Very Berry Solar Cells

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Introduction

Solar energy (the conversion of light to electricity) has become an increasingly important source of clean energy. However, even with gaining attention over the years, it still provides less than 2% of the energy in the United States (1). Part of the challenge has been that the traditional materials used for generating solar energy like silicon, germanium and arsenic are not environmentally friendly. Moreover, the fabrication methods require very specialized conditions. Organic solar cells offer a better alternative. They can be made with low to medium-purity materials using low-cost processes. They can also be made with materials that can be processed as a solution that can be coated on to flexible surfaces. The push for organic solar cells gained momentum with the publication of the paper on dye sensitized solar cells (DSSC) by Brian O'Regan and Michael Graetzel (2). Since then, the field has burgeoned with researchers seeking higher efficiencies and greater lifetimes for these cells.
This module helps students get an appreciation for solar cells by fabricating and testing a solar cell that uses the dye from blackberries. This is the same kind of cell that O'Regan and Graetzel fabricated. It is called a Dye Sensitized Solar Cell (DSSC).

Although the module is written to be used in a Physics classroom, extensions of the module can be used to demonstrate the reactions that take place in the solar cell in a Chemistry curriculum. It can also be used as part of a Biology curriculum to compare the workings of the solar cell to photosynthesis.

Module objectives

Objective: To fabricate solar cells with titanium dioxide and various berries using inexpensive materials and a process that can be completed in two to three hours.

Student learning objectives

Physics

- Learn lab techniques to safely fabricate working solar cells using titanium dioxide and berries.
- Measure the current-voltage characteristics of the solar cell.
- Measure the open circuit voltage (V_{oc}) and the short circuit current (I_{sc}) and understand what the peak power point represents on the graph.

Chemistry

- **Learn to fabricate an organic solar cell using dyes.**
- Understand the oxidation-reduction reaction that enables the working of the solar cell.

Biology

- Understand the relationship between photosynthesis and the working of the berry cell.
- Investigate other pigments to use in the solar cell.

Key words : Solar Cells, Dye Sensitized Solar Cells (DSSC), Graetzel cells, Clean Energy, oxidation- reduction, Nanotechnology, Photosynthesis and solar energy conversion

Module data

Type of module: Experiment

Intended grade level: High School, Freshman and Sophomore college level;

Time required: Basic Level: One Lab session of two hours

Advanced/College level: Two lab sessions of two hours each.

Pre-requisite knowledge Basic Lab skills such as weighing chemicals, reading and following instructions.

List of equipment and supplies

Materials		Vendor
Blackberries	4-6	Any grocery store (fresh preferred but frozen may be used).
Ring stand for funnel	1	Any Chemistry lab
Buchner funnel with rubber hose	1	From Chemistry Lab This is used to filter the crushed blackberries. But it takes a long time and the yield does not seem like a lot. An easier alternative might be to dip the titanium dioxide coated slide directly on the juice of the crushed blackberries and wash off any seeds that may stick to the slide.
Filter paper	To fit funnel	Needed for filtration (see above). Not needed if going with direct dipping in crushed berries. Source: Chemistry Lab
10 mL measuring cylinder	2	
Scoopula	1	Source: Chemistry Lab
Indium Tin Oxide coated Glass Slides	10 (to make 5 cells)	Institute of Chemical Education (see reference 3). They cost roughly a dollar a piece.
Colloidal titanium dioxide powder	6g is much more than needed for 5 devices. But decreasing this amount will make it difficult to form a good suspension.	AEROXIDE (20g). From Evonik Degussa Corporation, 379 Interpace Parkway, Parsippany, NJ 07054; (973) 541 8106. OR Alternative: From Acros Corporation

Soap solution	Micro-90	Daigger Scientific, https://www.daigger.com/micro-90-cleaning-solutions-15664-group?gclid=CjwKCAjwj6SEBhAOEiwAvFRuKJdBSWq1GGk-jKQTHeT0yPSr6B0zFiuLN7m7izTgC_m3YI6AYjM14hoCgqoQAvD_BwE
Acetic acid solution pH 3-4 in de-ionized water	10mL	Prepare prior to Lab.
Syringe		https://www.daigger.com/
Parafilm		Chemistry Lab
Ceramic top Hot Plates that can go up to 450^{0}C	1 per group	Chemistry Lab
Forceps		Chemistry Lab
Transparent tape		Chemistry Lab – simply use gift wrap tape. Scotch tape will work as well but make sure no tape residue is left behind on glass.
Glass stirring rod (small)		Chemistry Lab
Cotton swabs	~10	Chemistry Lab
Plastic dropper	1	Chemistry Lab
Mortar and pestle	1 medium	Chemistry Lab
Plastic spatula	1	Chemistry Lab
Microspatula	1	Chemistry Lab
Petri dish	2	Chemistry Lab
Candle and matchbox	1	Chemistry Lab
Timer	1	Any stopwatch or could use a cell phone
Binder clips	Medium – 10	Any office supplies store
Potassium Iodide solution	A few mL per station	Prepare in Chemistry Lab prior to the start of the fabrication – 0.5 M Potassium

		iodide mixed with 0.05 M iodine in water-free ethylene glycol.
Multimeters	2	Can get inexpensive multimeter for approximately $10. One multimeter will be used for measuring the voltage and one for measuring current (for the I-V curve). If measuring only the output voltage, need only one multimeter.
Leads with alligator clips	Several	Possibly available in the Physics lab.
Potentiometers	1	Only needed for characterization (I-V curve). http://www.ietlabs.com/rs-200.html
LED white light source	1	In principle any bright light source will do for the purpose of an introductory lab. To measure the I-V curve, it would be good to have a white LED light source. Here are some alternatives: Overhead projector with a parabolic reflector. This gives mixed results so not strongly recommended. A halogen lamp with a parabolic reflector (Sylvania PAR 38 Halogen, GE 12 Or MB-JDR-75 (available at hardware stores). Need an IR filter when using a halogen lamp to prevent the cell from heating up and degrading. According to the institute of Chemical Education (ICE), an IR filter can be made using a petri dish filled with 0.1 M $CuSO_4$ solution. The solution will absorb most of the IR light

		but will allow most of the visible light to pass through. The important thing is that it has to be a white light source of sufficient intensity. Better to use a simple source (not one connected to a power supply). We are not varying the intensity.
Safety goggles	1 for each student	Chemistry Lab
Ring stand and Clamps	1	Chemistry Lab
Forceps with broad tips	1	Chemistry Lab. Used to hold the slides while erasing part of the carbon layer.
Ethanol in wash bottles		Chem Lab
Isopropanol		Chem Lab
De-ionized water in wash bottles		Chem Lab
Kim wipes		Chem Lab
Small Zip Loc bags to store the cells overnight.		
Latex Gloves – different sizes		

Table 2: Materials for the common table

Module Procedure

Outline:

The procedure consists of the following main steps:

1) Preparation of Blackberry juice.
2) Preparation of the titanium dioxide suspension.
3) Deposition of the titanium dioxide film.
4) Annealing of the titanium dioxide film.
5) Staining of the film with the dye (blackberry juice)
6) Making the carbon electrode.
7) Assembling the device.
8) Testing!

Steps 1) through 4) can be done during one two-hour lab session. Steps 5) through 8) can be done the next day OR all steps can be done in a long lab session.

Each step is detailed below.

Detailed Procedure:

Preparation of blackberry juice:

- Crush 6-8 blackberries in a mortar.

- Option1: (may take longer time) Place a Buchner funnel in the mouth of a conical flask using a rubber stopper to create a tight fit. Select an appropriately sized filter paper and place it in the funnel. Attach a vacuum hose to the outlet of the funnel and attach the other end of the hose to the vacuum outlet in a fume hood. The weight of the hose is enough to topple the conical flask so support the funnel either with a weighted ring or attach it to the fume hood with a clamp.

- Transfer the crushed berries to the funnel, add 2mL of deionized water to the funnel and turn on the vacuum. You should have enough juice in about 30 minutes. If this is not the case, add 2mL of deionized water and stir occasionally.

OR

- Option 2: (Quicker) Simply transfer the crushed blackberries to a petri dish. This method will result in some seeds sticking to the slides but they can be rinsed off later without a great decrease in performance.

Preparation of the Titanium Dioxide suspension:

This is a very important step. Making a good titanium dioxide suspension is critical to the performance of your solar cell. It is important to be as quantitative as possible.

- Measure 6g of titanium dioxide powder. This is not a very dense substance so you will need a large weigh boat for this process.
- Transfer the powder carefully to a medium sized mortar.
- Very carefully, add 9mL of acetic acid solution (pH 3-4 in deionized water) in 1mL increments to the 6g of titanium dioxide powder. After each addition of the 1mL of acid solution, gently grind the powder to remove all lumps. Add each increment of the dilute acid solution only when the previous mixing and grinding has removed all lumps.
  - Grinding will cause the material to accumulate on the sides of the mortar. Use a flexible spatula to return the material to the center of the mortar. Then add the next 1mL of water and so on…

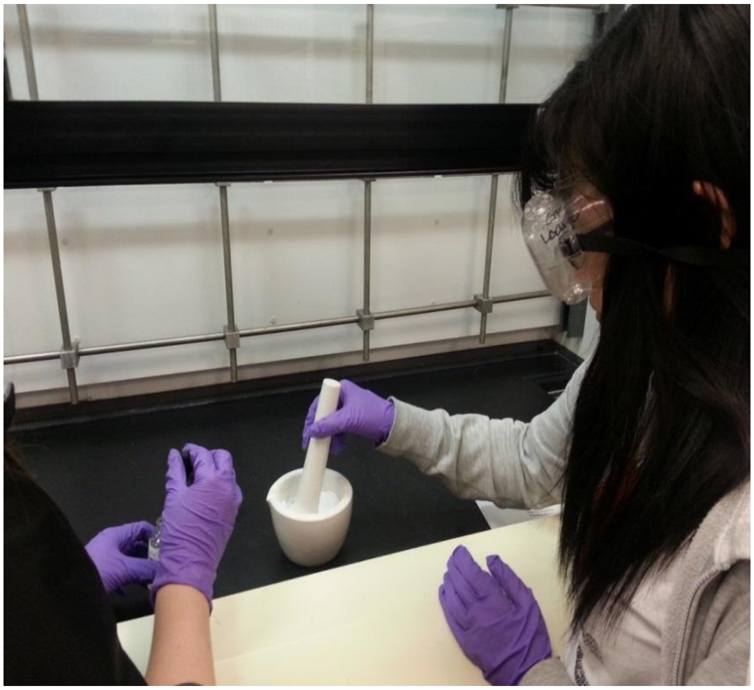


Photo Credit: Natalie Young, used with permission.

The final product must be a uniform and lump-free suspension with the consistency of paint as shown below:

Photo Credit: Natalie Young, used with permission.
Completed TiO_2 suspension

- Add a drop of a surfactant (soap solution). Do not grind or agitate the suspension after this step.

  We will be using a syringe to store and apply the suspension on the glass substrates. You could store in a bottle with a dropper cap and use the dropper cap but the syringe is a convenient way to push the suspension out in drops.
- Start with a new syringe. Seal the nozzle of a syringe tightly with two layers of parafilm.
- Remove the plunger from the syringe and using the microspatula, **gently scoop** the suspension into the syringe.
- **Very gently**, push the plunger slightly into the syringe. If you push it too hard, the suspension might push the film out and you will have to start all over again.
- Wipe off the excess titanium dioxide with a Kimwipe and let the syringe sit for 15 minutes. If any bubbles are visible after 15 minutes, allow them to come to the surface before using the suspension. If the suspension is too thick, the layer will peel away after application on the substrate. If it is too thin, the solar cell will not absorb enough light.

Applying the TiO_2

While you are waiting for the titanium dioxide to be ready, prepare the glass substrates. These substrates will serve as the electrodes for the solar cell. The glass substrates are coated with a very thin layer of Indium Tin Oxide on one surface. The advantage of

Indium Tin Oxide is that it is both conducting and transparent. The coated side of the slide is therefore, the conducting side.

The first step is to determine which side of each glass slide is the coated (and therefore the conducting side).

- Pick up a glass substrate. Use a multimeter to check the resistance of both surfaces of a substrate. The conducting surface will have a very low resistance (a few Ohms). Place the substrate conducting surface up on a clean surface (a sheet of wax paper or a lab soak sheet-may be used.
  - Repeat this with five more substrates. Place the substrates in a 2x3 array.
  - Tear off a small piece of tape (about two inches long) and tape the substrate to the surface along the two parallel lengths of the substrate so as to cover about 1mm of the substrate.
  - Take another similar piece of tape and cover about 4-5mm of the substrate to the surface. The tape will form a 40-50 micron deep channel. The titanium dioxide can flow into this channel to form a layer of the same thickness.

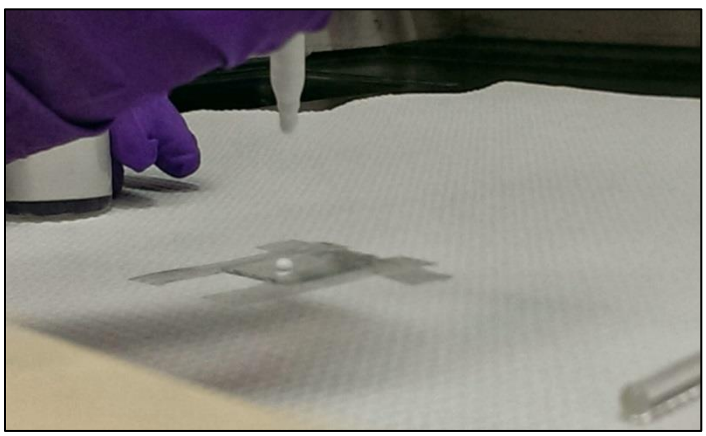


Photo Credit: Natalie Young, used here with permission.

  - Remove the parafilm from the syringe and push the plunger gently out while holding the syringe over a paper towel (away from the substrate). This is to ensure that the flow of the titanium dioxide is smooth before you apply it to the actual substrate. Be very gentle while doing this as there is a good chance that the titanium dioxide suspension will spurt out.
  - Very carefully, push the plunger out while holding the syringe over the substrate so a single drop (or two) is released on the substrate (see above).
  - Using a glass rod, roll out the titanium dioxide on the substrate. This must be done within 5 seconds of releasing the drop on the substrate. For best effects, sweep the

rod rapidly towards the bottom of the substrate, lift the rod and sweep again in the same direction.

- Repeat the sweeping action two or three times until you get a uniform application.
- If the layer appears uneven, you may wipe it off with a damp tissue and start the application again with a clean glass rod.
- Once the titanium dioxide layer is formed, carefully remove the tape. Place the substrate in a petri dish and close the dish.
- Repeat the process with four more substrates.
- Wash and dry the glass rod. You may use the same titanium dioxide for other substrates. Seal the syringe tightly with parafilm and put it away. Clean the glass rod as well.
- Allow the titanium dioxide to dry for a minute. The next step is to anneal the titanium dioxide film.

Annealing the titanium dioxide film

- The titanium dioxide film is annealed at very high temperature on a hot plate. Using forceps (this may need some practice), transfer each slide to the surface of the heater. The forceps should grab the edges and not the surface of the slides to avoid scratching the titanium dioxide application.
- Turn the hot plate on to the maximum setting. Be very careful as the heater will get very very hot.
- Keep the substrates on the surface for 30-60 minutes (Might be worthwhile experimenting with this time). As the substrates heat up, the titanium dioxide film will brown and then return to its off-white color. This color change is needed for the cells to work well.
- Switch off the hot plate and let the substrates cool completely – this is a good time to take a break!

Dyeing the titanium dioxide film

- By now, you must have collected enough blackberry juice in the flask. Pour the juice into a petri dish. If you did not filter the juice (option 2), you can use the unfiltered juice in the petri dish.
- Very carefully (touching only the edges with your gloved hand) transfer the substrates to the petri dishes so that the titanium dioxide layer is submerged in

the juice. Move the substrates around until all the white film is coated with the juice.

- Soak the titanium dioxide coated side for 10 minutes in the berry juice. There should be no trace of white titanium dioxide after the 10 minutes while viewing the slide through the petri dish. If there is an unstained portion, soak for an extra 5 minutes until the white disappears. While the substrates are being stained, you can apply the carbon coating to the other electrodes (see below for the procedure).
- Wash the film (now stained purple) in deionized water, and then in ethanol and isopropanol.
- Gently blot the film with a tissue. The dyed substrates can be used immediately. If not, they can be stored in acidified deionized water (pH 3-4, acetic acid) in a closed, dark-colored bottle.

Preparing the carbon electrode

We are now ready to prepare the carbon electrode.

- Clean five more glass substrates by rinsing them with ethanol (over a funnel in a waste bottle) and patting them dry with Kimwipes.
- Using a multimeter, check for conductivity.
- Place the slides on a clean petri dish or surface with the conducting side facing up.
- Light a tea-light.
- Place a stopwatch/timer on the table so you can measure the time comfortably.
- Using a pair of forceps gently pick up one of the slides with your dominant hand. The best way to do this is to grab a corner of the slide with the forceps.
- Very carefully flip the slide and hold the conducting side of the slide over the flame. Start the timer with your other hand. Or have your teammate start the timer.
- Move the substrate back and forth for 30 seconds. Soot will be deposited on the conducting surface. Make sure this deposition is as uniform as possible. Try to cover the substrate fully. **<u>But do not exceed 30 seconds!</u>**

- Using a cotton swab, gently remove the soot from two edges of the substrate so you have a 5mm strip on either side of the substrate that is not coated with soot.
- Once the soot is applied, make sure you do not touch the surface. The substrates should be handled only at the edges with forceps.

Making the solar cell

The process has also been described in a YouTube video (link in the reference section at the end of the module), The video also describes how chlorophyll extract from spinach can be used as the active layer in the solar cell instead of blackberry juice. The process of extracting energy from the light hitting the cell is similar to the process of photosynthesis in plants. Students in a Biology class can make solar cells using Chlorophyll pigment instead of the dye in blackberries. The working of the solar cell can then be compared to the process of photosynthesis.

We are now ready to build our solar cell!
If you had stored the TiO2 coated substrate overnight or if it is staining, take it out and rinse it with de-ionized water.
Important! Dry the stained glass thoroughly. This can be done by rinsing it in ethanol or isopropanol and placing it on a tissue with the film side up.
Make sure the substrates are dried thoroughly.
Place the TiO2 coated substrate on a flat surface.
The following step should be done quickly to protect the TiO2 film from being exposed to the air for a long time.
Make sure the dropper bottle containing the iodide electrolyte solution is close by.
Take the carbon-coated electrode, holding it by one of the corners and gently flip it on top of the TiO2 coated substrates, leaving an offset for the leads. At each end, we must have 4-5mm exposed (this is the part of the substrate that is not coated with carbon)
Place two binder clips on the other two edges to hold the cell together.
Next, orient the cell so it is vertical. Place one or two drops of the iodide electrolyte in the gap between the substrates.

Very carefully open and close the binder clips, one clip at a time. The electrolyte will be drawn into the space between the substrates on to the TiO_2 film which will change color. Tilt the cell until the entire surface is coated.

Wipe off the excess electrolyte from the exposed clear glass areas. This is very important to get good electrical contact. Remove all the excess electrolyte completely from the transparent edges of the slides.

Testing

This is the exciting part – you get to test your cell!

Attach a red wire with an alligator clip to one clear end of the cell (where you removed the soot) and a black wire to the other clear end.

Attach the other end of the red wire to the positive end of the voltmeter (your instructor will show you which terminal to use).

Attach the other end of the black wire to the ground terminal of the voltmeter.

Place the cell with the TiO_2 electrode facing the white light LED source.

Record the voltmeter reading – this is called the open circuit voltage.

Show the reading below:

__________________volts.

(If you are teaching this as part of a high school course, this may be a good place to stop and talk about the conversion of solar energy to electrical energy. At the college level, you could go further and measure the current-voltage characteristics of the solar cell. You may not get the ideal curve but you can show that the solar cell does not obey Ohm's Law, i.e., the current is not directly proportional to the voltage. If you do get a reasonable curve, you could compare the efficiency of various cells relative to each other, as described below.)

College Level:

The relative efficiency of the cells can be measured using a simple circuit. Since a solar simulator (a light source that puts out light that mimics the solar spectrum) is very expensive and not readily available to all, it is not possible to measure the absolute efficiency of a solar cell. But it is possible to compare the efficiency of cells with each other. In other words, we can compare the efficiency of all the working solar cells that we have fabricated in this lab module.

In the procedure below, we will first measure the current-voltage (I-V) characteristics of a solar cell. If the graph of current vs. Voltage does not match the characteristic curve, then the fabricated device is not a working solar cell even if it produces an open-circuit voltage (the voltage measured directly across the electrodes of the cell and denoted by V_{OC}).

Measurement of the Current-Voltage Characteristics

To measure how the current in a solar cell varies with voltage across the solar cell, we set up a circuit as shown below:

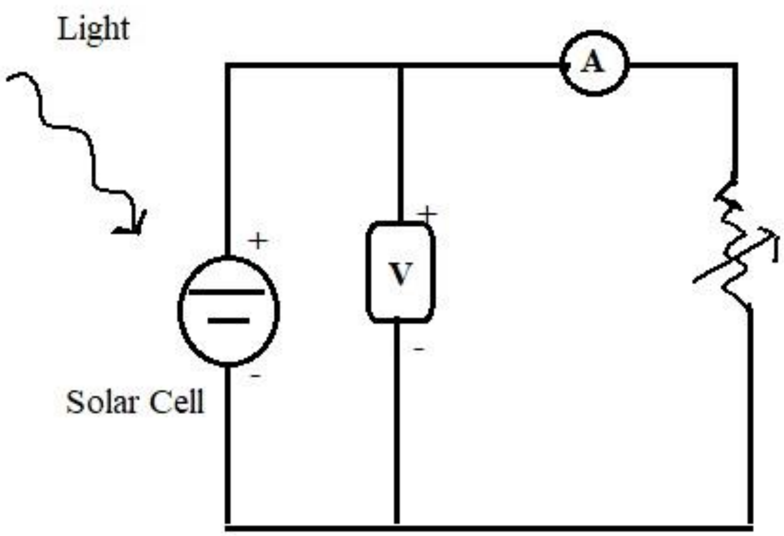


Fig.1 Circuit Diagram to measure the current-voltage characteristics of a solar cell

The light source is an LED that is powered by a power supply. The sample may be secured on the ring of a ring stand. It is important to keep the distance between the source of light and the sample holder the same for all measurements. This ensures that the same intensity of light is incident on all the samples.

The voltmeter is connected in parallel to the sample (the solar cell is the power source so it is like connecting the voltmeter to measure the voltage across the terminals of the battery. The ammeter, shown as 'I' in the figure above, is connected in series with the solar cell and a variable resistance box (shown as a potentiometer in the figure above).

Data for the current-voltage plot (I-V plot) is collected as follows:

1) Complete the circuit (without the solar cell)
2)Set the resistance to a low non-zero value. **Setting it to zero could short the cell.**
3) Set the voltage output of the power supply (not shown in the figure) such that the current output is less than 1.0A (this maximum current value is based on the ratings for the specific LED you are using, so adjust accordingly). After this, do not touch the current and voltage knobs to ensure that all measurements are made with the same intensity of light incident on the solar cell.
4) Now place the solar cell on the ring stand and connect the voltmeter leads to the two electrodes. The carbon electrode faces away from the light.
5) Measure the current and the voltage. Write down the current, voltage and the resistance values in a data table (typical data table shown below).
6) Change the resistance values by 20Ω and measure current, voltage and resistance. The current for a very low resistance is the maximum possible current through the solar cell and is called short circuit current or Isc.
7) Take as many measurements as you can especially for values of resistance where you see a rapid change in current. Keep increasing the resistance until you reach 1 or 3 MΩ or until you stop seeing a change in current. The voltage you measure at very high resistance is called 'open-circuit' voltage or VOC. The short circuit current and the open circuit voltage are important characteristics of the solar cell.

Sample table

Resistance (Ω)	Current (A)	Voltage (Volts)
20		
40		
…(more values)		
1000		
2000		
…(more values)		
…(more values)		
10,000		
…(more values)		
1MΩ		

Table 3: A Sample Table

8) Plot a graph of current in the y axis and voltage in the x axis.

Question: What kind of plot do you get? Does the solar cell behave like a resistance? Does it obey Ohm's law? Explain

9) We will now calculate the Fill Factor of the solar cell. This is a measure of the relative efficiency of the solar cell.

The efficiency of a solar cell, i.e., the measure of how much of the incident light energy is converted to electrical energy, is given by the Solar Power Conversion Efficiency.

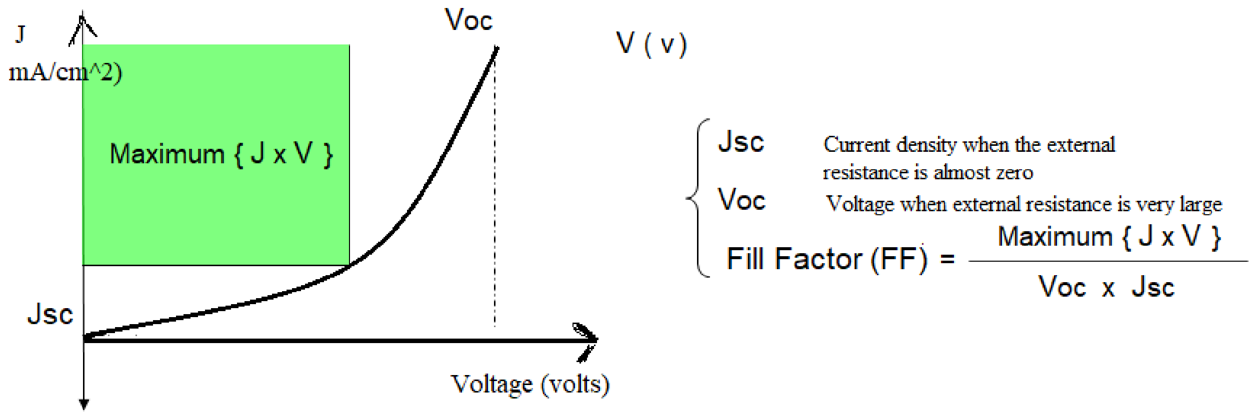
Solar Power Conversion Efficiency:

$$\frac{\text{Electrical Output Power}}{\text{Sunlight Power}} = \frac{\text{FF x Voc x Jsc}}{\text{Sunlight Power}}$$

$$= \frac{\text{Max\{J(mA/sq.cm) x V (v)}}{\text{100mW/sq.cm)}}$$

J is the current density, defined as

Current density J (mA/cm2) = Current (mA) / Active area (cm2). The active area is the rectangular stained area on the slide.



Graph of current density vs. Voltage. The fill factor (FF) is the ratio of the area of the green rectangle to the area formed by the dotted line.

Substituting the expression for the fill factor in the expression for the solar efficiency above, we can see that the fill factor is a measure of the relative efficiency (how much one cell is efficient compared to the other cells) as long as we keep the light source at the same intensity. We can do this by ensuring that the power supply to the LED puts out the same voltage and current and the distance from the light source and the solar cell is kept the same for all measurements and all cells.

Extensions: Students can experiment with raspberries, pomegranate, tea leaves and turmeric powder to compare efficiencies.

References

1) https://en.wikipedia.org/wiki/Solar_power_in_the_United_States

(Last accessed April 28, 2021)2) O'Regan, Brian and Gratzsel, Michael, Nature, 353, pp737-740 (1991)

3) Nanocrystalline Solar Cell Kit, Institute of Chemical Education.

https://ice.chem.wisc.edu/kits-and-publications

4) Video demonstrating the process for making the dye cell using blackberries and Chlorophyll as an alternative.

https://www.youtube.com/watch?v=hwH_h_Zi3Vk

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