

Laboratory Handout

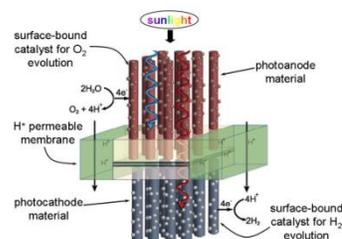
The Solar Energy Activity Lab

The goal of the Solar Energy Activity Lab (SEAL) is to find a fortuitous combination of metals to make a previously uninvestigated semiconductor with the ability to trap sunlight and use its energy to split water into hydrogen and oxygen. The hydrogen and oxygen could then be used in a reverse reaction that combines the hydrogen and oxygen to extract either electrical energy (*e.g.*, fuel cell) or heat energy.

BACKGROUND

For centuries the world has been run by energy produced from fossil fuels. Not only are these sources becoming harder to obtain, but the by-products given off by using these energy sources has and are continuing to pollute our planet. Considering the magnitude and expected growth of worldwide energy demand, sunlight has perhaps the best chance of any renewable resource of satisfying our energy needs. Most importantly, the sun has the ability to meet our energy needs since as much energy from sunlight hits the earth in an hour than is currently use worldwide in a year! However, one problem with using the sun as an energy source is that it only illuminates half of the earth's surface at any one times. Thus in order to use solar energy at night, one must be able to store it during the day. As a result, one active area of chemistry research is that of solar energy storage where the sun's energy is transformed to a useable chemical energy source.

Among the many schemes proposed for storing the sun's energy is one that mimics the process of photosynthesis. Using techniques belonging to the discipline of photoelectrochemistry, scientists have proposed systems for electrolyzing water – splitting it into hydrogen and oxygen gas – using sunlight as an energy source. The schematic shown here is a model for such a system and is currently under development by several the California Institute of Technology (Caltech) research labs in collaboration with scientists at several other institutions, which include UW-Oshkosh (<http://www.ccisolar.caltech.edu/>). This week you will begin participating in this research project aimed at discovering new types of photoelectrochemical water oxidation materials.

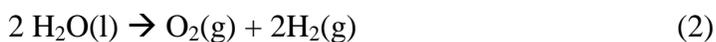


Electrochemistry and Materials Science

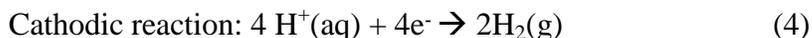
The electrode at which oxidation occurs is called the anode and the electrode at which reduction occurs is the cathode. We then defined the cell potential, ΔE_{cell} , according to Eq. 1, where E_{cathode} is the reduction potential for the half-reaction occurring at the cathode, and E_{anode} is the reduction potential for the half-reaction occurring at the anode.

$$\Delta E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \quad (1)$$

Cells for which $\Delta E_{\text{cell}} > 0$ produce electricity and are known as galvanic cells. Cells for which $\Delta E_{\text{cell}} < 0$ are known as electrolytic cells; these require a source of electrical energy for operation. Consider an electrochemical cell in which water (H_2O) is split into its elemental constituents, hydrogen (H_2) and oxygen (O_2) –



Using platinum wires as electrodes, we can represent this cell as: [Pt | O₂, H₂O || H⁺, H₂ | Pt]. The half-reaction proceeding at the anode (oxidation) is described by reaction 3. The half-reaction proceeding at the cathode (reduction) is described by reaction 4. If the acid concentration in the cell ([H⁺]) is 1 M,



and we bubble oxygen gas at 1 atmosphere of pressure at the anode, and hydrogen gas at 1 atmosphere pressure at the cathode, we would measure a cell potential of -1.23 V (Eq. 1.5, reduction potentials are given versus SHE). Since $\Delta E_{\text{cell}} < 0$, this is an electrolytic cell: in order to produce H₂ and O₂ gas, a voltage of at least 1.23 V must be supplied by an electrical power source. More current will flow through the cell (keeping the areas of the electrodes constant) if we increase the applied voltage above 1.23 V. The total standard free energy change for decomposing 2 moles of H₂O is then

$$\Delta G^\circ = -nF\Delta E^\circ = -4(9.65 \times 10^4)(-1.23) = 4.75 \times 10^5 \text{J}$$

If we hope to drive the water splitting reaction using sunlight as the source of electrical energy, then we must generate a voltage greater than 1.23 V. Ideal photovoltaic devices can produce this voltage using photons of energy greater than 1.23 eV, corresponding to light in the near-IR region of the electromagnetic spectrum. A considerable portion of the solar spectrum includes photons above this energy threshold; consequently, the fundamental thermodynamics of water electrolysis are amenable to the use of sunlight as an energy source.

Semiconductors

Semiconductors are solids that have electrical conductivity intermediate between that of an insulator and a conductor. The conductivity properties of semiconductors are described in terms of electronic energy bands. In molecules, two atomic orbitals from adjacent atoms can interact to form two (bonding and anti-bonding) molecular orbitals. A similar interaction takes place in many crystalline solids, but in this case, a large number of atoms (~10²³) interact to form dense bands of orbitals that extend throughout the entire crystal.

Just as in molecules where different types of atomic orbitals can interact to form different types of bonds, different atomic orbitals in solids interact to form different energy bands. The bands are composed of orbitals that are very close in energy. The bands are formed from both filled and empty atomic orbitals that give rise to bands that are either filled or empty. The bands that are most important to the properties of the crystals are the highest energy filled or valence bands (VB) and the lowest energy unfilled or conduction bands (CB).

The energy region between the VB and CB is known as the band gap. If the VB and CB overlap in energy, the crystal is electrically conducting (like a metal); if the two bands are very widely

separated in energy, the crystal is an insulator. Semiconductors are intermediate between conductors and insulators, having band gaps in the range of 0.5 to 4 eV. In most semiconductors there are few or no energy levels in the band gap. The bands for a semiconductor are shown in Figure 1. Normally we don't show individual bands and only mark energies of the top "edge" of the valence and bottom "edge" of the conduction band levels. These appear in Figure 1 as dark lines.

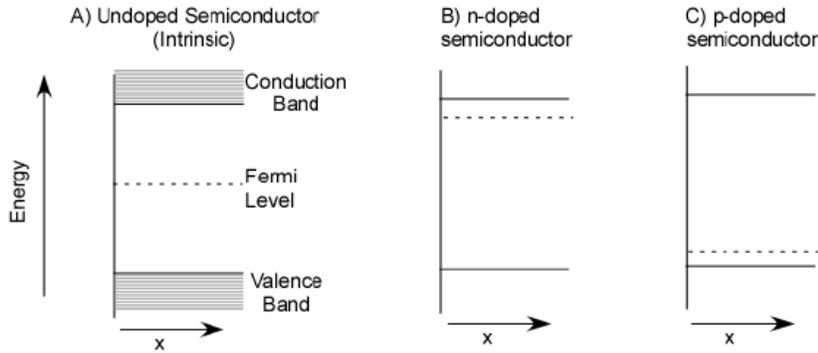


Figure 1 Semiconductor band diagrams. Increasing energy is up and the horizontal axis, x , is distance into the semiconductor as you move right, the vertical line represents the edge of the semiconductor. A) An undoped or intrinsic semiconductor showing multiple levels in the valence and conduction bands. B, C) Diagrams for semiconductors doped with donors (n) or acceptors (p), respectively, showing only the highest energy valence band and lowest lowest energy conduction band levels.

At absolute zero temperature, all of the VB levels are filled with electrons and the CB is empty. At higher temperatures, thermal energy can excite electrons from the valence band the conduction band. When this occurs, mobile CB electrons and mobile VB holes are formed. These mobile charge carriers (*i.e.*, electrons and holes) can move readily and provide electrical conductivity to the crystal. For very pure semiconductors, however, the gap between the valence band and conduction band is large, so even at room temperature (~ 300 K) there are few mobile electrons and holes, and the conductivity is very poor.

Doped Semiconductors

Semiconductors can be doped by introducing impurity atoms into the crystal lattice. If these dopant atoms have filled levels just below the conduction band, they serve as electron donors, known as n -type dopants; if they have empty levels just above the valence band, they serve as electron acceptors, known as p -type dopants. For example, you can dope Silicon with Phosphorous (an n -type dopant) or Boron (a p -type dopant).

Semiconductor	Fixed Charge	Mobile Charge
n -type	Positive, ions	Negative, e^-
p -type	Negative, ions	Positive, holes

Table 1 Table of semiconductor types and their fixed and mobile charges

For an n -doped semiconductor, the donor's electrons can be easily thermally excited to produce mobile electrons in the conduction band. These donor electrons are so close in energy to the

conduction band that virtually all of them populate the conduction band. Thus for an n -doped semiconductor each dopant atom contributes a mobile electron to the conduction band with a fixed positive charge remaining on the dopant atom. This fixed charge cannot move in the crystal lattice since it is attached to the dopant atom (see Table 1).

For a p -doped semiconductor, unoccupied orbitals on the acceptor atoms are very close in energy to the valence band. Thermal energy can excite an electron from the valence band to the acceptor, creating mobile holes in the conduction band, and fixed negative charges in the lattice. Thus for a p -doped semiconductor each dopant atom contributes a mobile hole to the valence band with a fixed negative charge remaining on the dopant atom. Again, this fixed charge cannot move in the crystal lattice since it is attached to the dopant atom (Table 1).

The number of mobile and fixed charges are equal, but opposite in charge. Thus, doped semiconductors, although still neutral, are much better conductors than undoped ones.

Photoelectrochemical Water Splitting

Doped semiconductors are important materials for solar water splitting schemes. When light hits a doped semiconductor, an electron is promoted across the band gap, and a hole is created from where the electron was removed. For an n -type semiconductor, this hole (h^+) moves towards the surface, and if it's at the right potential, oxidizes water to produce O_2 . For a p -type semiconductor, when light hits the surface, electrons move towards the surfaces, which are used to produce H_2 from the solution. Examples are shown in Figure 2.

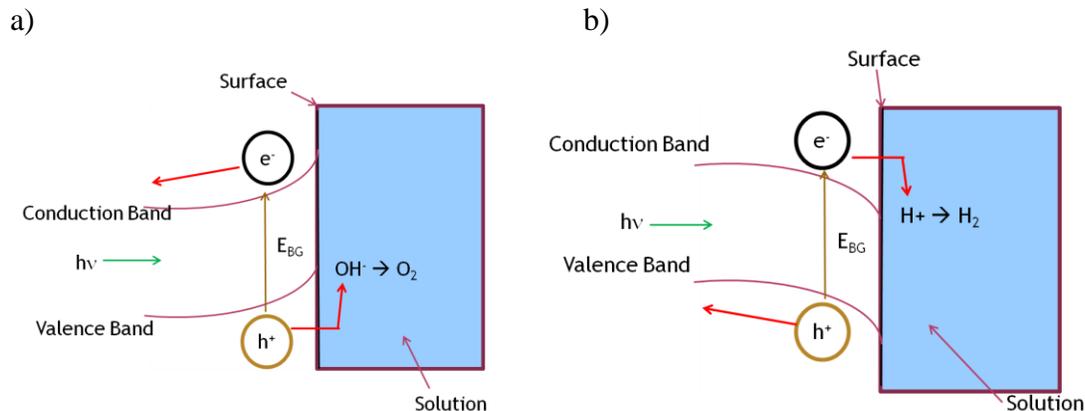


Figure 2a) a n -type semiconductor is shown which produces O_2 using holes. b) a p -type semiconductor is shown that uses electrons to produce H_2 .

Either a combination of n -type and p -type semiconductors may be necessary to split water, where the two electrodes would be side by side or one in front of the other. Another option would be for a semiconductor to be combined with a counter electrode metal (such as platinum or graphite) where the semiconductor would do either the oxidation or reduction of water and the counter electrode would do the opposite reaction.

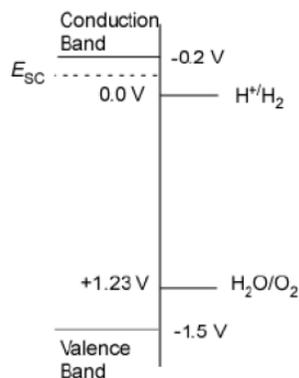


Figure 3 Near ideal water splitting band energies, all potentials vs. SHE.

An ideal situation would be for the semiconductor to make by H_2 and O_2 at the same time from water by absorbing visible light. One complication in photoelectrochemical water splitting is that while we have focused on the band gap of the semiconductor, it is the absolute positions of the valence and conduction bands that are important. The energetic of water splitting under standard conditions ($pH = 0$, $[H^+] = 1 \text{ M}$) are shown in Figure 3. The semiconductor energy levels depicted are those of a hypothetical ideal water splitting material. If a single semiconductor material is to be used for water splitting (oxidation and reduction), its bands must have energies that straddle the potentials for proton reduction and water oxidation.

In 1972, Fujishima and Honda reported that water could be decomposed into H_2 and O_2 upon irradiation of a crystalline TiO_2 semiconductor electrode in an electrochemical cell. Unfortunately, TiO_2 suffers from two shortcomings that prevent its use in solar energy devices: the band gap is too large and the conduction band edge is too close to the thermodynamic H^+/H_2 reduction potential. As discussed earlier, photons with energies greater than 1.23 eV ($\sim 1000 \text{ nm}$) have enough energy to drive the water splitting reaction. Some extra energy would be required in any real water splitting device, but this still leaves a considerable portion of the solar spectrum that can be used to produce H_2 and O_2 (Figure 4).

Unfortunately, only a very small fraction of solar photons striking the Earth's surface have energies greater than 3 eV. So a practical photoelectrochemical water splitting material must have a smaller band gap than TiO_2 . Titanium dioxide is used as a base in white paint and powdered donuts! For solar energy conversion, we need a material that is highly colored and thus light absorbing. The second problem, the location of the conduction band edge is a little more subtle. The electrons that are excited into the conduction and by light absorption will be used to reduce H^+ to H_2 , and the holes left behind in the valence band will oxidize H_2O to O_2 . As discussed earlier, we know the thermodynamic potentials for H^+/H_2 (0 V vs. NHE) and the O_2/H_2O (1.23 V vs. NHE) couples (Fig 3).

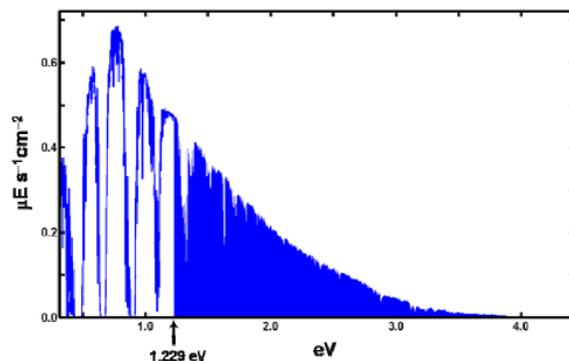


Figure 4. Flux of solar photons striking the Earth. The region corresponding to photons with energies greater than 1.23 eV is shown in blue.

Hence, electrons in the conduction band of a photoelectrochemical water splitting material must have potentials more negative than 0 V and the holes in the valence band must have potentials more positive than 1.23 V (Figure 3, Figure 5).

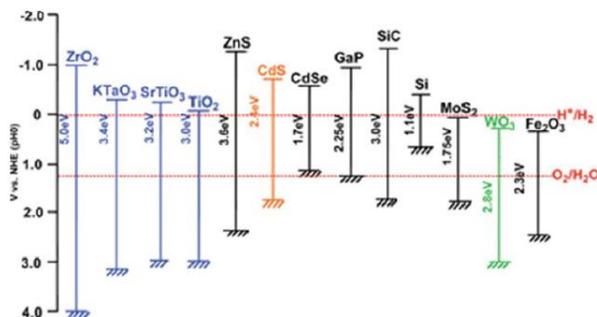


Figure 5. Band gaps and band energies relative to the water splitting potentials for several different semiconductor materials.

As you can see, none of the materials shown in Figure 5 has both the proper band gap and band edge locations to perform as a practical photoelectrochemical water splitting material. That is why we need to look for NEW materials! In this lab, we will specifically focus on exploring photoanode materials whose valence bands are positive enough for the holes to oxidize water to oxygen.

Materials

Although many different combinations of elements will form semiconductor materials, metal oxides are believed to be the best candidates for photoanodes in water splitting devices because they are able to tolerate the strongly oxidizing conditions required for O₂ production from H₂O. All elements of the periodic table will form “oxides” with the exception of fluorine and the noble gases. Binary metal oxides adopt a large number of different structures. In the transition metals, oxides are known for metals in oxidation states ranging from +1 to +8. Consequently, there is a

great deal of variety in the stoichiometries of metal oxides. Some of the major forms are listed below.

- Monoxides- MO
 - Monoxides are known for all M^{2+} transition metal series except scandium and chromium. Monoxides are also formed by some elements of the second series (Zr, Nb, Pd, and Cd), as well as Hg in the third. Most transition metal monoxides adopt rock salt structures, but other crystal forms (e.g., wurtzite) are known.
- Dioxides- MO_2
 - Many M^{4+} elements from the first (Ti, V, Cr, Mn), second (Zr, Nb, Mo, Tc, Ru, Rh), and third (Hf, Ta, W, Re, Os, Ir, Pt) transition series form metal dioxides. Most transition metal dioxides crystallize in either the rutile or fluorite structure.
- Sesquioxides- M_2O_3
 - The sesquioxide stoichiometry has the metal in the M^{3+} oxidation state and forms with metals of the first transition series through iron (Sc, Ti, V, Cr, Mn, Fe), as well as two second row (Y, Rh), and one third row metal (La). Crystals of these compounds have the corundum structure that is also found in alumina (Al_2O_3).
- Spinels- M_3O_4
 - The spinel stoichiometry requires two metals in the M^{3+} oxidation state, and one in the M^{2+} state. Binary oxides of Mn, Fe, and Co can adopt spinel structures. A large number of mixed metal oxides can also form the spinel structure (e.g., $MgAl_2O_4$).
- Pentoxides- M_2O_5
 - The pentoxide stoichiometry is found for M^{5+} ions of the vanadium group (i.e., V, Nb, Ta). These materials can adopt a large variety of structures including layered and chain structures.
- Trioxides- MO_3
 - This stoichiometry appears in the Cr^{6+} , Mo^{6+} , W^{6+} , and Re^{6+} oxides. Cubic, layered, and chain structures are found in these oxides. One of the most remarkable cases of polymorphism (multiple crystal forms) is presented by WO_3 , which has as many as eight phase transitions up to $900^\circ C$. All of the phases are distorted structures of the highly symmetric cubic ReO_3 .
- Heptoxides- M_2O_7
 - Oxides of Mn^{7+} , Tc^{7+} , and Re^{7+} show this stoichiometry. Mn_2O_7 is a deeply colored oil at room temperature, whereas Tc_2O_7 and Re_2O_7 are yellow volatile solids. Mn_2O_7 and Tc_2O_7 are molecular species even in the crystalline state.
- Tetroxides- MO_4
 - There are only two transition metal tetroxides: RuO_4 and OsO_4 . Both compounds are molecular materials. The solids have low melting and boiling points.

Given the wide variety of binary metal oxides that are known, it is clear that there is a vast number of possible mixed-metal oxide combinations. The stoichiometries of the different metals in mixed oxides do not necessarily have simple integer relationships. Hence, not only are there many possible combinations of metal, there is a virtually limitless number of stoichiometries to be explored.

A Combinatorial Search for Photoactive Metal Oxide Materials:

We are interested in discovering new metal-oxide materials that have better photoelectrochemical water-splitting properties than TiO_2 . Preliminary experiments have shown that combinations of 3 or 4 metals in the oxide semiconductor can be used to produce a photocurrent when hit with visible light. As many as 60 elements in the periodic table are capable of forming semiconducting oxides, and with the need for multiple metals, there are millions of different combinations possible, which all must be screened for photoelectrochemical water splitting activity. How do we find the combination and stoichiometry that are optimum for photoelectrochemical water splitting?

The best way to address this search is to utilize combinatorial chemical methods aimed at performing this screening process as rapidly and thoroughly as possible. Combinatorial chemistry involves the rapid synthesis and activity screening of a large number of different but structurally related molecules or materials.

In this lab, mixtures of three metal salt solutions will be prepared with systematically varied compositions. These mixtures will be applied to conducting glass plates, dried, and sintered to form mixed metal oxides. This fulfills the first requirement of combinatorial chemistry: rapid synthesis of a large number of materials.

You will then carry out a rapid screening by testing these different combinations of elements for photoelectrochemical activity. To test the materials performance as photoanodes in water-splitting photoelectrochemistry, we will illuminate the different combinations of metals and measure their electrochemical response. Illumination will be accomplished with 8×8 light-emitting-diode (LED) arrays in which the LEDs are illuminated sequentially and the electrochemical response is recorded. The LED array pattern matches the spotting template that you used for sample preparation, so there will be a one-to-one correspondence between a given LED and a particular metal-salt mixing stoichiometry.

The readout electronics consist of a two-electrode potentiostat. Your spotted samples on conducting glass will serve as the working electrode: a wire will be attached to the conducting glass surface for easy connection. As mentioned above, we are investigating these materials for their ability to successfully oxidize water to oxygen. The counter electrode will be a small piece of graphite rod. Ideally, the reaction taking place at the counter electrode is the reduction of protons. The electrolyte will be 0.1 M KOH. A small positive potential will be applied to this electrochemical cell. The potential will be low enough so that there is not too much background (dark) current flow, but high enough to assist any photoresponse. This voltage will be determined experimentally. The readout system will integrate the current that flows during the time that each LED is illuminated and will subtract the dark current that flows during that time.

Data will be collected using the Solar Materials Discovery Software and saved. These results will be uploaded to an online database, where you will be able to compare your results to those of other participants in this project.

PROCEDURE

WEEK 1: Precursor Preparation

Metal nitrate solutions are used as precursors to the metal oxide semiconductors. Metal nitrate salts decompose upon being heated to very high temperatures to form the metal oxides we are seeking.

1. As a lab group, determine the three metal salts you would like to use from those available. You may consult the online database at <http://bilrc.caltech.edu/solmatdisc/> to see what materials have previously been explored and get new ideas.
2. From the salts you selected, prepare 0.04 M solutions for each metal. Additionally, you will need to prepare two standard solutions – Iron Nitrate and Copper Nitrate. Make 0.04 M solutions of iron (III) nitrate and copper (II) nitrate. These will be deposited on to each plate.
3. If solubility appears to be a problem (i.e., the solution is cloudy), add 0.015 M nitric acid (about one drop of concentrated nitric acid) to acidify the solution.
4. Next clean three conductive glass plates. First wash with deionized water, then with isopropanol and lastly with acetone. Be careful not to cut your fingers on the sharp edges of the plates. Dry the plates thoroughly.
5. Identify which side of the glass is conductive – this means which side of the glass is coated with fluorine-doped tin oxide (FTO). Using a voltmeter, set it to measure resistance (Ω), touch both leads to one side of the glass slide. The side that indicates a small resistance value is the conductive side (or the voltmeter beeps). This is the side that should be placed face up to deposit your sample on.
6. Prepare a control plate using your Fe^{3+} solution. Deposit the samples in the following pattern shown in Figure 6. Place a glass plate over a paper spotting template of the 8×8 array onto a cool hot plate.
7. Using a 10- μL pipettor, place 10- μL spots of the Fe^{3+} solution *onto the conducting side of the glass plate* according to the pattern shown in the left side of Figure 6. Once you have spotted the plate, turn on the hot plate to about 100°C to allow the spots to evaporate to dryness.
8. Next prepare two plates of your combinatorial mixtures of the three metal salt solutions. Using a 96-well mixing plate and a 10- μL pipettor, prepare the mixtures of the three salts according to the pattern indicated in the right side of Figure 6.
9. Place the glass plate over a paper spotting template and pipet 10 μL of each mixture over the corresponding circle on the template. Put the glass plate onto the hot plate and allow the spots to dry. You should prepare two identical plates to test reproducibility.

10. After your plates have dried, give them to your instructor. They will fire your plates at 500°C and return them to you next week.

11. Lastly, prepare the electrolyte solution, or 250 mL of 0.1 M potassium hydroxide. This should be stored in a plastic bottle.

COL \ ROW	1	2	3	4	5	6	7	8
1								
2		10 μL Fe ³⁺		10 μL Fe ³⁺		10 μL Fe ³⁺		
3			10 μL Fe ³⁺		10 μL Fe ³⁺		10 μL Fe ³⁺	
4		10 μL Fe ³⁺		10 μL Fe ³⁺		10 μL Fe ³⁺		
5			10 μL Fe ³⁺		10 μL Fe ³⁺		10 μL Fe ³⁺	
6		10 μL Fe ³⁺		10 μL Fe ³⁺		10 μL Fe ³⁺		
7			10 μL Fe ³⁺		10 μL Fe ³⁺		10 μL Fe ³⁺	
8								

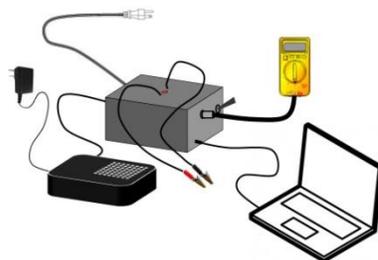
COL \ ROW	1	2	3	4	5	6	7	8
1	0 : 90 : 0	0 : 80 : 10	0 : 70 : 20	0 : 60 : 30	0 : 50 : 40	0 : 40 : 50	0 : 30 : 60	0 : 20 : 70
2	10 : 80 : 0	10 : 70 : 10	10 : 60 : 20	10 : 50 : 30	10 : 40 : 40	10 : 30 : 50	10 : 20 : 60	10 : 10 : 70
3	20 : 70 : 0	20 : 60 : 10	20 : 50 : 20	20 : 40 : 30	20 : 30 : 40	20 : 20 : 50	20 : 10 : 60	20 : 0 : 70
4	30 : 60 : 0	30 : 50 : 10	30 : 40 : 20	30 : 30 : 30	30 : 20 : 40	30 : 10 : 50	30 : 0 : 60	
5	40 : 50 : 0	40 : 40 : 10	40 : 30 : 20	40 : 20 : 30	40 : 10 : 40	40 : 0 : 50		0 : 10 : 80
6	50 : 40 : 0	50 : 30 : 10	50 : 20 : 20	50 : 10 : 30	50 : 0 : 40		10 : 0 : 80	0 : 0 : 90
7	60 : 30 : 0	60 : 20 : 10	60 : 10 : 20	60 : 0 : 30		80 : 0 : 10		
8	70 : 20 : 0	70 : 10 : 10	70 : 0 : 20		80 : 10 : 0	90 : 0 : 0		

Figure 6. (Left) Spotting pattern for the Fe³⁺ solution for the control plate. (Right) Three-chemical mixing pattern for combinatorial metal-oxides synthesis. The ratios indicate the number of microliters of each metal salt to add to the indicated well on the 96-well plate, i.e., $\mu\text{L MA}:\mu\text{L MB}:\mu\text{L MC}$.

WEEK 2: Photoelectrochemical Responses from Combinatorial Materials

Assembly of the Instrument

1. Connect the components of the instrument as shown below in Figure 7. Do not yet connect the leads to the electrodes (the sample plate and the graphite rod counter electrode). It is generally a good idea to plug the experiment box and the LED array into different outlets. The “ground” lead of the BNC cable connects to the “COM” port of the voltmeter. Reversing the leads will makes all the voltages read the opposite sign.
2. Use tape to secure the graphite rod (counter electrode) to the side of the crystallization dish. Use liquid electrical tape to secure the graphite tape to the FTO-coated side of the glass plate (working electrode). The conducting side of the graphite tape (not the plastic side) must be in contact with the conducting glass plate.
3. Fill the crystallization dish with electrolyte (e.g., 0.1 M KOH) such that the plate is completely immersed and that some part of the graphite rod is submerged. The level of electrolyte should not be so high that the alligator clips come in contact with electrolyte; they should only attach to the dry parts of the electrodes.



4. Activate the power (toggle) switch on the current integrator box. You will notice the LEDs might activate and blink. This blinking might not occur if it previously transpired when the LED array was plugged in to the wall outlet.
5. Activate the voltmeter. Set the voltage range to 2 V.
6. Start the Solar Materials Discovery program. The program takes several seconds to start up as various drivers are installed.
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. You should enter the voltmeter reading **in units of volts** (e.g., "0.035"). 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 materials, multiple biases can be scanned. Ideally, we would like to not apply a bias, so we should screen "0.00 V" first. Enter "0.00" to set the bias potential to 0 mV. Wait a few moments and note that the voltmeter now reads +0.00 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 Rest Current". 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). The y-scale is volts because there is a current-to-voltage conversion in the box. This process can take several attempts/clicks and a little waiting. High rest currents unfavorably decrease your signal-to-noise ratio.
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.
4. Click "Perform a Scan". Enter the number of cycles desired (e.g., "3"). Each cycle takes 1–2 minutes. Note that the LEDs will blink and the progress of the scans is reported on the monitor. The data are reported in a 3D plot in real time. The menu will re-open when

the scanning is complete. Note: you can rotate the chart in 3D using the rotation option on the toolbar (looks like a curvy arrow).

5. On the menu, click “Save Data to a File” and enter the appropriate information as prompted by entries in the save data menu, from top to bottom. Data will be saved locally as *.smd files that can be uploaded to the Caltech Solar Materials Discovery online database. Make sure to record the order of how you entered your data into the database. This will help you when filling in the information.
6. Re-initialize the LEDs and again click on the button “Apply Voltage” to set the bias potential **in volts**. Now instead of no bias, we will apply a positive bias (0.100 V) and then repeat the experiment with a negative bias (-0.100 V). Wait a few moments after the bias is applied and note that the voltmeter now reads +0.100 V or -0.100 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.
7. If your bias causes a rest current that is too high, lower your bias by 0.005-0.1 Volts.

DISCUSSION

1. Which metal-oxide combinations gave the largest photocurrents?
2. Do you notice any correlation between dark current and applied voltage?
3. The iron-only sample was intended as a control- did any of your mixed-metal oxides give higher photocurrents than the Fe sample?
4. What is the photocurrent value for the mixtures that show the highest potential?
5. In general a material with a photocurrent of at least a factor of two higher than the Fe standard will be considered promising. What can you conclude about your metal oxide mixtures as potential photoanode materials?

Adapted from the Caltech Chem 3x Laboratory Manual (Jay Winkler, Bruce Brunschwig, James McKone), the Solar Materials Discovery Kit User’s Guide (Jay Winkler), The SHArK Project Manual (Jennifer Schuttlefield Christus, Bruce Parkinson, Craig Markum), and the SHArK Project Pasadena Handbook (Jillian Dempsey, James McKone)