Using the SEAL Kit to Test the Photoactivity of Mixed Metal Oxide

Samuel R. LeFevre*[1], Eamon Patamasing[1], Angelina Ye[2]

[1]Crescenta Valley High School, 2900 Community Avenue, La Crescenta, California 91214, United States
[2]Northwood High School with Concordia SEAL, Concordia University, Concordia, Irvine, California 92612, United States

ABSTRACT: A promising area of research in renewable fuel sources is in the discovery of metal oxide catalysts for the breakdown of water. The SEAL (Solar Energy Activities Lab) kit is used to detect photocurrent, a required step in the splitting of water. Unfortunately, these catalysts are not always easy to find or cheap (platinum is well known for its catalytic abilities, but it is far too rare and costly to be used efficiently). The discovery of cheap, earth-abundant metal oxides is of paramount importance. Iron(III) oxide is considered among the most promising, but on its own cannot produce a strong enough current. The answer may not lie in one single oxide, but in a combination of two or more. The exploration of mixed metal oxides has been the aim of this research period. Several different metal oxides were mixed in different ways and tested, among them the promising bismuth vanadate. Experiments were performed to examine the role that oxide color plays in photoactivity, as well as concentration, mixing methods and surface area. It was found that bismuth vanadate achieved very high results when allowed to dry, before adding cobalt to the already dried spots. However, research into mixed metal oxides is ongoing and hopefully newer, better combinations will be found in the future.

1. INTRODUCTION

With the rapidly growing human population and their expanding energy needs, cleaner, more abundant sources of power are necessary.[4] Fossil fuels are being exhausted and contribute to the growing threat of global climate change. One of the most spoken about and researched renewable energy sources is solar, and the benefits are immediately clear. The sun is permanent, pollution-free and radiates 4.3 x 10^{20} J of energy to the Earth's surface in just one hour.[4] However, solar panels, the most common source of solar power, are expensive, inefficient and detrimental to the environment to build. One intriguing, promising alternative to solar panels is the use of metal oxide photocatalysts to catalyze the breakdown of water, thereby creating hydrogen fuel. This process occurs in multiple steps, with several measurable occurrences along the way to indicate successful hydrolysis.[1] One of these indicators is photocurrent, the production of electric current from the breakdown of water molecules. Electrons are released and transferred from the oxygen molecules to the hydrogen, forming hydrogen and oxygen gas. The SEAL (Solar Energy Activities Lab) kit was developed to measure these electrons. It tests for photocurrent generated by the breakdown of water catalyzed by metal oxide photocatalysts. These catalysts are annealed in a kiln to a fluorine doped tin oxide (FTO) plate according to a "spotting" pattern; the FTO plates resemble polka dot patterns when kilned. The plate is placed in a glass dish and covered with a 0.1 M NaOH solution. The spots are aligned over an LED array, which, when flashing, simulates sunlight. Hopefully, when the LEDs flash over a spot, the metal oxide photocatalyst catalyzes the breakdown of the water in solution. The electrons freed by this reaction are carried by the electrolytic NaOH through a circuit created by attaching a lead to the plate and a lead to a graphite rod. An attached multimeter records the current generated and displays the results in a computer program (Solar Materials Discovery). Computer readouts show higher currents as red, lower as blue.[1]

There is more than one consideration involved in finding suitable metal oxide photocatalysts. The oxide must have an appropriate band gap, the difference in energy between an atom's two outermost electron bands that permits photons from the LED to excite the oxide's electrons to its outer bands, catalyzing the reaction (this quality characterizes a semiconductor). This band gap should correspond to an energy associated with visible light in photons (iron(III) nitrate's strong photocatalytic properties are attributable to its red color).[2] Additionally, the oxide should be cheap and earth-abundant. With this in mind, suitable mixed metal oxide catalysts, based on artful combinations of different oxides by different means, were explored in hopes of making solar energy more efficient and affordable.

2. METHODS

2.1 The SEAL kit

The SEAL kit comes with the computer program (Solar Materials Discovery), a current integrator box, a multimeter, a graphite rod, and an LED display, as well as epoxy, some wire and copper tape. The current integrator box and LED display both require electrical outlets. A plug is

provided to connect the multimeter to the current integrator box. The kit's USB plug was plugged into the computer with the program loaded on it. Once the current integrator box and multimeter were turned on, the program was opened, and after entering the multimeter's initial reading, the LEDs began to flash, indicating the program's initialization. Once a plate was made (detailed below), a piece of wire was stripped at both ends, and a small piece of copper tape was added to one end of the exposed wire in order to totally cover it. This wire was taped to the conductive side of the plate, away from any spots. The epoxy was mixed on an expendable surface, and applied to the tape at the top of the plate. The epoxy entirely covered the tape and the wire connected to it. Once the epoxy dried (after ~10 minutes), the plate was placed in a glass dish. To submerge the plate, 0.1 M NaOH was added to the dish. The graphite rod was secured to the inside wall of the dish using Scotch tape. The red alligator clip from the current integrator box was connected to the other end of the exposed wire, and the black clip was attached to the top of the graphite rod. The dish was placed on top of the LED display, and the spots on the plate were aligned with the LEDs. At this point, a bias potential of 0.1 V was applied across the circuit, and the "dark current", that is, the electrical current in the dish before testing, was measured. Generally, the dark current started higher than 0.5 μA, but decreased after a short time (thirty seconds or less, if there were no problems with the plate). Once it was safely below 0.5 μA, a test (usually three scans in a row) was performed. When the test finished, the bias potential was turned off and the plate was removed. The electrolyte solution was disposed of, and the used plate was washed with distilled water and stored. The data from the test were saved. For future reference a screenshot was taken of all the data.

2.2 Making a plate

A plate was first etched on the non-conductive side with its name, based loosely on the plate's future contents. The non-conductive side is distinguished from the conductive side (the side upon which metals are spotted) by the presence of small grooves on the sides of the plate, which point to the conductive side. The plate was washed first with distilled water, then acetone, then isopropanol and dried. Since the surface of the plate is naturally hydrophobic, spots of metals tend to flee the center of the spot and coagulate around the edges, creating unsightly "coffee rings" that interfere with testing since the light from the LEDs cannot travel through the metals. Several methods have been proposed to solve this issue. In this project, an ozone cleaner, donated by the SEAL team from Oakwood High School in North Hollywood, was used. The ozone cleaner housed a powerful UV lamp that converted oxygen in the cleaner to ozone. This stripped the FTO plate of minute impurities untouchable by less precise cleaning methods and rendered the plate hydrophilic. However, if the entire plate were hydrophilic, metal spots would simply slide all over the surface, creating puddles, so plastic templates roughly matching spotting patterns were added to the plates before they were cleaned. A drop or two of distilled water was added to the plate, and the plastic template was pressed on the plate, which was above a paper spotting pattern, to which the template was aligned. The plate, with the template attached, was placed in the ozone cleaner for ten minutes. Once finished, the template was removed and the plate placed above the paper spotting template for spotting. Only the surface of the plate exposed to the cleaner by the template is hydrophilic, which has the added benefit of causing spots almost to move there on their own. Since spots tend to reflect their own lights into neighboring spots, they were generally added in a "checkerboard" pattern, of six rows and three columns, saving the top right corner for the epoxy later. Generally, plates were completed with seventeen spots. The plate was then placed on a hot plate (usually) for five to ten minutes at 40 to 50 degrees Celsius until the water from the added solutions had evaporated. After drying, the plate was placed in a kiln and the spots were annealed for three hours at 500 degrees Celsius. The heat of the kiln converted the salts in the spots to their oxide forms, and adhered the spots to the plate. When annealing was finished, the above steps were taken before the plate is tested.

2.3 Spotting Methods

One of the primary areas of exploration of this research was the use of different mixing and spotting methods, usually involving the "analog" micropipette, to add salts to plates. Once an idea for a plate was formulated, the appropriate solutions were made (0.4 M solutions were made and diluted in small quantities to the desired concentration). A micropipette (usually P 20 or R 100) was used to add spots to the appropriate areas as shown by the ozone cleaner and the template. As this project pertained to the use of mixed metal oxides, different mixing methods were explored. The simplest way to mix salts was to spot one salt to a space and then add another salt to it immediately afterward. This seemed to ensure that the metals were uniformly mixed, but actually upon drying and kilning, it became clear that the different drying speeds of metals caused them to form layers over one another, which was mostly undesirable, especially when the two metals were starkly different colors. Therefore, another method used was that of mixing the salts prior to spotting. Wells were used for this. Small quantities of each salt, rarely exceeding 100 μL, were added to a well. For example, if a plate called for two metals to be mixed in a one-to-two ratio, 50 μL of one salt were added in a well to 100 μL of the other using a micropipette. The well was thoroughly mixed, and from this a spot was extracted. Generally, spots mixed in this way were more homogeneous and less prone to layering out than in the other method. Bismuth vanadate was mixed in wells in this way; it was made by mixing solutions of $Bi(NO_3)_3$ and NH_4VO_3 in a well, which stood out due to its bright orange color.

However, there were situations where the layering effect was desirable. Bismuth vanadate's photocatalytic activity[3]

tends to be undermined by its uncontrollable reactivity to ambient light. This situation often necessitated crudely covering the SEAL kit mid-test with a cardboard box to keep the spots dark. Cobalt(II) oxide is a black oxide that has some catalytic potential but has an undesirable band gap. If bismuth vanadate was spotted and allowed to dry, cobalt(II) oxide could be added on top of those spots and dried again to create very pronounced layers. After kilning, spots were orange on the bottom and black on top. Not only was this found to be an ample partnering of a reactive metal with a photocatalytic one, the black cobalt layer helped to prevent ambient light from interacting with the bismuth vanadate, which was still able to react with the LEDs since its layer was on the bottom.

3. RESULTS

3.1 Iron(III) standards

The project began with iron(III) nitrate, since it is known to produce good photocurrent. The first plates made were those composed of varying ratios of 0.2 M iron(III) nitrate, cobalt(II) nitrate and chromium(II) chloride, mixed manually on the plates. Most of these results were dark blue, though iron(III) nitrate was noticeably better without any added metals. Cobalt and chromium paled in comparison. However, as stated, mixing spots manually on the plate often led to disruptive layers of metals after kilning, so the method of mixing the solutions before spotting was used to avoid this. This method resulted in less layering, and slightly higher results (0.2 to 0.8 mA, whereas mixing manually resulted in 0.1 to 0.4 mA). Another problem specific to iron(III) nitrate was that when it became iron(III) oxide in the kiln, it tended to crystallize into its mineral form, hematite, which did not allow light to travel through it. One method thought to alleviate this was to add glycerol to each spot, but glycerol did not dry, and actually exacerbated the "coffee ring" effect by driving the salt in solution to the edges of the spots. It was resolved that not allowing iron(III) nitrate to dry too quickly (on settings of 40 degrees Celsius or below on the hot plate) would help this problem the most. Additionally, a plate made with varying concentrations of iron(III) nitrate from 0.05 to 0.25 M revealed that higher photocurrent (1.5 mA in this case) is derived from the lower concentrations of iron(III) nitrate. Higher concentrations either flaked away or crystallized into hematite. 0.05 M iron(III) nitrate not only showed the highest photoactivity but tended to show the least crystallization. From then on each plate was made with a 0.05 M iron(III) nitrate standard.

3.2 Bismuth vanadate

Bismuth vanadate is well known as one of the most photoactive metal salts of all. Sure enough, the first bismuth vanadate plate tested showed high red spikes, in the 5 mA range. From this, a large number of permutations and combinations of bismuth vanadate with itself and other metals were tested. First was a combination of bismuth vanadate and 0.2 M iron(III) nitrate made by mixing them together beforehand. It was found that increasing the concentration of iron in bismuth vanadate decreased its photoactivity. Other metals were considered, but another problem became apparent: that of the bismuth vanadate, as stated, reacting with ambient light in the room. It was thought that adding a layer of 0.1 M cobalt(II) nitrate and chromium(II) chloride, whose oxides turns very dark, on top of already-dried bismuth vanadate might block out some of the ambient light while preserving bismuth vanadate's photoactivity. Results from this test were strongly positive in the cobalt region, in the 5 μA range, able to "compete" with bismuth vanadate on its own. The chromium spots were not as high, so cobalt was selected for future experiments. A subsequent test compared this layering method with mixing bismuth vanadate and cobalt on the plate in various percentages (all percentages are by volume, so "30%" cobalt means 7 μL of bismuth vanadate with 3 μL of cobalt). The highest results came from a 40% cobalt-bismuth vanadate region. It was suggested that these results be given to HARPOON for analysis of oxygen evolution. HARPOON discovered the most oxygen evolution in the 40% region, a highly encouraging discovery. Later tests showed that copper(II) nitrate exhibited similar photoactivity to cobalt(II) nitrate when layered in the same way on bismuth vanadate. These results were encouraging, but the bismuth(III) nitrate solution used to create bismuth vanadate became contaminated through some unknown means, requiring freshly made solutions. This new bismuth(III) nitrate solution was made at 0.1 M, while the new ammonium metavanadate was made at 0.05 M. This combination led to some interesting results. It was found that when 8 μL of 0.05 M ammonium metavanadate was mixed with 2 μL of 0.1 M bismuth(III) nitrate (an unequal stoichiometric ratio of bismuth to ammonium in bismuth vanadate), the highest photo activity was consistently generated.

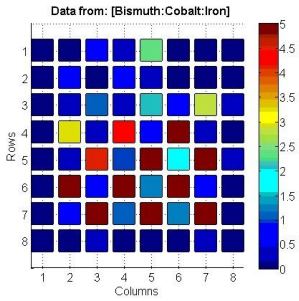

Figure 1: Results from a plate spotted with increasing concentrations of cobalt with bismuth vanadate. Note the highest results in row 7, representing 40% by volume cobalt (entry 8 in table 1).

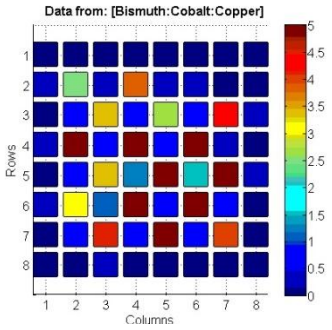

Figure 2: Results from a plate that was spotted with bismuth vanadate, allowed to dry, and spotted again with cobalt(II) and copper(II). The middle two rows are cobalt, the bottom two are copper. The top two rows are iron(III) and bismuth vanadate standards, respectively (entries 9 and 10 in Table 1)

Table 1: The components, mixing methods and results of the above mentioned plates.

Metal salt(s)	**Ratios (µL metal 1: µL metal 2, etc.)**	**Spotting method**	**Avg. photocurrent (µA)**
0.2 M iron(III) nitrate	n/a	No mixing	0.1507
0.2 M iron(III) nitrate, 0.2 M cobalt(II) nitrate	10:0, 8:2, 6:4, 4:6, 2:8, 0:10	Mixing on plate	0.4434 (highest 0:10, 0.609)
0.2 M iron(III) nitrate, 0.2 M cobalt(II) nitrate	10:0, 8:2, 6:4, 4:6, 2:8, 0:10	Pre-mixing in wells	0.1559 (highest 10:0, 0.5)
iron(II) nitrate	Various concentrations: 0.25, 0.2, 0.1, 0.05 M	No mixing	0.5979 (highest 0.05 M, 1.5369)
0.1 M bismuth vanadate	n/a	Mixing bismuth(III) nitrate and ammonium metavanadate before spotting	7.3285
0.1 M bismuth vanadate, 0.1 M iron(III) nitrate	0:10, 2:8, 4:6, 6:4, 8:2, 10:0	Mixing on plate	1.5799 (highest $BiVO_4$ 5.9344)
0.1 M bismuth vanadate, 0.1 M cobalt(II) nitrate	8:2, 8.5:1.5	Mixing on plate	7.51
0.1 M bismuth vanadate, 0.1 M cobalt(II) nitrate	9.9:1, 9:1, 8:2, 7:3, 6:4	Mixing on plate	4.01 (highest 6:4 6.2966)
0.1 M bismuth vanadate, 0.1 M cobalt(II) nitrate	10:5	Layering	4.609
0.1 M bismuth vanadate, 0.1 M copper(II) nitrate	10:5	Layering	4.72
0.1 M bismuth(III) nitrate, 0.05 M ammonium metavanadate	7:3, 8:2, 9:1	Pre-mixing in wells	5.3

4. CONCLUSION

This research project involved the spotting and testing of no less than 60 plates, through which valuable data on mixed metal oxides was gathered. As expected, bismuth vanadate produced the most consistent results, although the low solubility of its constituents meant that premixed solutions of bismuth vanadate did not last long. A simple solution was to mix small amounts of bismuth(III) nitrate and ammonium metavanadate in a well before spotting, though both of these substances were prone to contamination and had to be remade regularly. Adding layers of dark oxides, specifically catalytic cobalt(II) oxide after bismuth vanadate had dried was shown to reduce bismuth vanadate's reactivity with ambient light while not affecting its photoactivity and even increasing it. Similar metal salts such as copper(II) oxide should be pursued in this manner to corroborate these findings. Though some unique combinations of metal oxides were found, nothing was discovered that could outpace bismuth vanadate's success as a catalyst, only alleviate some of the minor problems associated with the process. There are still many catalysts to be found in many combinations that may yet prove to be as effective as or more effective than bismuth vanadate.

ACKNOWLEDGMENT

This work would not have been possible without the continued financial support of the National Science Foundation and the Center for Chemical Innovation. Thanks to the California Institute of Technology, Dr. Harry Gray and Allison Moore for providing a space for this research as well as support and advice.

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