

# Testing the photoactivity of metal oxides and investigating where the current originates from by using optical bandpass filters

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*Supporting Information Placeholder*

**ABSTRACT:** In the search for a catalyst that can be used to split water, the Solar Energy Activity Lab (SEAL) kit is used to apply a current to a sample plate, and the current is measured when the sample is subjected to a flash of LED light. To ensure that the current measured is from the reaction and not from photocorrosion, optical filters were used to specify which wavelengths of light the catalysts were exposed to. The optical filters used include glass: blue, green, orange; and plastic: red, orange, yellow, green, and blue. There were different results for iron oxide, nickel oxide, cobalt oxide, copper oxide, and their different combinations, due to the varied band gaps and each element's ability to absorb light. The photoactivity of several scans of a single plate using different filters and without a filter, when compared, show that photoactivity is greatest when the plate is scanned without any filter. The optical filters investigate whether the metal oxide catalysts are photoactive at the correct wavelengths, and that the current measured is coming from the reaction taking place.

## 1. Introduction

As time goes on, the demand for energy continues to grow even faster than the world population [1]. A sustainable resource that can work to meet that demand is solar energy: photovoltaic solar energy (PV), which is the direct conversion of sunlight into energy, is already used around the world. The problem with relying on PV as a main source of energy is its unreliability [1], as PV energy cannot be stored as current, which makes it difficult to use at night or in areas that do not receive enough sunlight daily. An alternative power source that is similar to PV is solar water-splitting, which works to split hydrogen and oxygen in water. The hydrogen gas is able to be stored, and when needed, it is recombined with oxygen to create an electric current. To effectively develop this alternative power source, there is an ongoing

search to find a combination of earth abundant catalysts that will perform efficient and inexpensive photoelectrochemical water-splitting (PE). In this search, there are 71 possible elements that can work together in combinations of three or more to perform varying degrees of PE [1].

The Solar Energy Activity Lab, or SEAL project, allows small groups of scientists to participate in this global search. The SEAL kit includes an LED array unit, a current integrator, and transparent conducting fluorine-doped tin oxide (FTO) plates [2], where the possible photocatalyst is to be spotted. The plate is submerged in an electrolyte solution and connected to the current integrator while being exposed to direct light from the LED box as shown in Figure 1 [3]. The light induces the water oxidation reaction and electrons released flow into the current

integrator unit to be measured. There has been concern that the current measured is from photocorrosion rather than photoactivity, as the SEAL kit is unable to identify where the electrons originate from.

The elements chosen that have the greatest photoactivity are usually those with the ability to absorb light and the lowest relative band gap. Iron oxide is used as a base for this search, as it has a relatively low band gap of  $\sim 2.18$  eV [4], which means it must be excited by light with a wavelength of at least 569 nm. This wavelength of light is visible in the form of the color green-yellow, and wavelengths with higher energy include the visible colors green, blue, and purple. The understanding of exciting the metal oxide sample is that a smaller band gap energy means more wavelengths of light are able to excite the electrons to become conductive. The use of optical filters with varying wavelengths over the LED light will specify the wavelengths used to excite the material. When the wavelength of light is less than required to excite an electron in the light absorber, the current measured has the possibility of coming from photocorrosion of the spots while in the electrolyte solution. If corrosion does occur, the electrons released can create a current of a similar order of magnitude as the current produced by the reaction.

## 2. Method

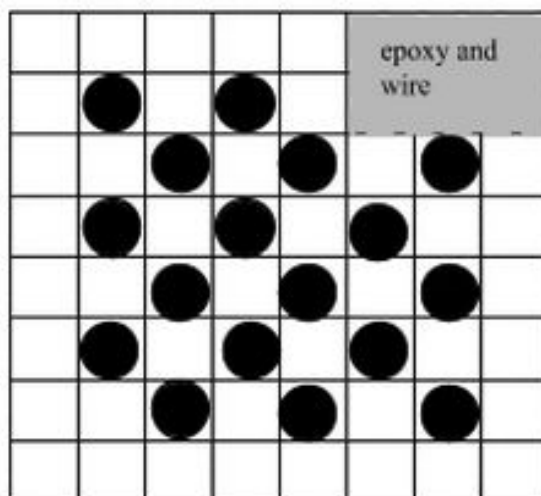
### 2.1 Preparing the FTO plate to spot the solution

To analyze the plates using the SEAL kit, solutions of metal oxides (including iron nitrate, nickel nitrate, cobalt nitrate, and copper nitrate) were created with varying molarity. Starting with iron nitrate ( $\text{Fe}(\text{NO}_3)_3$ ), 20 mL of 0.4M of the solution was made. The molarity was decreased to 0.2 because it was found that a higher molarity solution crystallizes and takes longer to dry. An FTO plate was labeled using a glass etcher on the nonconductive side, which was tested using a multimeter. Once the plate was cleaned by rinsing its surface with deionized water, acetone, then isopropanol, and wiped dry with a kimwipe, the FTO plate was then spotted. The LED light box

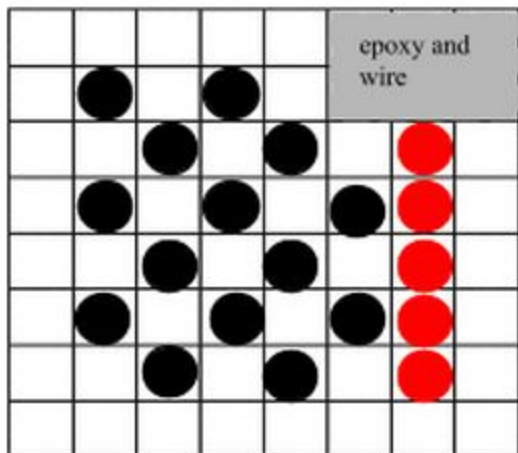
has an array of LED light bulbs which is 3 inches by 3 inches, with 64 small LED bulbs ordered in a grid pattern, ordered 8 by 8 bulbs.

### 2.2 Spotting the FTO plate in varying patterns

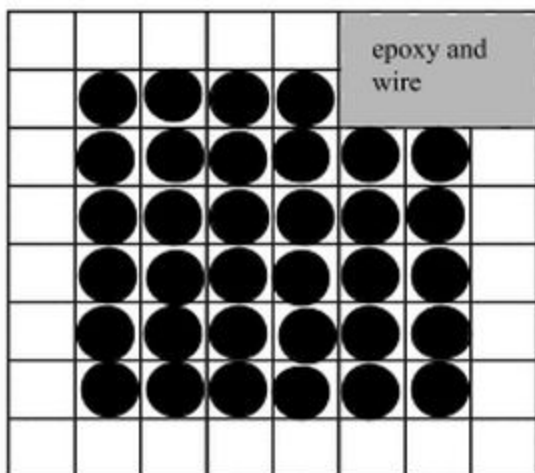
Using a template that outlines the light pattern of the LED light box, 10  $\mu\text{l}$  per spot was spotted in a checkerboard pattern shown in Figure 1, onto the charged side of the FTO glass plate. Depending on the solution used, an iron standard was spotted with the same molarity of the solution used for the rest of the plate, either 0.4M or 0.2M as shown in Figure 2 and on sample plate NiFe 1 in Figure 4. An additional method for spreading solution on a sample plate is to use a 20  $\mu\text{l}$  micropipette and add solution in 20  $\mu\text{l}$  increments. Using the template, add solution and spread the solution by tilting the plate or using the micropipette tip to stretch the solution to spread. Leave the edges of the FTO plate clear, as well as the 2 by 3 corner of the plate for the epoxy and wire as shown in Figure 3. FTO sample plates were ozone cleaned using a UV Ozone Cleaner ProCleaner Plus. The plates were cleaned for 15 minutes and were spotted with solution immediately after being removed from the ozone cleaner. Ozone cleaning the plates made the FTO layer more hydrophilic making the solution spread over the surface of the plate to increase surface area.



**Figure 1:** Solution pattern without iron standard. Each black dot represents the area where the solution was spotted.



**Figure 2:** Solution pattern without iron standard. Each black dot represents the area where the solution was spotted. Each red dot represents the area where the iron nitrate was spotted to be used as a control.



**Figure 3:** Solution pattern spread without iron standard. Each black dot represents the area where the solution was spotted and spread.

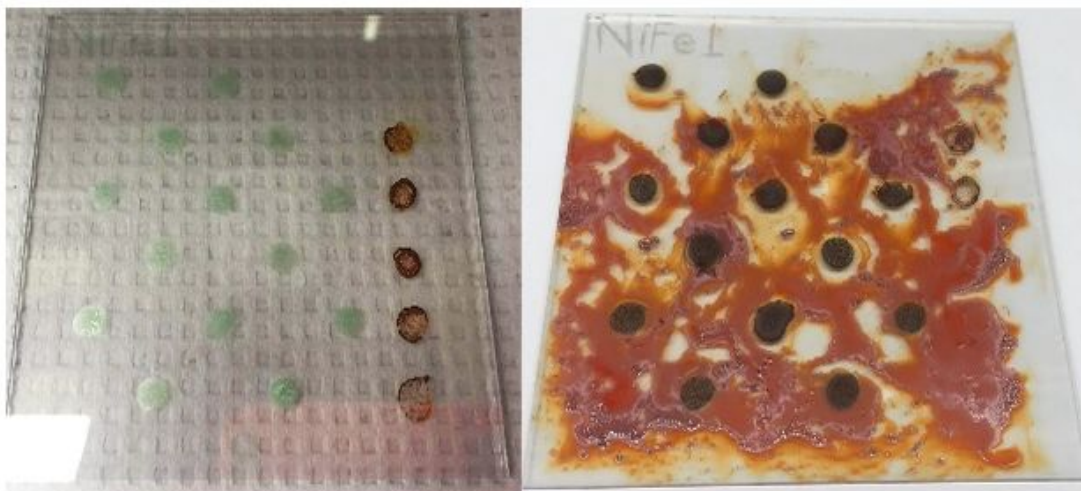
### 2.3 Preparing the plate for scanning

Once the plate was completely air dried, placed on the hot plate at 45°C, or placed in a desiccator for approximately 30 minutes, it was fired in a kiln at 500°C for about 5 hours to anneal the material to the plate. After being removed from the kiln, a 5” piece of wire with 0.5” of the insulation on each end stripped was attached to the plate in the upper

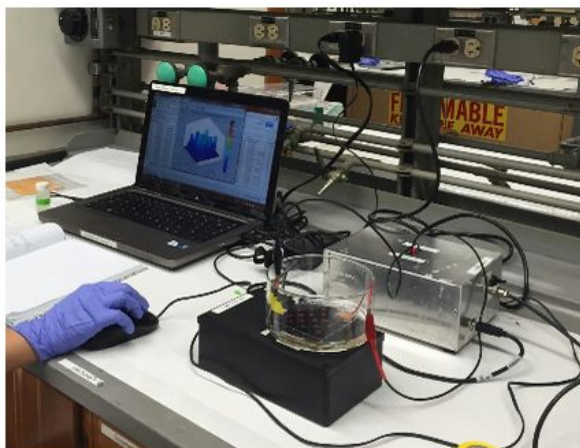
right hand corner where solution was not spotted. The wire is attached using a small piece of copper tape that completely covers the exposed wire, and by using 5-minute epoxy to cover both the tape and wire. Once the epoxy is dry, the plate is placed in a crystallization dish, with the wire and sample facing away from the base of the dish. A graphite rod was taped to the inside of the dish perpendicular to the base so it is touching the base, but the tape is not touching the solution. NaOH solution of 0.1M was poured to cover the plate.

### 2.4 Scanning the plate

Following the SEAL User Guide [3], the SEAL kit was assembled as shown below, the current integrator turned on, and multimeter set to 2V. Once the Solar Materials Discovery (SMD) program was started, the current voltage reading was entered to calibrate the equipment. The alligator clips were attached, red to the wire attached to the plate, and black to the graphite rod taped to the crystallization dish, and a voltage of 0.100V was applied through the SMD program. Before each scan, the dark current or rest current was checked using the program, and the plate was not scanned until the current was below 0.5V. Optical filters were placed on the LED light array box below the crystallization dish and the sample spots were aligned with the lights of the box. The optical filters used include glass: blue ( $T_{\max}$  at 420 nm), green ( $T_{\max}$  525 nm), orange ( $T_{\max}$  at 550 nm); and plastic: red ( $T_{\max}$  at 390 nm), orange ( $T_{\max}$  at 375 nm), yellow ( $T_{\max}$  at 365 nm), green ( $T_{\max}$  at 500 nm) and blue ( $T_{\max}$  at 410 nm), their transmittances shown in Figure 10. Each scan had 3 cycles, and the data was saved to the SMD database and according to the filter used. The data was then uploaded to Google Sheets to better identify the average current measured from the spots of each scan.



**Figure 4:** Sample plate (NiFe 1) spotted using pattern from Figure 1 with iron standard. Nickel nitrate (green) was spotted and annealed with iron nitrate (brown) control on the left, then iron nitrate spotted to make a second layer and annealed shown on the right. The iron nitrate formed one large layer of iron oxide and increased the photocurrent measured.



**Figure 5:** SEAL kit set-up. Sample plate being scanned using the Solar Materials Discovery program.

### 3. Results

Over 30 FTO sample plates with different solutions and mixtures of solutions were created, and 15 sample plates were scanned with the optical filters and without the optical filters at least twice, depending on the results of the first scan without a filter.

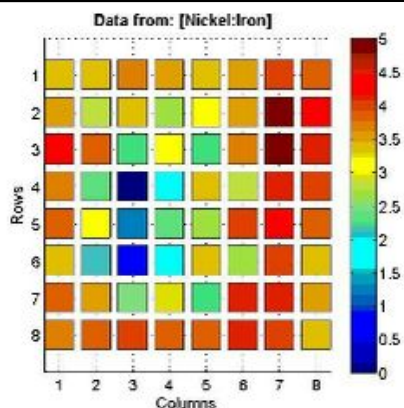
#### 3.1 Sample plates with highest photoactivity

Once the sample FTO plates were created and fired in the kiln, the scans showed the plates with layered iron oxide had the highest levels of

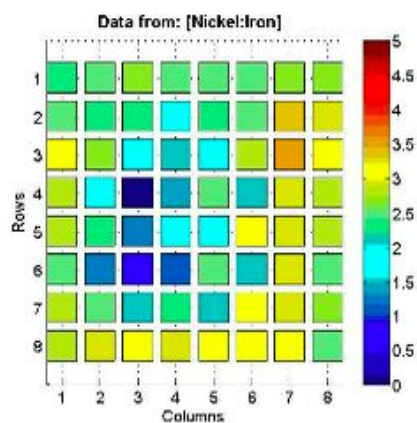
photoactivity. Sample plate NiFe 1, in Figure 4, had the highest photoactivity, with a plate average of 3.275 mA. In comparison to plates with only single layer spots of solution, the double layered plates had a much higher photoactivity. Other plates, including those with copper oxide, cobalt oxide, and nickel oxide, had much lower photocurrents, less than half of the current measured of the iron oxide standard on the same plate. Once the focus was placed on iron and the surface area of the spot was increased, the scans produced a more distinguishable result.

Sample plates spotted with  $\text{BiVO}_4$  produced a high photocurrent. Two plates, both created by another SEAL group, were created and spotted with  $\text{BiVO}_4$ , one which had a much higher photocurrent than the other, which had a molarity of 0.1 and bright yellow in color. The  $\text{BiVO}_4$  sample plate was made using ammonium metavanadate, and the bismuth vanadate plate with a lower molarity and lower current was made with sodium vanadate. The bandgap of  $\text{BiVO}_4$  is similar to iron oxide (2.18 eV) and estimated to be about 2.4-2.5 eV [6]. The current measured averaged 5.932 mA for scans without a filter, 4 times higher than scans of CON 2, a plate of iron

oxide with a similar pattern with an average of 1.46 mA.



**Figure 6:** Image from NiFe 1 plate scan without an optical filter. Results show a very high current measured. This plate was spotted as shown in Figure 1 with an iron standard, and with nickel nitrate in a checkerboard pattern.

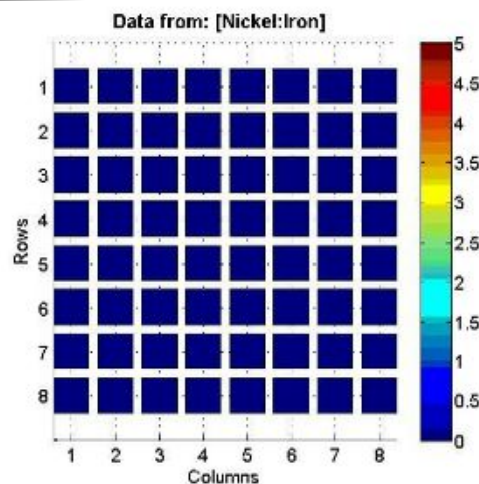


**Figure 7:** Image of scan of NiFe 1 plate with a blue glass filter. Results show a high photocurrent, but not as high as the results from the scan without a filter.

### 3.2 Optical filters and their effect on photoactivity

For plates that were scanned using all optical filters (8, both glass and plastic), the scan with the blue glass filter most often had the highest average photocurrent measured. The blue glass filter provided a higher photocurrent than the blue plastic filter. In order from highest photoactivity to lowest, the filters were blue glass, blue plastic, then slight variations of yellow plastic, orange glass, orange plastic, green glass, green plastic,

then red plastic. For plate NiFe 1, the scan without a filter in Figure 8, with a blue glass filter in Figure 9, and with a red plastic filter in Figure 10 are shown.



**Figure 8:** Image of a scan of NiFe 1 sample plate with a red plastic filter. The results are much lower than results from scans without a filter or with a blue filter, showing a very low photocurrent measured.

### 3.3 Results of ozone cleaning the plate before spreading

FTO plates that were ozone cleaned prior to being spotted had a higher photocurrent than plates that were spotted in a pattern with single spots. Ozone cleaning the plates made the FTO layer on the glass plate more hydrophilic allowing the solution to spread over the plate. The scans of these plates, as shown in Figure 9, showed a higher photocurrent measured even when scanned with a red optical filter.

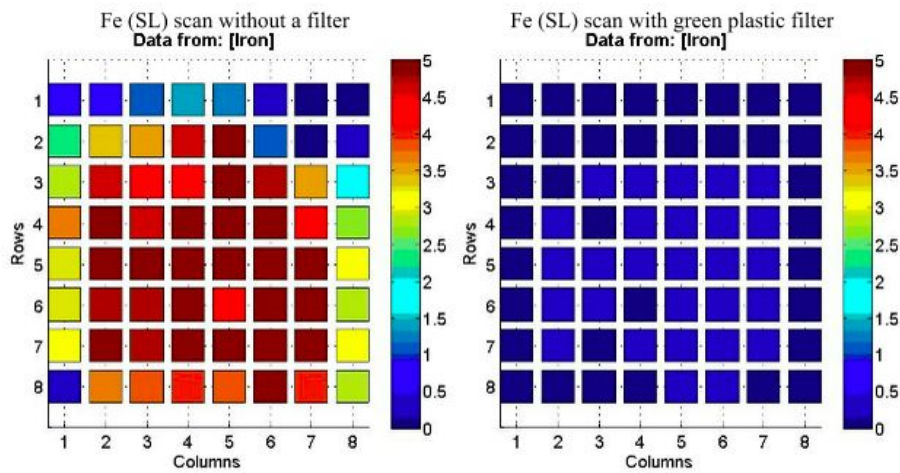
### 3.4 UV-Vis of Optical Bandpass Filters

The optical bandpass filters varied in color and material. The filters were scanned using the UV-Vis spectrophotometer and the transmittances are shown in Figure 10. In total there were 8 filters, 3 glass and 5 plastic. The optical filters used were glass: blue ( $T_{\max}$  at 420 nm), green ( $T_{\max}$  at 525 nm), orange ( $T_{\max}$  at 550 nm); and plastic: red ( $T_{\max}$  at 390 nm), orange ( $T_{\max}$  at 375 nm), yellow ( $T_{\max}$  at 365 nm), green ( $T_{\max}$  at 500 nm) and blue ( $T_{\max}$  at 410 nm).

Average current measured in mA

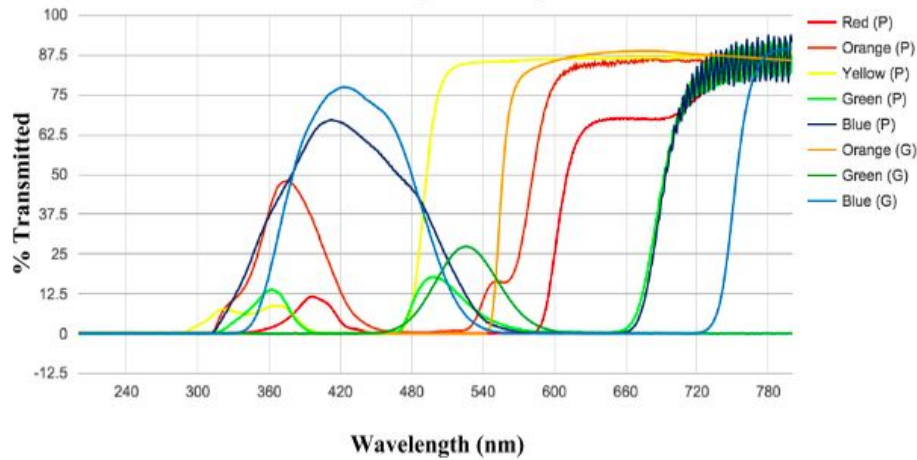
Plate name	Orange (G)	Green (G)	Blue (G)	Red (P)	Orange (P)	Yellow (P)	Green (P)	Blue (P)	No Filter
NiFe 1	0.212 mA	0.275 mA	2.422 mA	0.070 mA	0.296 mA	0.930 mA	0.180 mA	2.380 mA	3.329 mA
BiVO <sub>4</sub>	0.037 mA	0.128 mA	5.163 mA	0.132 mA	0.384 mA	0.119 mA	0.057 mA	5.390 mA	5.923 mA
Fe (SL)	0.122 mA	0.250 mA	2.977 mA	0.073 mA	0.302 mA	0.302 mA	0.142 mA	2.519 mA	3.668 mA
Cu 1	0.103 mA	0.457 mA	0.113 mA	0.017 mA	0.034 mA	0.121 mA	0.014 mA	0.072 mA	0.242 mA
CON 2	0.085 mA	0.136 mA	1.547 mA	0.304 mA	0.176 mA	0.345 mA	0.031 mA	0.994 mA	1.460 mA

**Table 1:** Results for each plate with each optical bandpass filter were averaged. These measurements are in milliamps and are listed for NiFe 1, BiVO<sub>4</sub>, Fe (SL), Cu 1, and CON 2. NiFe 1 is a layered plate with nickel nitrate and iron nitrate. BiVO<sub>4</sub> is a sample plate of bismuth vanadate that was yellow in color. Fe (SL) is a sample plate that was ozone cleaned with a double layer of iron oxide. Cu 1 is a sample plate with copper oxide. CON 2 is a plate of only iron oxide spotted in a checkerboard pattern.



**Figure 9:** Results for Fe (SL) sample plate. This plate was ozone cleaned and spotted with iron nitrate, annealed, then spotted with iron nitrate and annealed again to make a double iron oxide layer. The left shows the results of a scan without an optical bandpass filter. The right shows the results of a scan of the same plate with the green plastic filter.

Transmittance of Optical Bandpass Filters



**Figure 10:** Percent of light transmitted by the optical bandpass filters for each wavelength. Measurements taken by the UV-Vis spectrophotometer.

## **4. Discussion**

Results from the scans using different filters supports the idea that the current measured is not coming from photocorrosion. As the scans not using a filter and those with a blue filter are much higher than the scans with a red filter, the current is more likely to be originating from actual photoactivity rather than photocorrosion. If the sample plates were undergoing photocorrosion, the scans with filters of longer wavelengths would produce similar results to those using the blue filters with a shorter wavelength or not using a filter.

### **4.1 Plates with higher photoactivity**

Plates with higher photocurrents measured were those with a larger layer of iron oxide or with a higher molarity of solution. A larger surface area of the catalyst led to increased current measured because each flash of LED light illuminated a larger area of the catalyst. As more of the catalyst was exposed to light, the reaction took place on a larger scale creating more current. FTO sample plates with a sample of a higher concentration had a higher current as more material was able to anneal to the plate. With more material, the sample was able to induce the reaction and create more current. Sample plates with copper oxide, cobalt oxide, and nickel oxide did not have as high of a photocurrent as iron oxide for several reasons. The SEAL kit works to identify an element that would be a good catalyst and a good light absorber, which limits the amount of chemicals that will have a higher photocurrent. To investigate whether this current came from photoactivity and not photocorrosion, samples with a higher photocurrent are preferred. With a higher consistent photocurrent the differences in the current measured for each filter of a single sample are seen more clearly.

### **4.2 Effects of optical filters**

The optical bandpass filters used had varying wavelengths and amount of light transmitted at those wavelengths. Filters with a higher amount of light transmitted produced results from scans with a higher photocurrent. Blue filters that had a more light transmitted at a shorter wavelength had higher results from scans, but green filters did not

have a current as high because less light was transmitted through the filter and through the sample.

### **4.3 Different results with different cleaning methods**

Plates that were ozone cleaned for 15 minutes prior to being spotted with solution produced a current that was higher. We think this is due to the increased surface area of the sample, as well as causing the plate to be cleaner than when wiped with alcohol and isopropanol. Different methods of spotting were used in spotting sample metal nitrates onto the FTO plates which changed the results of the scans.

### **4.4 Effect of amount of light transmitted for each filter**

The optical filters were scanned using the UV-Vis spectrophotometer which analyzed the amount of light transmitted at each wavelength for the filters. In comparison to the results, we found that the amount of light transmitted directly affected the results. When more light was transmitted through the filter, the sample was more photoactive, which caused the measured current to be higher. The green filters, both glass and plastic, had a much lower amount of light transmitted than expected. The filters were darker in color, and the low amount of light transmitted caused the scans with these filters to have a lower current measured, despite the shorter wavelength that was transmitted. The LED light array box emits a certain set of wavelengths that we were unable to measure, and these wavelengths could be unequally distributed. This would give certain optical filters an advantage over others.

## **5. Conclusion**

In the case of current measured being caused by photocorrosion, results of the scans using the different optical filters indicate that the current is caused by photoactivity. Current is increased by the increased surface area of the sample spots, because the LED light is exposed to more of the sample. Iron oxide had much higher results because it is a good light absorber and a good catalyst, while the cobalt oxide, copper oxide, and nickel oxide are not both. In future work, a further investigation into finding the wavelength

spectrum emitted from the LED light array box would help to identify if any optical filters have an advantage over the others. By using the spreading method rather than working with sample spots, the increased photocurrent allows the differences to be identifiable between sample plates.

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