



The Caltech Solar Materials Discovery Kit (Aka Solar Energy Activity Lab or SEAL)

User's Guide

Last Revised: 08 July 2014

Materials Checklist

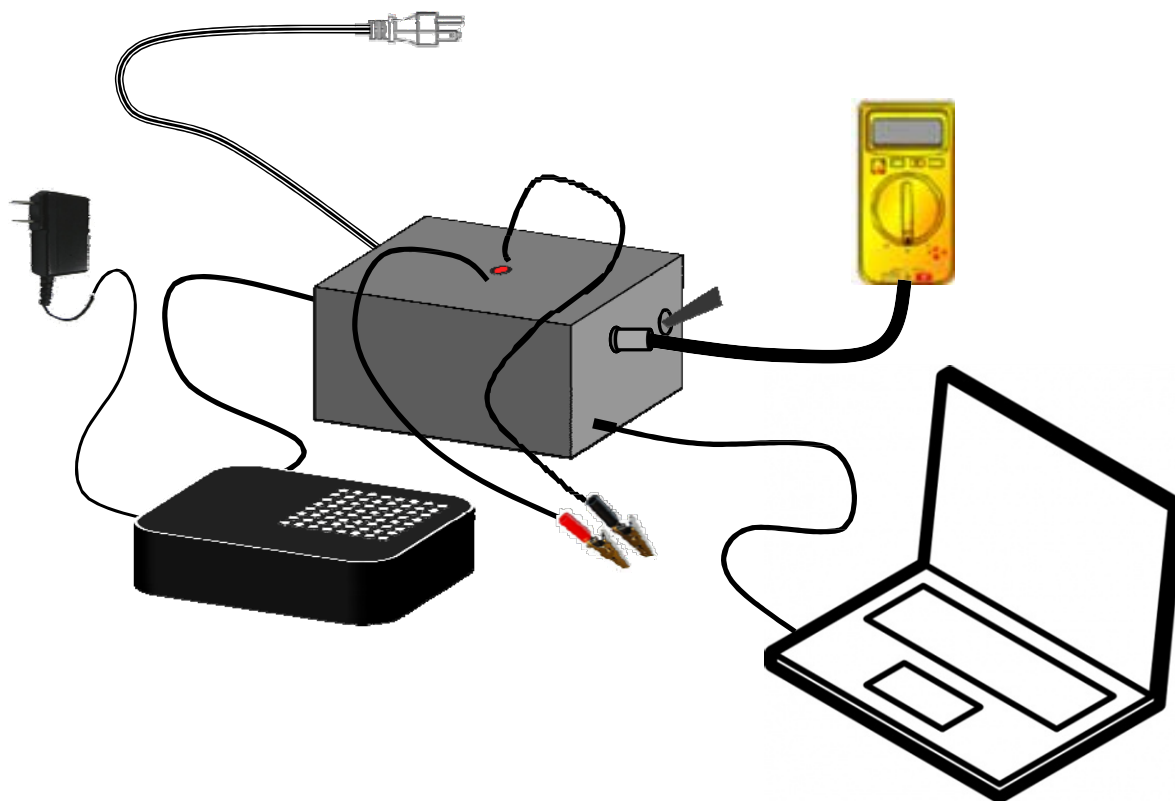
Items included with the kit:

- USB Flash Drive with National Instruments hardware drivers, standalone SMD software, excel templates and User's Guide
- LED Array Unit (black box)
- Current Integrator (aluminum box, with electrode leads)
- Digital Voltmeter/Multimeter (small red box)
- CAT 5 ethernet cable (connects LED to integrator)
- USB Cable (connects integrator to PC)
- BNC Cable (connects integrator to voltmeter)
- 6 FTO-coated glass slides, 4" x 4" or 3" x 3" square (one pre-spotted with iron oxide standard)
- Copper Tape with Conducting Adhesive (McMaster-Carr: 76555A712, 1/2" wide)
- 5-min Epoxy (Devcon 20845 5-min epoxy)
- Insulated Wire (McMaster-Carr: 8054T22, stranded wire)
- 2 Graphite Rods (Wale Apparatus: 12-1201, 1/8" x 12")
- Spotting Template
- User's Guide

Items required but not provided with the kit itself:

- Computer running under Windows XP or 7 (NOT Windows 8 or Mac)
- Pyrex glass crystallization dish, 150 mm x 75 mm (125 mm x 65 mm dishes fit the 3" x 3" plates)
- Sodium Hydroxide, 0.1 M aqueous solution
- Isopropanol or acetone
- Micropipette (5-25 μ L range) and disposable tips (Cheap version with 25 μ L range: <http://www.flinnsci.com/store/Scripts/prodView.asp?idproduct=18990>)
- Jewelry kiln (Good, cheap version: Paragon SC2 - http://www.clay-king.com/kilns/paragon_kilns/paragon_sc2.html)
- Scotch tape

Figure 1. Schematic diagram showing the connectivity of the SMD instrument.



SAFETY

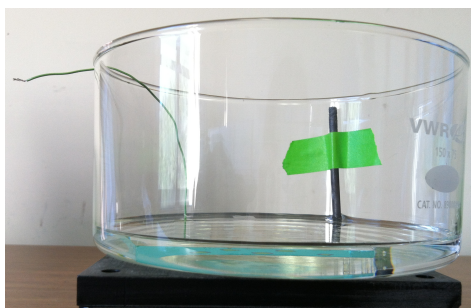
Always wear eye goggles and gloves when working with chemicals. The electrolyte solution (0.1 M NaOH) will burn skin and eyes. Flush eyes or skin with water for 15 min in case of accidental contact. Avoid skin and eye contact with epoxy resin. Can cause irritation and bonding of skin to itself or other materials.

Assembly of the Instrument

- 1) Connect the components of the instrument as shown in Figure 1. Do not yet connect the leads to the electrodes (the sample plate and the graphite rod counter electrode). It is generally good practice to plug the silver Current Integrator electronics box (the box that connects to the voltmeter) and the LED array (black plastic box) into different outlets. The LED array may light up depending on the order the devices are connected. This is perfectly fine. The “ground” lead (black) of the BNC cable connects to the “COM” port of the voltmeter and the other lead (red) into the “VΩmA” port. Reversing the leads will make all the voltages read the same numerical value, but with opposite sign.



- 2) Use tape to secure the graphite rod (counter electrode) to the side of the crystallization dish. The rod should be vertical on the side of the dish with the bottom of the rod touching the bottom of the dish. Be sure the tape is at least an inch above the bottom of the electrode so that the electrode makes contact with the sodium hydroxide solution (next step) in the dish. Place the plate in the bottom of the dish with the metal-oxide spots (with epoxied wire) facing upwards.



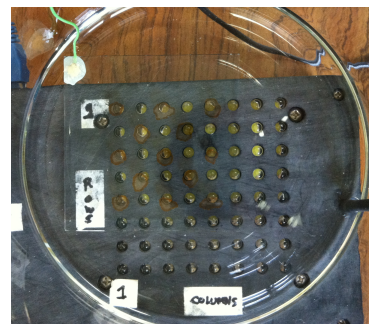
- 3) Fill the glass dish with electrolyte (e.g., 0.1 M NaOH) so that the plate is completely immersed and that some part of the graphite rod is submerged. A large quantity of electrolyte beyond this minimum is not required. The level of electrolyte should NOT be so high that the alligator clips will come in contact with electrolyte; the clips should only attach to the dry parts of the electrodes.
- 4) Make sure that the alligator clips have still not been attached yet, then activate the power (toggle) switch on the current integrator box. The LEDs might activate and blink at this step. (Note: Having the alligator clips attached and the circuit completed when powering on the current integrator may cause too high of a voltage to pass through the system and fry the electronics).
- 5) Activate the voltmeter. Set the voltage switch to 20 DCV range.
- 6) Start the Solar Materials Discovery program by clicking on the Solar Materials Discovery shortcut. Select "yes" to override any warnings that pop up. The program takes several seconds to start up as various drivers are loaded.
- 7) Eventually, you will see a prompt in the open window asking for the reading on the voltmeter. This step is intended to calibrate the applied voltage, and set the equipment to a zero position before beginning any experimental work. You should enter the voltmeter reading in units of volts (e.g., "0.035" V corresponds to 35 mV). After entering the value, the voltmeter should read 0.000 V (or within a few mV of this value). If it does not read close to zero, you may have incorrectly entered the voltage reading. Exit the program and try again.
- 8) Now connect the leads to the electrodes: connect the counter electrode (the graphite rod) to the black alligator clip; connect the working electrode (the conducting glass sample plate) to the red alligator clip.
- 9) You will notice the LEDs turn on and off. This is an initialization sequence; wait for it to complete. A menu will open when the process is complete.

Scanning a Plate

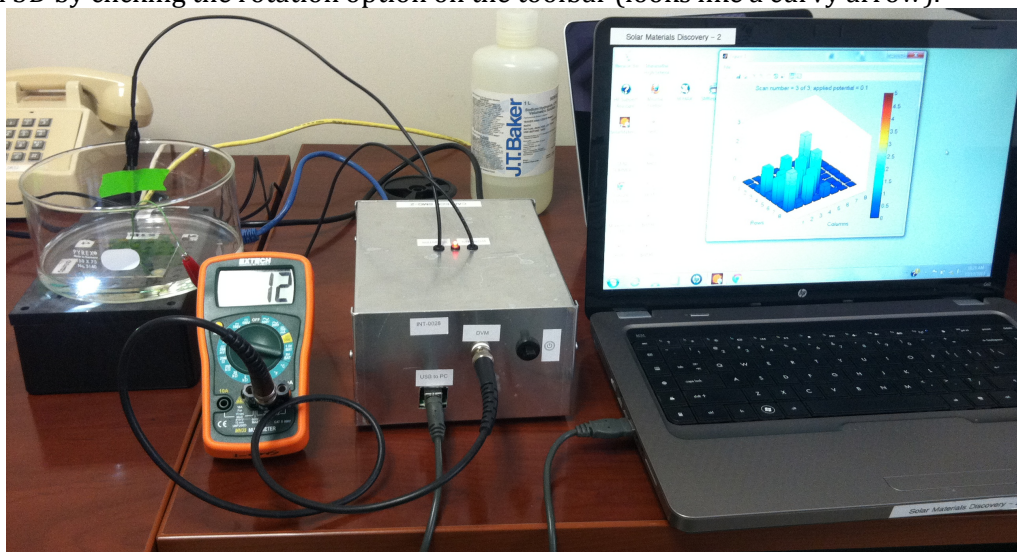
- 1) Click on the button "Apply Voltage" to set the bias potential in volts. For general scanning for water oxidation, enter "0.100" to set the bias potential to +100 millivolts. Wait a few moments and note that the voltmeter now reads +0.100 V (within ± 0.02 V). If the voltmeter does not read close to the value that you entered, there may be a calibration problem. Exit the program and try again.

- 2) Click on the button “Check Dark Current” (also referred to as rest current). This will generate a plot of volts vs. time on the screen and should stabilize to a low value (<0.5). The y-scale is volts because there is a current-to-voltage conversion within the equipment itself. Please remember that the units of current are typically microamps. Continue to periodically click on this button until the points stabilize around a common value. Ideally, the points will be low on the plot (<0.5). This process can take a little waiting (ca. 10 minutes), but you can periodically recheck the dark current as many times as you like over this period. If the rest current is large, try reducing the applied voltage to (0.05–0.10 V). High rest currents decrease the signal-to-noise ratio during the light-driven experiment that forms the basis of the results obtained from the kit, so the lower the Dark Current, the better your results will be!

- 3) Make sure the glass plate (i.e., the working electrode) has its spots aligned properly over the LED array and in the proper orientation relative to the row/column pattern you have used for spot composition. Improper orientation of the plate will result in mismatch errors when the data are reported for the semiconductor materials. Note: the cone of light emitted from any one LED may overlap with an adjacent spot if the spots are not well defined and sharp. This can lead to some “cross-talk”. With experience, you will be sufficiently adept at pipetting to form the individual spots that this will not be a major problem.



- 4) Click “Perform a Scan”. Enter the number of cycles that will be averaged for this scan (e.g., “3”). Each cycle takes 1–2 minutes. If you were to input “3”, then each spot will be scanned three times, and the responses for each spot will then be averaged by the software to give a single final value. Note that the LEDs will blink and the progress of the scans is reported in real time on the monitor in 3D. The menu will re-open when the scanning is complete. Note: you can rotate the chart in 3D by clicking the rotation option on the toolbar (looks like a curvy arrow).



- 5) On the menu, click “Save Data to a File” and then on “experiment information” in the next pop-up window. Enter the appropriate information as prompted by entries, from top to bottom (LED color will be white). The next pop-up will allow you to edit the “experiment information” again or “load chemical and pattern information from excel” or “manually load chemical and pattern information”. To load from a file, simply select the Microsoft Excel template that has been filled out with the chemical and pattern information previously and then verify the pattern is correct.

Finally, either “save data to a file” or go back and edit experimental information or the file chosen if necessary.

To manually load chemical and pattern information, follow the sequence of menus presented. First enter how many total elements were used on the plate. Select each element using the crosshairs on the periodic table. Be sure to note the order the elements were chosen. Then enter which metal salt was used for each element as well as the concentration of that solution. On the next menu, click “manually load pattern information” (or go back and edit experiment information or chemical information if desired). Pick a preexisting pattern or customize a blank template using the cross hair tool. Be sure to not click outside of the window while editing or the program may crash. Finally, either “save data to a file” or go back and edit experiment, chemical or pattern information.

Data will be saved locally as *.smd files that can be uploaded to the Caltech Solar Materials Discovery online database- <http://www.bilrc.caltech.edu/solmatdisc/index.php>, as *.fig files that can be opened from a graphics window in the data collection program, as *.bmp bitmap images and as *.xls excel spreadsheet. The spreadsheet is especially useful since it contains the data as numerical values for easy manipulation later.

- 6) Click on “Go to Solar Materials Discovery website” in the main menu to log-on to the website and upload data. The website also has downloads of the user guide, templates, software and other resources available. A temporary guest log-on is:

Username: smdvisitor
Password: SolarPhoton
(case sensitive)

If you do not yet have your own password, please contact Michelle Hansen by email at mchansen@caltech.edu to request one.

Spotting Plates

- 1) Clean your glass slide (both sides!) with water and isopropanol or acetone. Next, dry the slide.
- 2) Test for the conductive side of the glass using your multimeter on the 2000 Ω setting. The side with a measurable resistance is conductive (will measure in the 20-100 Ω range).
- 3) Place the glass plate conductive side up on top of the plate-spotting template. These circles will be the area in which to deposit the solutions.
- 4) Using a micropipette, deposit between 5-10 μL total of solution per spot. If using more than one solution, be sure to calculate ratios of metal salts based on both their molarities and volumes deposited.
- 5) When the spotting is complete, the solutions need to evaporate. It is optional to warm the glass plate on a hotplate set at 80-100°C (typically setting 2-3) for several minutes until spots evaporate. This method is faster and will help avoid the “coffee ring effect” which often occurs from air-drying, but is not absolutely necessary. Once the spots are evaporated, fire the plate at 500°C for approximately 3 hours. A small jewelry kiln works very well for this.
- 6) Cut a ~5” piece of wire and strip ~0.5” of insulation off of each end. Once the plate is fired and cooled back to room temperature, attach one end of the wire to the top left (1,1) corner of the plate using the copper tape. Be sure to splay the wire strand onto the plate to make as much

contact as possible. Then cover all of the copper tape and exposed wire with 5 min epoxy. If any copper or wire is exposed, the circuit will short and the plate will not work.

Suggestions for spotting

- Spot $\text{Fe}(\text{NO}_3)_3$ (iron oxide) on plates as a standard in a 3x3 square in one corner. The more uniform the data for these spots, more reliable the data for the whole plate.
- Note that a small amount of light from one LED can spillover into the adjacent spots on the slide. It is often is a good idea to leave a blank space between spots to get a checkerboard pattern.

For assistance setting up the SMD kit or help trouble-shooting any problems that may arise, please contact Michelle Hansen at mchansen@caltech.edu or (626) 395-2829