solar cell was placed on the overhead projector and the voltage was measured. The voltage obtained was 0.53 volts. This was near the center of the prediction interval for an individual predicted value at the optimal conditions, and confirmed the prediction of the model fit to the data of the screening experiment.

When interactions are identified as significant in factorial or fractional factorial designs, they normally (but not always) involve at least one of the main effects identified in the design. [Hamada and Wu \(1992\)](#) called this the *effect heredity principle*. The best-subsets regression method used to analyze the screening experiment identified two significant interactions that did not involve either of the significant main effects. This could be a rare

situation where this type of interaction occurs, or it could be caused by other important interactions that are partially confounded with the large unassigned effects. In this case it was not necessary to determine precisely which interactions were active, since the model predictions of the optimal factor settings were justified by the simple confirmation experiment.

4. Discussion and Conclusions

Statistics majors in experimental design classes may get some hands-on experience when they conduct an experiment for their term project, but many of these projects do not help them internalize the value of what they have learned in solving real-world problems. The purpose of many projects conducted by students in experimental design classes is to illustrate the use of some techniques they have learned in the class. These projects do not necessarily give students the confidence they need to be persuasive advocates of experimental design techniques in their future role as consultants. However, when the emphasis of a class project is to solve a real research question, the design and analysis of experiments becomes a tool rather than the end goal of the project. In this context students gain a greater appreciation for the tool.

This article described an experience where statistics majors and a chemistry TA worked together to solve a laboratory research problem. The problem was credible and the use of experimental design techniques (a variance component study followed by a screening experiment) allowed the students to quickly get to the root of the problem with limited resources. The experimental results permitted the students to identify conditions for producing Grätzel cells that produced voltages consistently at the maximum of the range reported in the literature. As a result of this experience, the students gained an appreciation for the value of experimental design and confidence that they could solve real problems with this tool. One student assessed his experience as follows:

It was very instructive to me to see the connection between the data gathering and analysis. Often when learning statistics in a classroom, the data is just given to us. This experiment showed us some of the difficulties that arise when trying to gather data. Once you've learned how to design an experiment, it's easy to describe how the experiment should be run, but it was very instructive to see how the design of the experiment translates into actually performing the experiment. In a traditional class project, I would likely choose an experimental design, and then try to forcibly to fit something I could do around my house into that design. With this project, we had the scientific question we wanted answered and we designed our experiments around answering those questions.

Another student offered the following assessment of the experience.

I feel that this project made the crucial connection between theory and application, between classroom and production room. We looked at the problem as any scientist might, but then took the experimental design principles learned over the semester and answered the question. The experience of being in a chemistry lab, watching the experiment performed, and seeing how other scientists with other backgrounds think about the same problem was invaluable in the learning process.

For me, the main difference between our class project and the traditional class project is that our class project actually convinced me that the methods we were learning in class were applicable and even crucial to real-world problems. The traditional project usually ends up being something that I throw together before it is due, rather than something that I've developed throughout the semester. The traditional class project usually involves a problem or question that the student creates to show some principle, whereas our project started with a question which we had to answer using a sequence of designs learned in the class. We were able to talk in class like we were actually part of a statistics team preparing to present our plan to developers in a lab, discussing what things might go wrong or might confound our results and how we might handle those situations.

We saw how performing one type of experiment leads naturally to another experiment to answer the new questions that are generated. We could have stopped after identifying the design elements which caused the most variability, but that knowledge was useless without knowing how to improve the solar cells. Consequently, we figured out how to control those elements to optimize our output. This project gave me a clearer view of how each aspect of theory learned in the course, or applied disjointly through homework, fit together to find answers to real problems in an actual situation. I feel that this project proved to me that what we'd learned about in class actually works, and even an inexperienced student like myself can apply them and make a difference through using statistics.

Students in applied science, where laboratory experiments are used, are often required to take one statistics class in their course of study. Many even take an elective course concentrating on experimental design; however, experimental design techniques are rarely used in their laboratory experience. Instead, most laboratory experimentation is conducted like

extended pilot experiments with little organization. Once a procedure has been run successfully, attempts at optimization usually follow a vary-one-factor-at-a-time procedure, or they follow a shotgun approach, varying factors that are easy to manipulate but not necessarily essential. After completing the exercise with the students in the experimental design class, the teaching assistant from the chemistry department made the following comment.

I learned the importance of experimental designs in giving a direction to the research. The statistical analysis of the resulting data helped provide a clear and concise description of the results and justification for the conclusion that was reached. It helped to reduce the number of experiments and avoided confusion that might have resulted from a haphazard approach. The carefully thought-out planning of experiments helps in explaining the results and answering the questions which otherwise might have been confusing to answer.

When I (the instructor) asked him how he would advise a chemist embarking on a research program in the lab with no training or experience in experimental design techniques, he said, "I will definitely advise that person to work in collaboration with a statistician. It helps to reduce the number of experiments and saves time".

Based on these observations, this class exercise appeared to be fruitful for the students involved. Although it takes more effort for a teacher of a design class to arrange such an exercise, I felt it was worthwhile and may be good model for collaborative learning. In this particular case, I had a small class and was able to use the funds normally reserved to pay a TA to grade homework to hire instead a TA from the chemistry department, and we were graciously allowed to use some bench space in his professor's lab. In the future, I would like to find at least one professor each term who would encourage ongoing collaboration with statistics students in his or her laboratory experiments. In that way, more students would be able to gain the insights that my students and TA gained in the trial experiment reported here.

Appendix: Pilot Experiment and Laboratory Procedures

The theory behind Smestad and Grätzel's solar cells is as follows: The colloidal TiO_2 is a semiconductor with a wide energy gap between the valence and conduction-band electrons. The photon from sunlight is not able to overcome this energy gap and transfer the electron from valence to conduction band. But this photon can easily excite the electrons in a berry juice dye adsorbed onto TiO_2 and transfer them to the conduction band in TiO_2 . These electrons then flow through the external circuit and produce electric current. This leaves the

dye in the oxidized (partially positive) state, which is neutralized by procuring an electron from iodide, resulting in iodine, or a triiodide formation. These lost electrons from iodide are replaced by electrons from the carbon-coated counter electrode. So, the TiO_2 acts as an electron acceptor, the iodide/iodine electrolyte solution is an electron donor, and the dye serves as a photochemical pump that excites electrons to a conductive state. The output voltage is the energy difference between the redox potential of the electrolyte and the conduction band of TiO_2 (Johnsen 2006).

A pilot test was made in an attempt to reproduce the demonstration experiment in our lab. We used the same procedure mentioned by Smestad and Grätzel (1998), with minor modifications. Twenty-five conductive (tin dioxide-coated) transparent glass slides (part no. CB-50IN-0107) were obtained from Delta Technologies Limited in Stillwater, MN. The colloidal titanium dioxide (TiO_2) powder (8-12 nm, anatase phase) was synthesized in one of the laboratories at Brigham Young University. Pomegranate juice was prepared by crushing the seeds over a sieve. The electrolyte solution was prepared by dissolving 0.127g of iodine in 10mL of water-free ethylene glycol, followed by the addition of 0.83g of potassium iodide. The solution prepared was stored in an amber-colored airtight bottle. The nano titanium dioxide suspension was prepared by mixing 1g of TiO_2 powder with 1.5mL of vinegar (added in small increments) until a smooth paste was formed, followed by the addition of a drop of dishwashing detergent, and then keeping the solution undisturbed for 15 minutes. The solution was then spread onto the conducting surface of a glass slide masked with tape on three sides. The film retracted many times while spreading so the final step was repeated until a uniform layer was formed.

The slides were dried for 15 minutes and then baked for one hour at 450°C in an oven to sinter the coated layer. The slides were left overnight to cool to room temperature. Contrary to the published descriptions of the experimental procedure, the layer of TiO_2 on the prepared slides was still too fragile to be dipped in a berry juice dye solution as described. To work around this problem, we stained the layer by placing two to three drops of berry juice on it. After the staining juice was allowed to dry overnight, the stained TiO_2 layer adhered very well to the glass slide. A counter electrode was prepared by depositing a layer of carbon onto the conducting side of another glass slide using a candle flame. Then the cell was assembled. The iodide electrolyte solution was allowed to seep between the slides by capillary action, and the voltage was measured by attaching the negative terminal of the multimeter to the titanium dioxide coated layer and the positive terminal to the carbon-coated slide. The measurements were recorded inside the lab using an overhead projector as a light source, as illustrated in Figure 8.

The test resulted in voltage readings that varied from 0.12 volts to 0.43 volts. The voltage reading was very sensitive to the placement of the electrodes. When a good connection was



Figure 8. Measuring the voltage on an overhead projector

made, the voltage readings would start above 0.30 volts and would rise as the solar cell remained in the light until a plateau was reached, usually in three to four minutes. If, when reconnecting the electrodes, one of the alligator clips touched the counter electrode, the circuit would short out and the voltage reading changed immediately to -0.00. If we could not increase the plateau voltage reading after several tries of reconnecting the electrode, we assumed we had found the best connection and used the maximum value to represent the test result.

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