Dye Sensitized Solar Cells

Sarah Collins

Esther Chapman

Our goal for this block was to continue research we started this summer on solar cells sensitized with an organic dye. We wanted to get all the equipment and instrumentation up and running so that the next research group can focus on improving cell construction and optimizing the dye used as a sensitizer. This entailed setting up the spectral response experiment and producing more cells to test construction methods. We also made measurements to determine the power output of the cells with white light, something we set up and were able to do this summer.


Sarah and Esther making solar cells.

IV Curve

An IV curve is a current versus voltage curve that can be used to determine the maximum power output of a cell. IV curves have two characteristic slopes which are determined by varying resistances inside the cell. The y-axis intercept is the cell's I_{sc} or short circuit current, and the x-axis intercept is the cell's V_{oc}, open circuit voltage. I_{sc} is the current through the cell with no load attached; that is just the cell in light with an ammeter reading current. V_{oc} is measured the same way, but with a voltmeter reading the voltage across the cell.
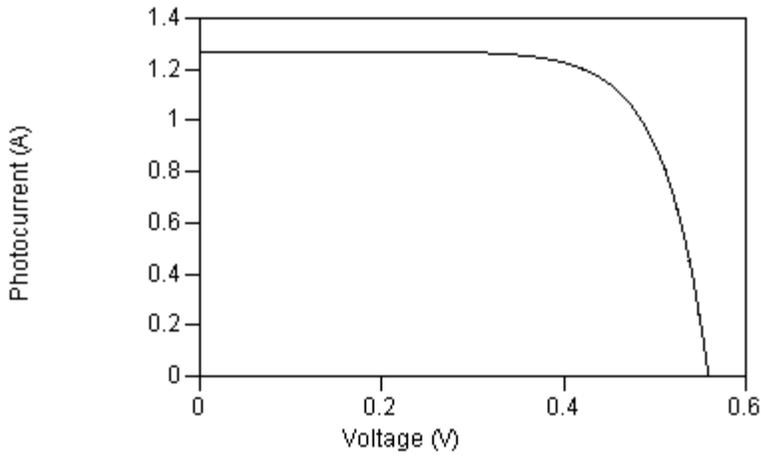
An example of an IV-curve
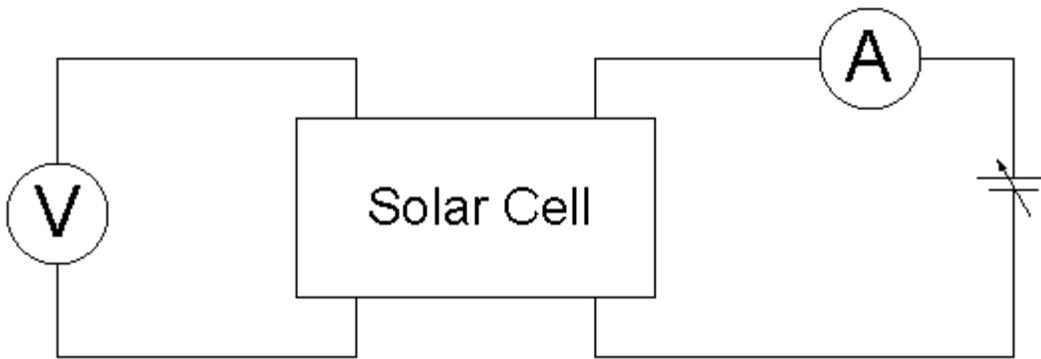
Set up for the measurement of an IV curve

To find an IV curve we must run current through the cell. To produce a varying amount of current we needed to add a resistance to our system. Most variable resistors are unreliable and imprecise, so we opted to add a voltage to our system to produce the change in current. The variable power supply as shown in our diagram above is provided by the lock-in amplifier's DAC options. The lock-in is connected to a computer running a Labview VI which can then automate the change in voltage running through the system. This same VI will measure and plot the voltage across the solar cell and the current through the cell each time the voltage from the lock-in changes.

IV Curve Raspberry Cell Feb. '06
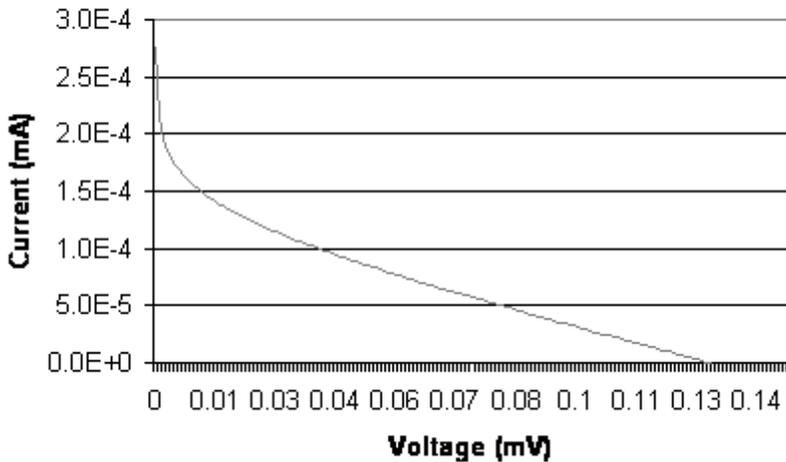
Graph of an IV curve for the cells made in February '06

This IV curve bears little resemblance to the silicon cell IV curve because of internal and external resistances. With more research and improved cell construction, hopefully we will construct dye sensitized solar cells which give us better IV curves.

Cell Construction

To make our raspberry cells, we followed an instruction manual intended for biology students (high school or lower level college) to understand the process of photosynthesis. We use the same knowledge to get a basic understanding of dye-sensitized solar cells (DSSCs) since plants are the original solar cell; they use light to produce energy. We modified the procedure a bit, trying to enhance the efficiency of the resultant cells, so we will touch on the modifications of the process. For the entire procedure, see the "Nanocrystalline Solar Cell Kit" from the Institute for Chemical Education.

Esther grinding up raspberries to make juice. The dye in the juice is used to sensitize the solar cells.

We kept a digital multimeter (DMM) handy to test the resistance of the glass. This allowed us to identify which side of the glass had the conductive tin oxide coating. We checked this every time we applied either the titanium oxide or the carbon counter electrode to the glass. It may seem silly to check this all the time, but if one of the glass substrates is upside down, the cell is rendered useless. We washed the glass substrates in ethanol any time we touched them and stored them under a Petri dish to prevent any airborne contaminants from landing on them, interfering with crucial contact points. Throughout the process, we tried to reduce the internal resistance of the cell at every interface to improve the shape of our IV curves.

We prepared the titanium dioxide (TiO_2) paste as described in the kit's instruction manual this summer, and it was still functional 6 months later when we resumed the experiment. This indicates that the TiO_2 paste has a shelf life of at least half a year. One little hint: *do not shake the paste to try to remove the small bubbles on the surface*. A surfactant (soap) is added so that the paste spreads evenly on the glass surface and shaking it will only cause it to bubble more, rendering it useless. Once the glass is ready to be coated in the TiO_2, instead of spreading the paste with a non-uniform glass stirring rod, we used a razor blade. We disposed of the blade after each use because the oxidation of the metal could potentially contaminate the cell. This process is called doctor blading, and is a common procedure for making DSSCs, based on our literature research. To sinter the TiO_2 paste onto the glass, we used a ceramic heater set to 450 degrees Fahrenheit. We monitored the temperature of the heater using a digital thermometer with its thin wire probe in the middle of the heater. After the cells were heated for 30 minutes, we placed them in an insulated covering so that they could cool slowly. This prevents the cracking of the glass and the TiO_2 coating.
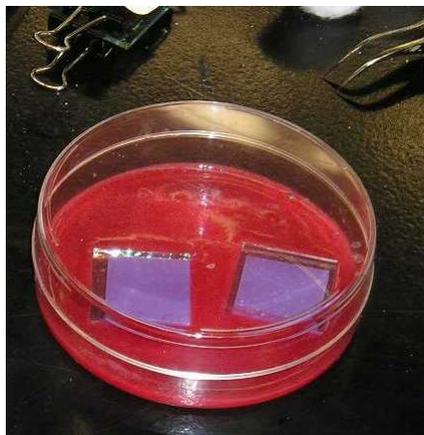
The solar cells soaking in the berry juice. The anthocyanine dye in the berry juice turns the cells purple.

The TiO_2 coated cells sat in the dye for 10 minutes to get fully covered with the sensitizer, and were then rinsed in water and ethanol to remove any excess dye from the surface. They were then blotted dry to remove all moisture from the heterojunction, preventing contamination of the electrolyte coating (reducing potential internal resistance). The carbon counter-electrode was prepared at the same time so that as soon as the cells were rinsed they could be assembled.
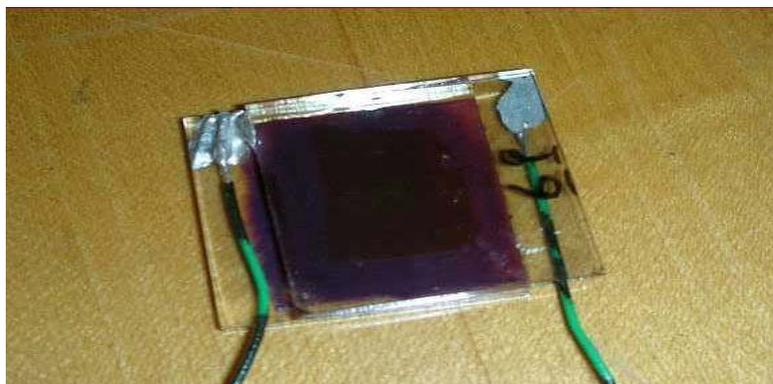
A finished solar cell.

To enable handling of the cells without the binder clips holding them together (which impedes data collection), we applied fast drying epoxy to the two sides which do not make electrical contact with wires. To prevent capillary action from drawing the epoxy into the cell, we placed the binder clips on the connection ends of the cells while the epoxy was applied and drying. It seems, though, that some chemical compound in the epoxy did indeed enter our cells, as the

short circuit current (I_{sc}) that we measured before applying the epoxy were dramatically different from those measured after the application. Some cells had a higher I_{sc}, some had a lower, and the amount they differed increased as the cells sat out.

Cells	Before epoxy (uA)	After epoxy (uA)	With epoxy 5 min (uA)	With epoxy 20 min (uA)
Rx	0.1	N/A	N/A	N/A
R1	4.0	11.3	11.9	12.0
R2	1.1	4.4	4.4	10.3
R3	2.2	6.4	7.3	22.1
R4	2.5	0.8	0.8	1.2
R5	14.8	13.6	12.4	130
R6	4.0	2.8	2.4	59.2

I_{sc} of raspberry cells with and without epoxy

Something in the epoxy adds instability to the cells and makes their behavior erratic. If we can isolate whatever it is that increases the I_{sc} of the cells, we may be able to improve efficiency in a predictable way. Another reason we wanted to use something other than the binder clips was again to reduce internal resistance of the cells.

There is another resistance we tried to reduce: the connection resistance between wire and the cells. We did two things to try to reduce this resistance; and we cannot say whether either of them worked. First of all, we used a conductive silver epoxy to affix the wires to the glass. We purchased the silver epoxy in the summer, and we noticed that the hardener (part B) was beginning to separate as we mixed the epoxy components together. This summer, we found that the ratio of hardener to resin should be slightly more than one to one; a little more hardener is needed to keep the wires attached to the cells throughout all the handling and experimenting. Secondly, we had a four prong wire system so that we could measure the voltage across the cell and the current through the cell independent of each other. We could only epoxy two wires at a time to a cell, so we waited quite a while to take data after the cells were made (the epoxy takes at least 24 hours to set per application, and there were two different applications per cell).

Dyes

This manual called for the use of an anthocyanin (sometimes anthrocyanin) dye which has necessary hydroxyl and/or carbonyl groups which chelate to a thin coating of titanium dioxide. It is the cyanin 3-glucoside and cyanin 3-rutinoside in the pigment of raspberries, blackberries, and bing cherries which fulfill this requirement. Knowing the names and structures of these pigments should aid in the future search for better dyes capable of producing more energy, making the cells more efficient. We crushed whole, fresh red raspberries then filtered out the seeds and skin to obtain this pigment with which to stain our cells.

Without thinking about what made a dye compatible with this experiment, we were led to try Prussian blue (ferric ferrocyanide) as a sensitizer, which we used in the form of laundry bluing. Prussian blue (PB) is a dark dye with remarkable electrochemistry which indicates that if it transferred electrons to the titanium dioxide it would last a very long time. We looked at previously conducted cyclic voltammograms (CV) of PB with the intent of finding peak ranges so that we could conduct our own CV, but the data we found online was sufficient. As we made cells with this

dye, however, we saw immediately that it did not adsorb onto the titanium dioxide coating, so we were skeptical about its performance as a sensitizer. Sure enough, once we finished the cell assembly and measured the I_{sc} of the PB cells, our hypothesis was confirmed in that the PB cells had an I_{sc} of 0.01uA. This is essentially an I_{sc} of 0A when taking background electrical noise into account. We had one raspberry cell that we dropped while adding our liquid electrolyte which yielded the same I_{sc} as the PB cells, indicating that the I_{sc} of the PB cells was in fact 0A.

Spectral Response

To optimize power output, we are looking for a dye sensitized solar cell that closely matches the spectral response of the sun, its primary light source for regular use. During this block, we found the relative spectral response of a small silicon solar cell. This measurement requires a chopped beam of monochromatic light directed on the cell. A monochromator takes light from an intense light source, focuses it with various mirrors and emits a specific range of wavelengths using an automated diffraction grating located inside the device. Readings suggest having a white bias light shining on the cell as well, however our equipment was not sensitive enough to account for the amount of light specified by our readings.

The cell is attached to a current to voltage converter built this summer, whose output is connected to a lock-in amplifier. The lock-in amplifier reads the signal and bias from the cell, flips the bias to a negative reading and averages out the overall signal. Output from the lock-in amplifier gives the voltage produced by the monochromatic light shining on the cell. A Labview Visual Interface (VI) was created to read the voltage from the lock-in amplifier and the corresponding wavelength from our Newport monochromator. From here, analysis in Microsoft Excel can be made to find the relative and absolute spectral responses of the cell.

Our initial focus for this block was to get our spectral response measurement system up and running. During the semester between our initial summer research and this block, our light source and pyroelectric information finally came in. Our new chopper came in as well, but without a chopper wheel. A chopper wheel is the blade that spins around at an adjustable frequency with a set number of openings allowing the light to be "chopped" (e.g. flashed very rapidly). A new one was express mailed to campus and arrived before the end of the first week.
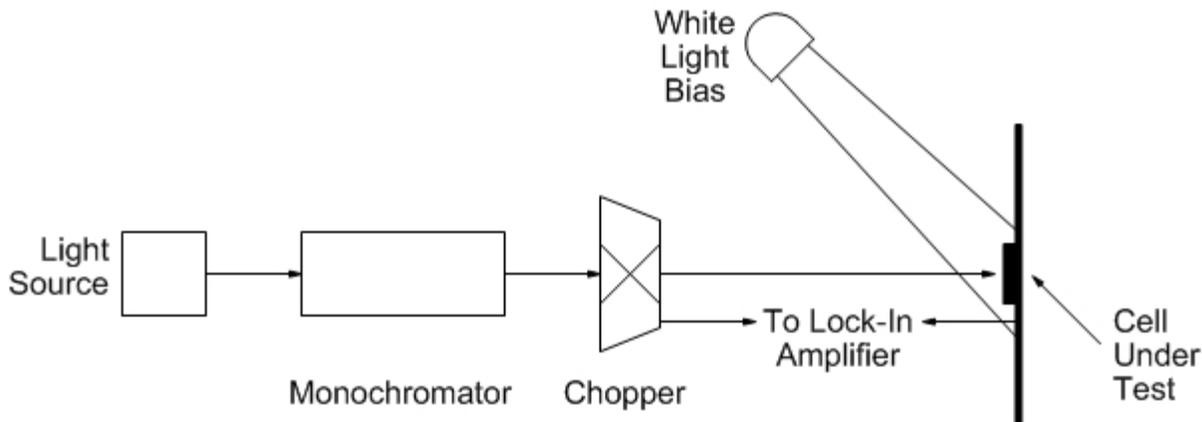
A simple diagram showing a setup of a spectral response measurement system. The lock-in amplifier detects the small amplitude changes due to the spectrally pure light shining through the monochromator.

We worked and researched during the first week to understand the purpose and output of the pyroelectric detector. A pyroelectric is a thermal device that measures the intensity of light by a change in temperature, this change caused by the chopped light. The pyroelectic allowed us to view the spectral emission of our monochromator and light source system. As you can see there are two peaks in our reading. After discussion with Professor Derin Sherman it was determined that one was corresponding to a peak wavelength of light from our quartz-tungsten halogen light source and the other from our monochromator gradient which had a blaze wavelength of 500nm. The information from the pyroelectric tells us the absolute energy in our chopped beam of light, and is used in determining the spectral response

of the cell being tested.

Pyroelectric Response
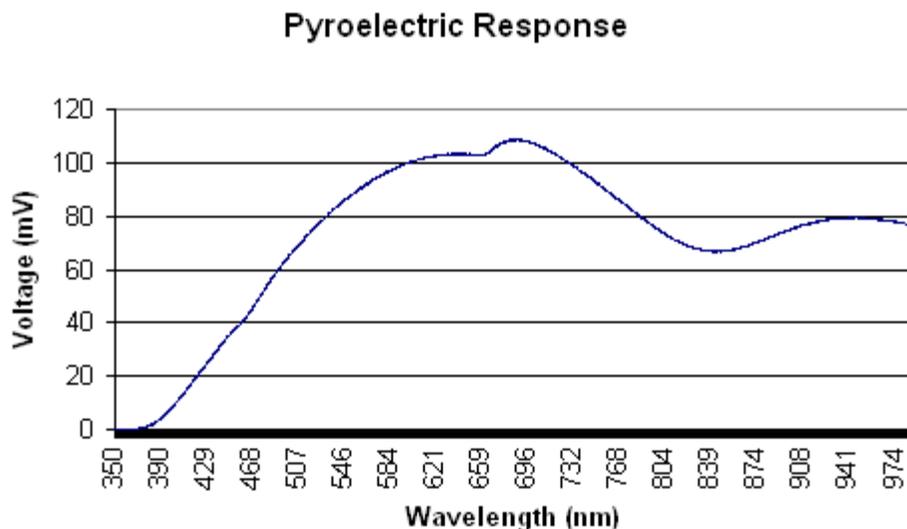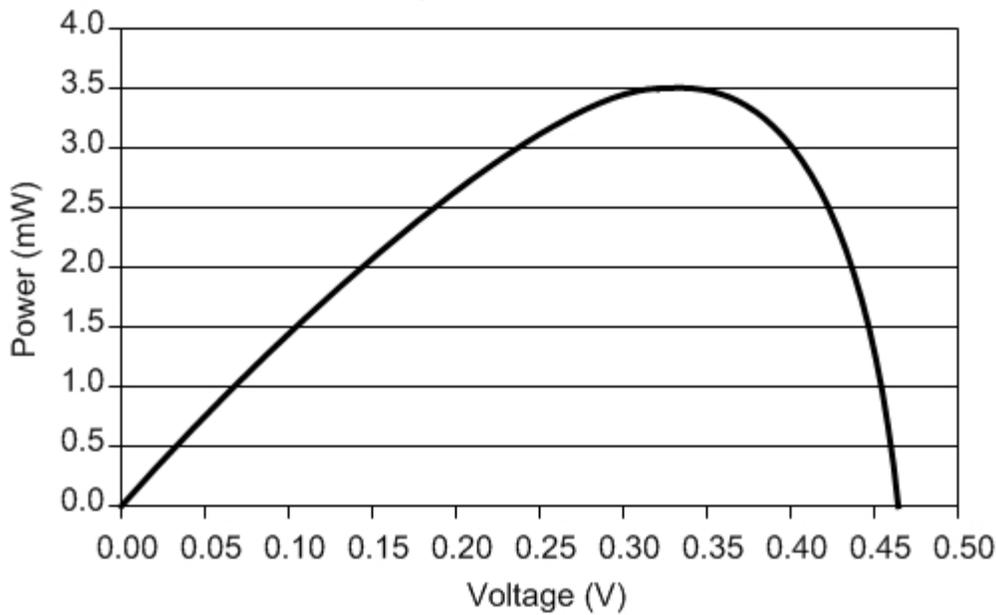

Graph of pyroelectric output

In the last few days of class we finally had the resources to actually take a measurement. Initially we attempted to measure the relative spectral response of a raspberry dye-sensitized solar cell, but the current coming out of our cell was too small for accurate measurement. We hope that future research students work with the lock-in amplifier further to find an optimum sensitivity setting in order to obtain accurate readings from our raspberry cells. In the mean time, to test our equipment we used a standard silicon solar cell. Our calculations were derived from an ASTM (American Society for Testing and Materials) report on the "Standard Test Methods for Measuring Spectral Response of Photovoltaic Cells."

Our readings were made using a cell that was illuminated by monochromatic light on over 25% of its cell area. As suggested by Prof. Kara Beauchamp, a voltage was put across the cell during the measurements. This voltage was determined by a Current-Voltage (IV) curve, which was then manipulated to produce a power curve. The voltage corresponding to the maximum power output of the silicon cell was the voltage that we used in our spectral measurements. These measurements were made during the summer. A voltage of 0.34mV was provided by the lock-in amplifier through its various DAC options. This voltage would assure us that our cell would be producing optimum power output when our spectral response measurements were taken.

Average IV Curve
### (Using a Silicon Cell)
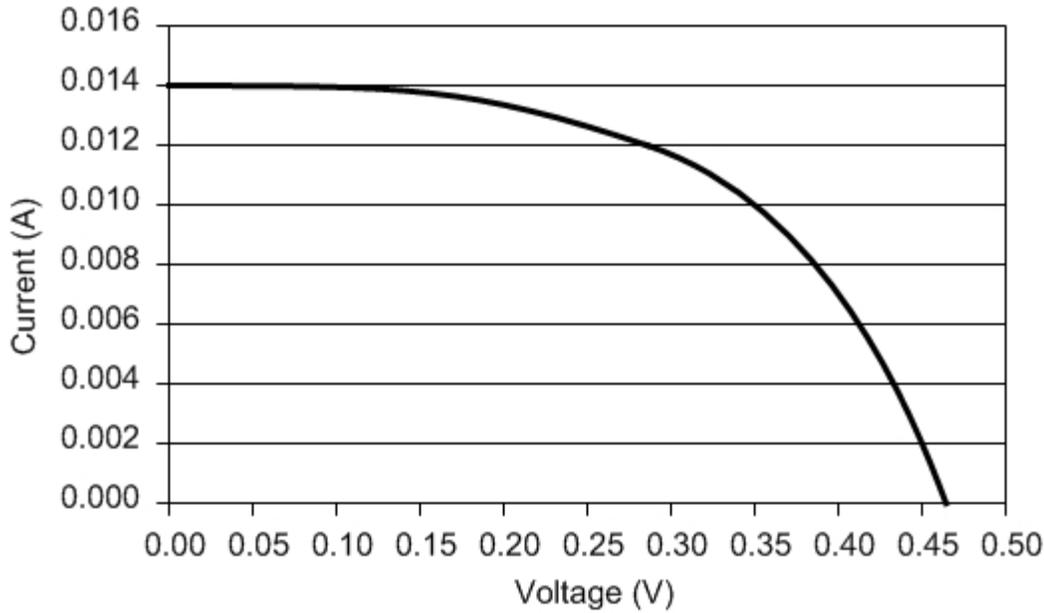
Average Power
(Using a Silicon Cell)

Graphs of Silicon cell IV curve and power output

An irradiance normalization constant A was found by dividing the maximum pyroelectric output by the output at each wavelength. Next our voltage output from the lock-in amplifier was converted back into current (1000V/A). The relative spectral response is equal to this current (in amperes) multiplied by the irradiance normalization constant, $R_r = I$ x A, and is plotted versus wavelength.
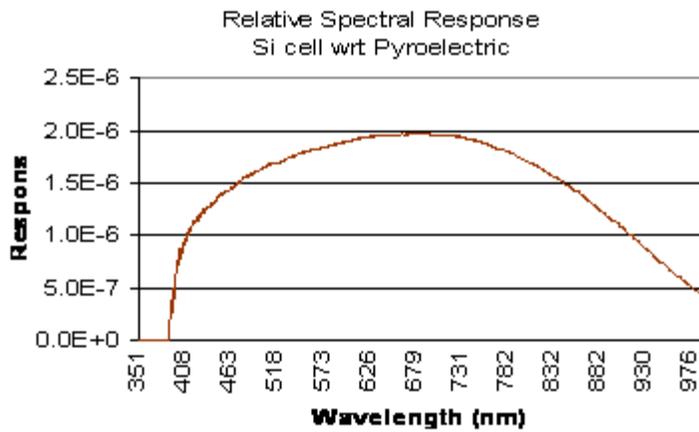
Graph of Si cell relative response

An absolute spectral response measurement is the "short-circuit current density per unit irradiance at a given wavelength" as described by our ASTM guidelines. A measurement of the cell without the provided voltage is required to find out the absolute response. These measurements were taken and then destroyed by Excel. Unfortunately, we are unable to reproduce these results within the limited amount of time left in the class. The absolute spectral response can be found by dividing the current (A) of the cell by the product of the illuminated area of said cell (m^2) and the pyroelectric irradiance (Wm^{-2}), $R_a = I / (aE)$. The spectral response is plotted versus wavelength. This result can then be converted into the external quantum efficiency using a given formula. The next group of students will be able to easily manipulate their measurements to get the absolute spectral response and its corresponding external quantum efficiency hopefully without any trouble from Microsoft products.

Conclusion

We were successful in getting this research project to a point where the next group can come in and continue the research part of this project. All the equipment is set up and communicating with the computer. We made raspberry cells with which they can take data and see ways in which to improve upon our design. We have laid the ground work for this project in setting up the electrical equipment necessary for taking the data. Now someone can come in and focus on making DSSCs and accurately measuring their efficiencies.