PROJECT REPORT

An Examination of the Current Efficiency of Hydrogen fuel Cells and Dye Sensitized Titanium Dioxide Solar Cells

Submitted To
The RET Site
For

**"Sustainable Engineering for Urban Needs:
Research Experiences for Middle and High School Teachers"**

Sponsored By

The National Science Foundation

Grant ID No.: EEC-0808696

College of Engineering and Applied Science

University Of Cincinnati, Cincinnati, Ohio

Prepared By

Philip Mercatili, Masters Student, University of Cincinnati, Cincinnati, OH
Jonathan Souders, School for Scientific Studies, Glen Este High School, Cincinnati, OH

Reporting Period: June 22nd – July 31st

Project # 2: Renewable Energy System

An Examination of the Current Efficiency of Hydrogen fuel Cells and Dye Sensitized Titanium Dioxide Solar Cells.

Philip Mercatili, Masters Student, University of Cincinnati, Cincinnati, OH.

Vesselin Shanov, PhD, Assoc Professor, Chemical & Materials Engineering, University of Cincinnati, Cincinnati, OH.

Jonathan Souders, School for Scientific Studies, Glen Este High School, Cincinnati, OH.

Feng Wang, MS, Chemical & Materials Engineering, University of Cincinnati, Cincinnati, OH.

Abstract:

To date humans have enjoyed relatively inexpensive energy without regard to the economic or environmental impact of the fuel sources we have used. The 21^{st} century will be forced to see the end of this trend. The development of future energy resources will require a focus as much on the products and by-products of the reactions as the energy they provide. Hydrogen is the source of energy with a track record for being clean and efficient. Hydrogen provides the potential to have a system where the only product is water vapor. Closing the reactant product loop will provide an endless fuel supply for our energy needs. This study examines the effect temperature has on the efficiency of a proton exchange membrane (PEM) hydrogen fuel cell. Also we look at the impact of dye selection on the efficiency of dye sensitized TiO_2 solar cells. Maximizing these two factors will help lead to a system that allows for the capture of solar energy for use in buildings and to create hydrogen that can be used in fuel cells. Improving the energy conversion efficiencies of these devices will go a long way to making the technologies useful to the vast consumer market.

Keywords: ALTERNATIVE ENERGY, GREEN TECHNOLOGY, PROTON EXCHANGE MEMBRANE, DYE-SENSITIZED SOLAR CELL, TITANIUM DIOXIDE

1. INTRODUCTION

The un-renewable energy resources currently in use are beginning to dwindle and are causing environmental damage on a global scale. Many of these technologies have their roots many years ago and were chosen over other renewable resources due to their low cost and availability. Fossil Fuels have injured the environment on a global scale and if this practice is continued the overall effects could be irreparable. Also, fossil fuels are causing problems to the world's economies because of the rising demand and falling supplies are causing the price to skyrocket.

These societal changes have begun to raise interest in green technologies that have the potential to solve many of the societal problems as well since free, cheap energy has the potential to remove one of the main causes of war: resources. These energy production methods are experiencing a renaissance in light of modern technological advances and in the near future will most likely be able to sustain a large amount of the world's power.

The hydrogen fuel cell works to turn hydrogen in diatomic form into protons and electrons by use of a catalyst. The protons are then pulled toward the cathode by way of an external circuit. This external circuit runs through an electrical device and provides the power to run it. The protons are pulled across the Proton Exchange Membrane (PEM) which is usually made of a material called Nafion®. Once the protons reach the other side of the membrane they are combined with oxygen to produce water vapor. This is how the hydrogen fuel cell produces electricity without any carbon emissions.

2. LITERATURE REVIEW

These two topics are popular at the moment due to the environmental crisis and the exploding price of fossil fuels. As these two problems continue to get worse the interest in alternative will continue to grow.

2.1 Hydrogen Fuel Cells

Proton exchange membranes (PEM) offer the ability to produce low- to zero-emission electrical energy from virtually limitless reserves. The main technical problem with these membranes is their inability to hold efficiency at higher temperatures. Higher temperatures have been shown to improve many aspects of the PEM fuel cell such as the thermal management and the heat utilization of fuel cell stack (Yang et al., 2001). The downside of this higher temperature is that it causes the PEM to dry-out. This, in turn, causes the membrane to lose efficiency because hydrogen fuel is able to leak across the membrane. This has three deleterious effects on the overall cell including: fuel efficiency reduction, cathode depression, and production of peroxide radicals (Cheng et al, 2007). This has direct implications for the continued use of the fuel cell and can create dangerous situations if allowed to continue. The crossover of diatomic hydrogen can allow for the formation of hydrogen peroxide radicals which can eat away at the catalyst and poke holes in the membrane. This can cause safety hazards and an overall reduction of efficiency or ceasing of operation altogether (Cheng et al, 2007). Methods for improving these membranes (Yang et al, 2001) have been attempted and have shown an increase in the ability of membranes to retain their relative humidity which will in turn allow for higher temperature operation. In this study we aimed to look at the temperature limits of a fuel cell stack used for educational purposes and determine which temperatures would show a reduction in efficiency. A schematic of a PEM hydrogen fuel cell is revealed in Figure 1

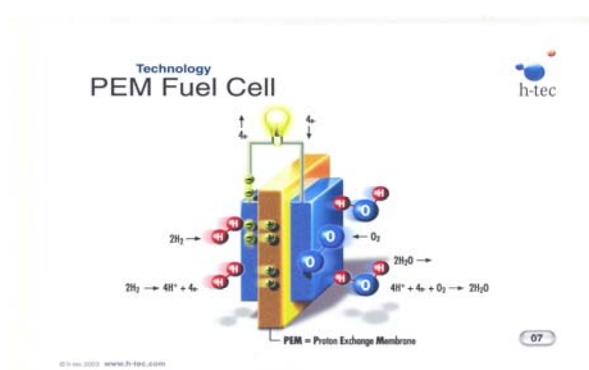

Figure 1. Schematic of a Proton Exchange Membrane (PEM) Hydrogen Fuel Cell

2.2 Dye-Sensitized TiO_2 solar cells

The current procedure for the production of TiO2 Nanocrystalline Dye Sensitized Solar Cells in use by the University of Cincinnati undergraduate chemistry lab has been resulting in DSSC with efficiencies far below expectations. The typical student result has a maximum power efficiency of approximately .025 %. Our goal has been to discover the source of this discrepancy. In investigating the process it was discovered that the Heat Gun being used for the annealing process failed to reach the appropriate Temperature of 450 degree C. The maximum temperature achieved with the Hest gun furnace was 283 degree C. Annealing is the process which causes the Tio_2 crystals to become closely aligned. It is this alignment that allows electrons to be efficiently passed through the cell and along the circuit (Mor et al., 2005). A secondary factor aided by the annealing process is the removal of water from the Nanocrystalline film.(Ehret et al., 2001) By driving of all the water from the surface of the Nanocrystalline film before placing it in the dye you improve the absorption of dye to the surface of the DSSC. It is believed that improving the annealing process in the lab procedures will result in improved performance of the DSSC. The principle of the DSSC is illustrated in Figure 2.

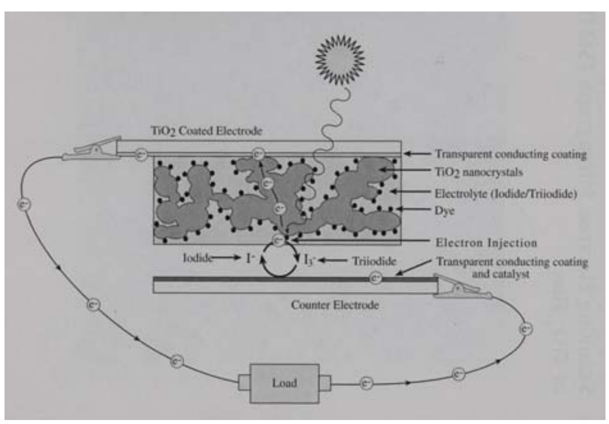

Figure 2. Schematic illustrating the principle of the DSSC

After locating an oven with the capabilities of annealing the DSSC to the proper temperature we prepared 8 samples for testing. We heated the TiO2 coated Glass Slides to 450 degrees C over a 2 hour time period. The Ramping of the heat was needed to assure that the glass would not crack do to extreme temperature changes. Once the temperature reached 450 degrees C it was held there for 1 hours to assure annealing and water removal. Then the Glass was allowed to cool over time in the oven, again to protect from glass breakage. Once the annealing process was complete the DSSC were assembled according to the standard procedures, with the exception of one set of slide which was allowed to soak in the dye solution for 12 or 24 hours instead of the standard 1 hour.

3. GOALS AND OBJECTIVES

The goal of our project is to determine how to increase the efficiency of some basic green technologies. One specific project aims to look for the prime temperature at which a hydrogen fuel cell will work most efficiently. The other main experiment being conducted is testing dyes for dye-sensitized TiO_2 solar cells to determine which of these is the best electron transporter for the cells. Our overall goal in these experiments is to not only improve these experiments for the engineering students at UC but also to be able to carry our research over into our classrooms.

4. MATERIALS AND METHODS

We have been utilizing a hydrogen fuel cell to do experiments on the efficiency of these cells. We measured the hydrogen put into the system and then measured the power, current, and voltage output. We then calculated the total amount of power that could be generated from the used hydrogen and in turn used that to determine the efficiency of the fuel stack. We also did these same tests at four different temperatures (30C, 35C, 40C, and 45C). The used hydrogen was UHP grade (99.999%) from Wright Brothers.

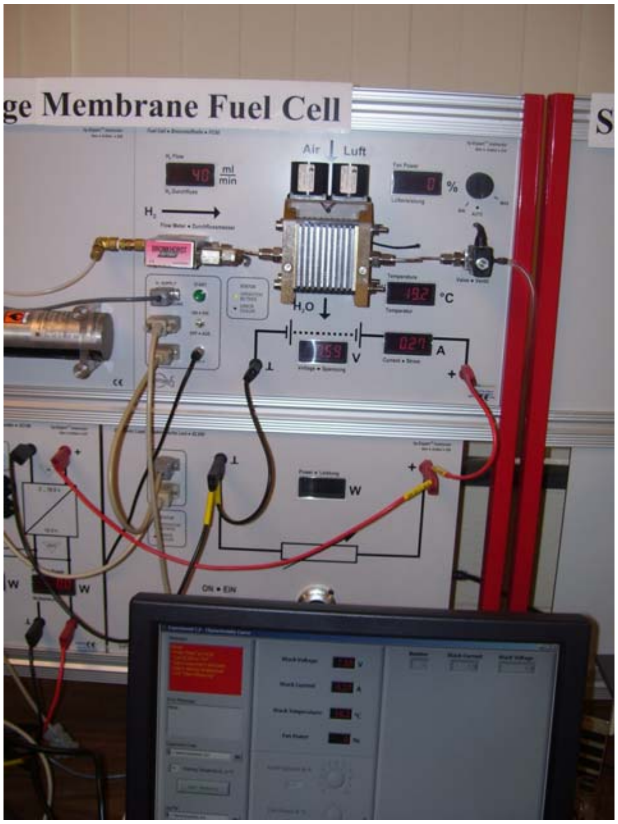

Figure 3. Photograph of hydrogen fuel cell apparatus

We also did a similar experiment using dye-sensitized solar cells where we created 4cm2 solar cells and tested them for their power and power efficiency along with voltage and current. We used blackberry dye that has a compound called anthocyanin that works as a electron transporter. Our plan right now is to test a bunch of these dyes both natural and synthesized to see what kinds of these dyes works best at converting the light energy into power.

Figure 4. Photograph of two of our dye-sensitized solar cells

5. ANALYSIS; RESEARCH RESULTS

For the hydrogen fuel cell project we measured power, voltage, current efficiency, voltage efficiency, and energy efficiency for the cell stack at different temperatures. Our results show that all of these aspects of the fuel cell remained steady until the cell has reached a temperature of 45C. At 45C the cells power, voltage, voltage efficiency, and energy efficiency all start to fall off compared to the other temperatures.

5.1.1 Power as Temperature is Increased

Our measure of power as amperage is increased shows that there is a linear trend to the graph (Fig. 5). As amperage increases so does power. As we near the top of the graph however there is a leveling off which indicates that with increased amperage power is going to reach a plateau between 55 and 60 watts.

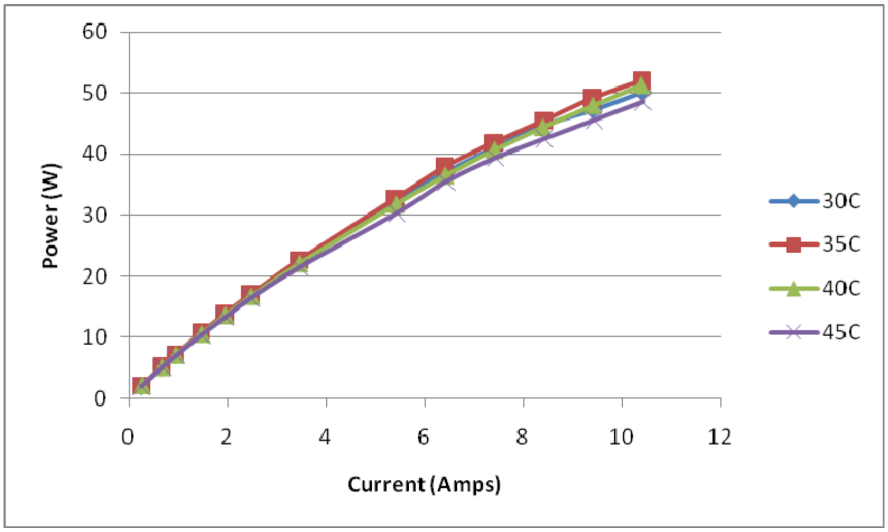

Figure 5. The power as a function of current shows that for the first three temperature points the power falls off neglibly, but at 45C there is a more pronounced dropoff.

After our experiment we also measured a few other aspects of the fuel cell. In this graph we looked at the voltage as a function of current. Figure 4 shows a similar trend to that of Fig. 1 in that the first three temperature points stay relatively consistent while the measurements at 45C begin to fall off quicker.

5.1.2 The Effect on Voltage of Increased Current and Temperature

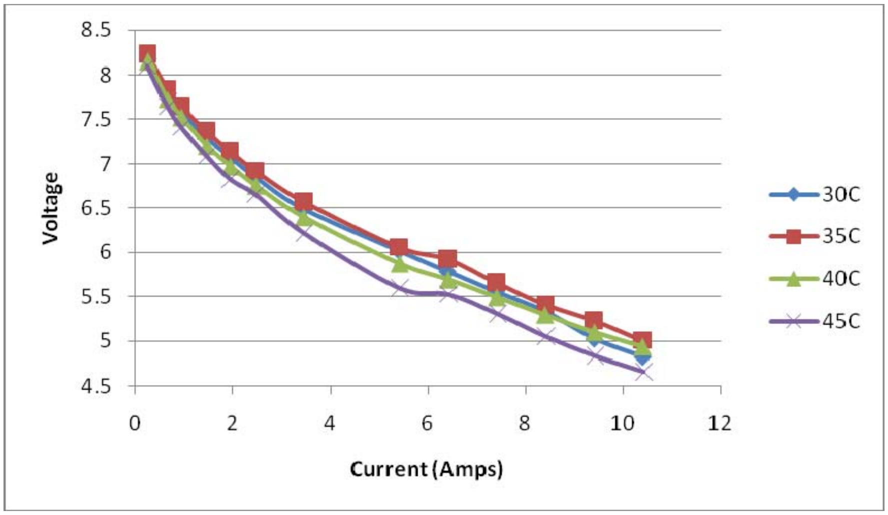

Figure 6. Voltage falls off considerablyquicker as the temperature is increased past 45C.

5.1.3 The Effect on Voltage Efficiency of Increased Current and Temperature

Here we look at the voltage efficiency over the temperature range and again we see that the increased temperature had a similar effect: the quicker degredation of voltage efficiency at higher temperatures.

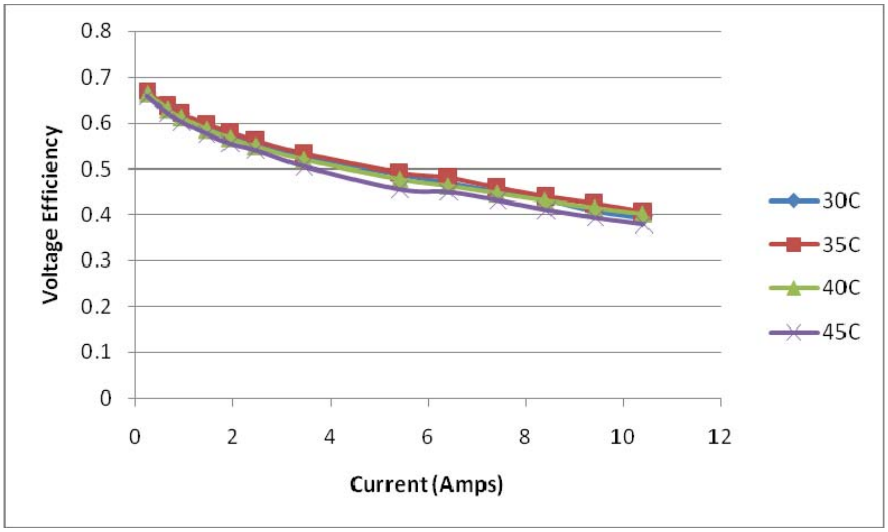

Figure 7. The voltage efficiency as a function of current shows a trend of decreased efficiency as the current is increased. This effect is exacerbated by the increase in temperature to 45C.

5.1.4 The Effect on Energy Efficiency of Increased Current and Temperature

In Figure 4 we show that an increase in temperature also has an overall deleterious effect on the energy efficiency as the current increases. Even though there is an overall drop off in efficiency as the current is increased the temperature causes this to worsen.

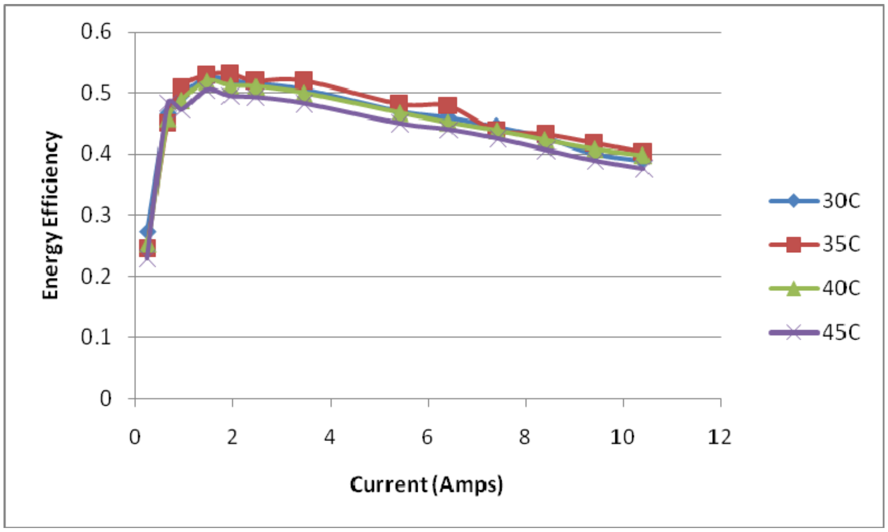

Figure 8. The energy efficiency over the temperature follows the trend of falling off quicker as the amperage goes up similarly to the other aspects observed.

5.1.5 The Effect on Current Efficiency of Increased Current and Temperature

The current efficiency however remained constant over the temperature range tested.

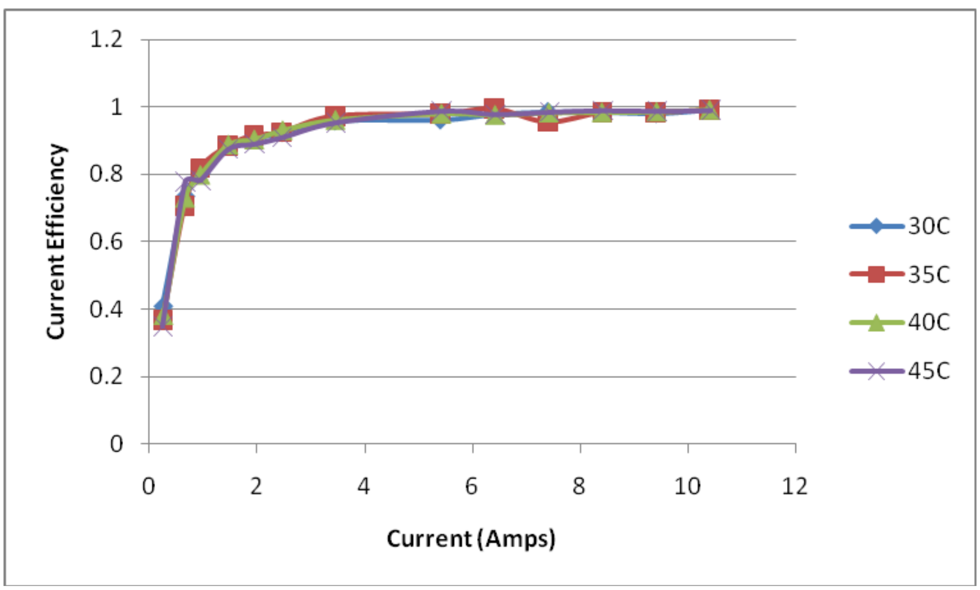

Figure 9. Current efficiency stays steady over the full range of tested temperatures.

5.2 *Titanium Dioxide Dye-Sensitized Solar Cells (DSSC)*

The dye sensitized solar cell project has many anthocyanin cells and one other using the dye from green leaves. Our main goals are to determine which of these dyes gives us a better result when used in the making of Titanium Dioxide Dye-Sensitized Solar Cells and to determine which of the two annealing methods result in a higher quality solar cell.

5.2.1 *TiO_2 Dye-Sensitized Solar Cells Using Blackberry Dye and Different Annealing Methods*

First, we took the original recipe the undergraduates used to create their solar cells and made a few cells of our own. We determined where we thought the process could be improved and modified them how we thought would be best. Here we used a heat gun that only achieved an annealing temperature of 285C. Here are the results of the cell that was annealed at this temperature and soaked in blackberry dye for 24 hours as opposed to the 1 hour that the original directions indicated.

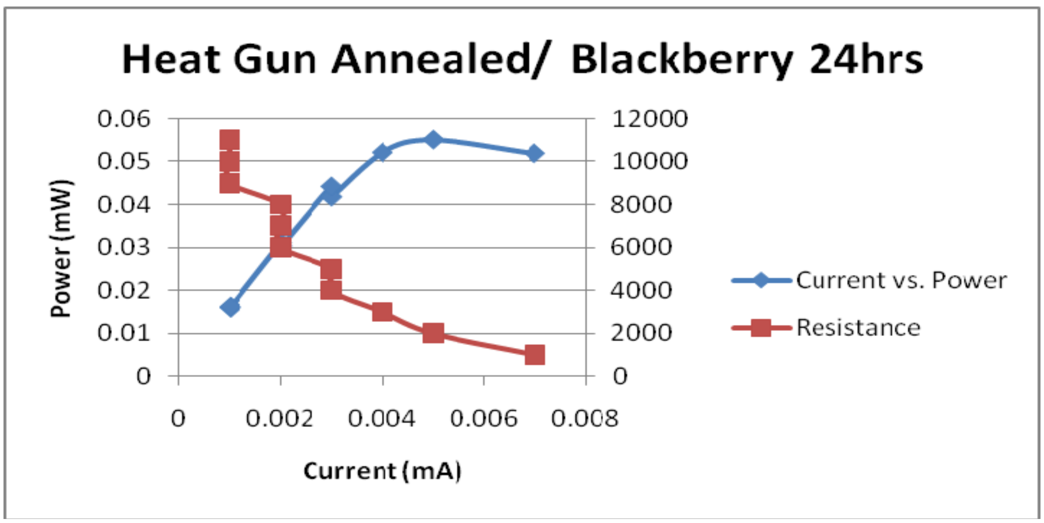

Figure 10. As the resistance falls the current and power increase but at intervals that are not realistic indicating problems with the production process

We determined after this experiement that not only the original length of incubation in the dye but also the temperature of annealing were very important to the efficiency of these solar cells.

Since the directions called for 450C we determined that we should see if there was a better heat source we could use to reach this temperature. We found an oven that reliably reached the 450C threshold that we thought was required to produce the best results and performed the experiment again to determine if there was a sizable increase in performance.

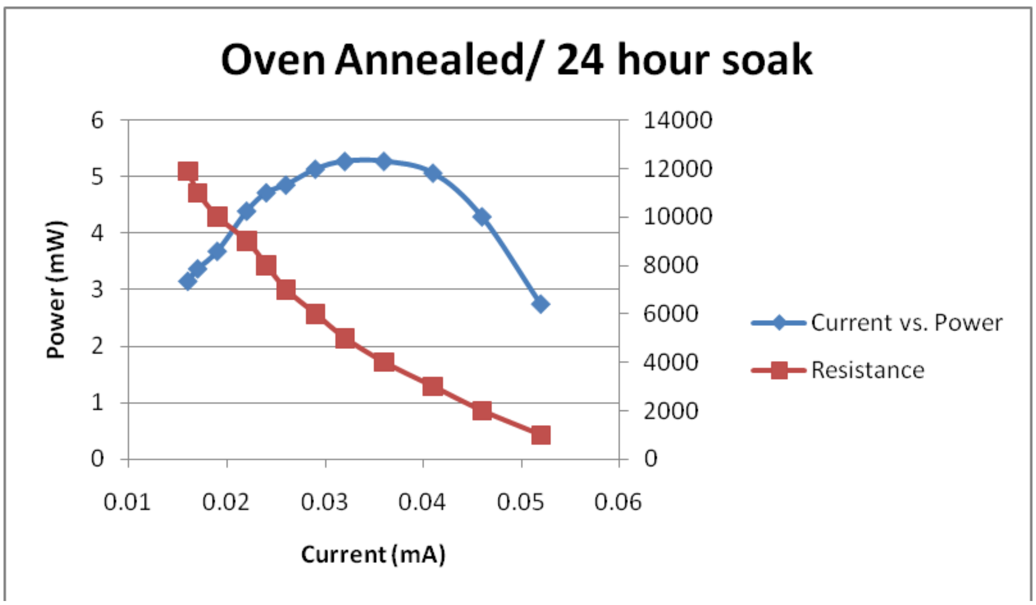

Figure 11. The cells annealed in the 450C oven produced much more power and current over the range of resistances we tested

We found that using the correct annealing temperatures in the production of these cells is integral in their proper function. The results we obtained from the oven annealed cells showed a two order of magnitude increase in efficiency compared to those annealed using the heat gun. This is shown in Table 1.

Table1. Efficiency of Oven and Heat Gun Annealed Cells

	Efficiency of Cells with different Annealing Methods (%)	
Resistance (Ω)	Oven	Heat Gun
1000	1.29	0
2000	2.00	0.03
3000	2.38	0
4000	2.47	0.02
5000	2.47	0.02
6000	2.41	0
7000	2.28	0
8000	2.21	0
9000	2.06	0
10000	1.73	0
11000	1.58	0

6. CONCLUSIONS

6.1 *Future of PEM Fuel Cells*

The increase in performance promised by the development of higher temperature fuel cell membranes is exciting as well as necessary if PEM fuel cells are ever to become a main stream energy source. These fuel cells offer a great deal but unless the basic problems are overcome and made much more resilient they will never be consumer ready. Before these fuel cells are put onto the global market they much be much better at retaining moisture to fend off membrane de-gradation because of the problems associated with hydrogen crossover.

Our study of fuel cells is centered on determining a top temperature for these fuel cells to show students that there is a real correlation between the temperature and the efficiency of the cell stack. With these investigations we hope to get more students interested in the field and therefore speed research to solutions of these problems.

6.2 *Future of TiO_2 Dye-Sensitized Solar Cells*

Our data would indicate that the impact of annealing is significant. The Power and I-V curve both indicate that DSSC annealed in the oven preformed substantially better than the cells annealed with the heat gun. The oven annealed cells performance is more in line with the expected results for TiO_2 dye sensitized solar cells.

The possibility of creating solar cells that achieve greater than 20 % power efficiency with a relatively low manufacturing cost has many positive implications for the future of solar power's wide scale distribution. To date Silicon has been the semi conductor of choice in solar cells. Research currently underway has produced TiO2 Dye Sensitized Solar Cells (DSSC) with an efficiency of 10.6% (Mor et al., 2005).

7. ACKNOWLEDGEMENTS

We would like to thank Dr. Vesselin Shanov and Feng Wang for helping us direct our I terests and training us in the use of the setups. Also, we'd like to thank them for helping us with reference material in relation to our project. Also,we would like to thank the NSF for funding: Research Experiences for Teachers Site for "Civil Infrastructure Renewal and Rehabilitation" (Grant ID No. is EEC-0808696).

8. BIBLIOGRAPHY

Cheng, X., Zhang, J, Tang, Y., Song, C., Shen, J., Song, D., Zhang, J., "Hydrogen cross-over in high-temperature PEM fuel cells," *Journal of Power Sources*, Volume 167, Issue 1, 1 May 2007, Pages 25-31

Ehret, A., Stuhl, L., Spitler, M.T. "Spectral Sensitization of TiO_2 Nanocrystalline Electrodes with Aggregated Cyanine Dyes," *J. Phys. Chem*. Volume105, pp.9960-9965 (2001)

Mor, G.K., Karthik, S, Paulose, M., Varghese, O.K.., and Grimes, C.A. "Use of Highly-Ordered TiO2 Nanotube Arrays in Dye Sensitized Solar Cells," *Nano Letters* 2006 Vol. 6, No 2, 215-218

Narayanan, S. R., Valdez, T.I.,* Firdosy, S. "Analysis of the Performance of Nafion-Based Hydrogen–Oxygen Fuel Cells," *Journal of The Electrochemical Society, volume*156 . pp.B152-B159 (2009)

Scrivano G., Piacentino A., Cardona F. "Experimental characterization of PEM fuel cells by micro-models for the prediction of on-site performance," *Renewable Energy* volume 34 (2009) pp.634–639

Yang C., Costamagna P., Srinivasan S., Benziger J., Bocarsly A.B. "Approaches and technical challenges to high temperature operation of proton exchange membrane fuel cells," *Journal of Power Sources*. Volume 103 (2001) pp.1–9