# Improving the Methodology of the HARPOON Experiment

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**ABSTRACT** In pursuit of an effective catalyst to aid in water splitting and production of chemical energy from solar energy, the HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) kit was developed. The HARPOON kit evaluates mixed metal oxides by observing the OER (Oxygen Evolution Reaction) half-reaction that occurs when they are put under an applied potential. However, the methods by which HARPOON tests the metal oxides are imperfect. The subject of this investigation was to improve upon these testing procedures. Because the high school students who work with HARPOON have limited access to the necessary equipment, improving the methodology of the experiment to make it more user-friendly is of great benefit. By running the HARPOON kit in varying configurations, several unique setups were assessed to determine the optimal testing procedure. The dish containing the system, the concentrations of the metal oxides used for testing, and the lighting system used to illuminate the setup were all investigated and modified through the experiments. With the improved technique and setup that has been developed, the HARPOON kit can be utilized to test mixed metal oxide catalysts more easily and effectively.

## 1. INTRODUCTION

The world's need for energy is constantly increasing due to the growing population and advancement of living standards.[1,2] As such, finding environmentally sustainable energy sources to meet these needs is crucial. Solar fuels are a promising source of sustainable energy that may provide a solution to the problem.[1,2] Currently, photovoltaic cells are used in solar panels around the world to convert light into electricity.[3] However, this energy either has to be used immediately, or must be stored in batteries in relatively small quantities.[3] This factor limits the usefulness of photovoltaics, so having an alternative method of producing clean energy that can be stored on a large scale is important. One such method is water splitting, which uses sunlight to transform solar energy into chemical energy in the form of hydrogen and oxygen gas.[2] In order to split water efficiently and effectively, the reaction must be catalyzed by oxygen evolving semiconductors.[2,4,5] The ongoing search to find a combination of inexpensive and earth abundant mixed metal oxides to serve this purpose is the motivation behind the Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization (HARPOON) experiment.[5]

Water splitting involves multiple steps, and the HARPOON experiment is centered on the discovery of catalysts for the Oxygen Evolution Reaction (OER) portion.[5] In OER, two molecules of water are converted to oxygen ($O_2$), and four protons and four electrons are released. The protons and electrons can then be used in the second half-reaction to produce hydrogen fuel ($H_2$).[5] The HARPOON kit tests the ability of mixed metal oxides to produce oxygen gas under an applied potential.[4,5] Metal oxides are drop casted onto a glass plate coated on one side with conductive fluorine-doped tin oxide (FTO), and the plate is submerged in an aqueous solution of sodium hydroxide (NaOH).[4] A piece of steel mesh coated with oxygen sensitive paint is placed over

the glass plate, which then changes color in response to the production of oxygen. The water splitting reaction is then driven by an applied potential, and catalyzed by the metal oxides. An ultra violet (UV) flashlight is used to light up the mesh, and allows the color change to be visually detected. Each mixed metal oxide spot is assessed based on the amount of oxygen it produces during the scan. The kit thus allows users to directly observe OER and understand the water splitting abilities of different catalysts, making it a straightforward project to be conducted by students everywhere.[5]

Although the current design of the HARPOON kit was formulated after a series of modifications due to consideration of several factors, the methodology of the experiment can still be improved in multiple ways. For instance, the container that holds the sodium hydroxide is wide compared to the FTO coated glass plate, so a great deal of sodium hydroxide is needed to fill the dish. Furthermore, the lighting system used to illuminate the painted mesh is not as effective as it could be. Presently, a UV flashlight is used to observe the mesh's change in color, but several issues with this method have been observed. A concentrated, direct beam of light, such as the one produced by this flashlight, is too bright to properly observe the OER transpiring in one place, but too dim to light up the entire mesh. Light needs to be cast over the system in a manner that is weaker than a direct beam, but still strong enough to completely illuminate the mesh. In order to investigate solutions to alleviate these types of problems with the HARPOON kit, experiments were run with three different sodium hydroxide containers, and three different lighting systems.

## 2. METHODS

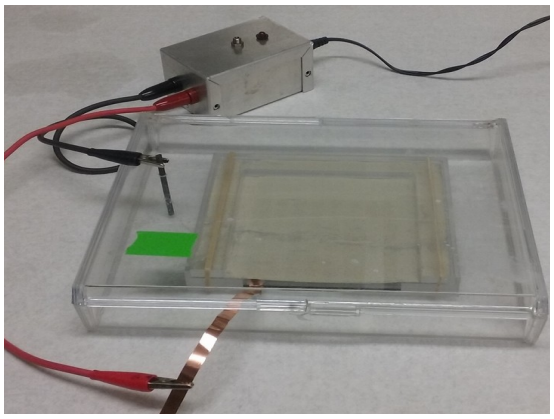

**Figure 1.** Original HARPOON kit setup.

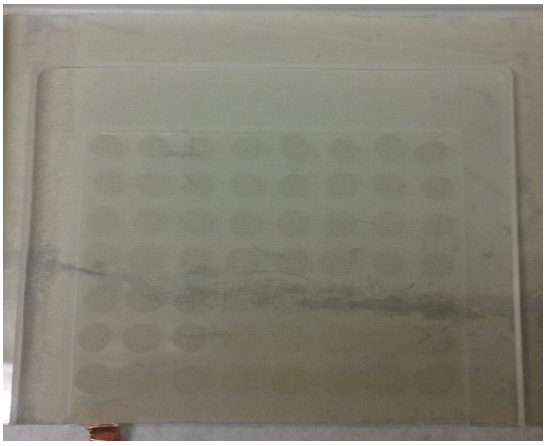

**Figure 2.** Acrylic holder with FTO plate and painted mesh.

### 2.1. The HARPOON Kit

The HARPOON kit was used to test mixed metal oxides for their ability to produce oxygen under an applied potential (Figure 1).[4] The mixed metal oxides were first prepared by making a mixed metal nitrate solution, and then using a 5 µl pipette to drop cast 5 µl aliquots onto a 3 inch by 3 inch glass plate coated with fluorine-doped tin oxide (FTO).[4] Then, the plate was annealed in a kiln for a total of 6 hours at 500°C, leaving behind a mixed metal oxide that could be tested. A piece of copper tape was attached to the corner of the FTO plate, and it was placed in an acrylic holder that surrounded the plate on three sides. Next, a piece of steel mesh with oxygen sensitive paint

was placed in the holder as well, and secured on three sides by a U-shaped acrylic piece that was held on by rubber bands (Figure 2). A small gap was left between the mesh and the plate. The acrylic holder was placed in a rectangular plastic dish, which was filled with a 0.1 M solution of sodium hydroxide (NaOH).

However, before the NaOH solution was poured into the dish, it had to first be purged of oxygen. This was achieved by using a nitrogen tank to vigorously degas the solution for 15 minutes before it was poured into the dish. Then, the solution was gently degassed for another 5 minutes once it was in the container. A graphite rod, which served as the counter-electrode, was inserted into the solution. The FTO plate served as the working electrode. The power supply was then connected to the system by attaching the negative (black) wire to the graphite rod, and the positive (red) wire to the copper tape coming off of the FTO plate. In order for the mesh's change in color to be detected, the oxygen evolution must take place in the dark, with only the UV flashlight illuminating the mesh. This situation was brought about by covering the entire container with a cardboard box, and shining a UV flashlight in through the side to cast light over the mesh. A small hole in the top of the box, covered by a yellow filter, provided a place to put a camera phone and take pictures of the mesh as it changed color. The power supply was plugged in, and pictures were taken of the mesh every 30 seconds for 5-7 minutes, depending on how much oxygen was produced. As the scan went on, the partial pressure of oxygen increased, causing the paint, which originally appeared yellow-orange, to appear green in the places where oxygen evolved. After the scan was complete, the pictures were put into the ImageJ software program. This program stacked all the pictures into one final image, and enhanced it so that the spots were more visible. The brightness values of the individual spots were recorded based on this final image.

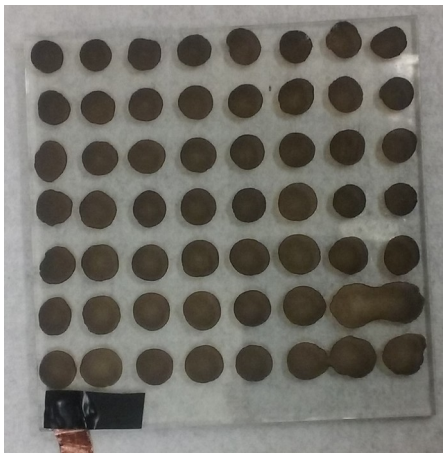

**Figure 3.** FTO plate spotted with first 0.005 M Ni:Fe:Co solution.

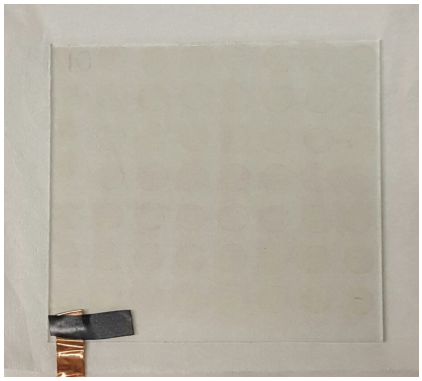

**Figure 4.** FTO plate spotted with second 0.005 M Ni:Fe:Co solution.

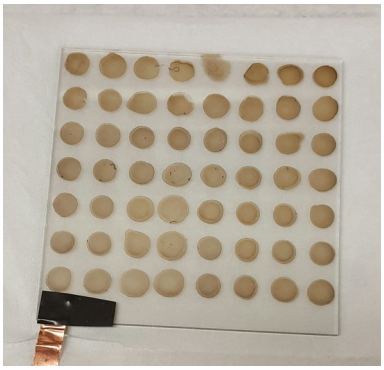

**Figure 5.** FTO plate spotted with 0.01 M Ni:Fe:Co solution.

### 2.2. Mixed Metal Oxide Solutions with Nickel, Iron, and Cobalt

Because the main focus of this project was on the methodology of the HARPOON kit, not the materials being tested, only one combination of metal oxides were used. The standard HARPOON solution, as designated by the HARPOON Experiment Instruction Manual, is a 0.005 M Ni:Fe:Co solution, combined in a 2:4:4 ratio.[4] This solution was made using nickel(II) nitrate ($Ni(NO_3)_2$), iron(III) nitrate ($Fe(NO_3)_3$), and cobalt(II) nitrate ($Co(NO_3)_2$).[4] However, the first attempt to make the standard was ineffective due to miscalculations, and the solution ended up being too concentrated. This fact was evidenced by the dark orange color of the solution, and the fact that after FTO plates with this solution drop casted on them were annealed, the spots turned completely black, instead of light brown as they should (Figure 3).[4]

In an effort to create a less concentrated solution that conformed to the HARPOON Instruction Manual, a new standard Ni:Fe:Co solution was made. First, 25 mL solutions of 0.005 M $Ni(NO_3)_2$, 0.005 M $Fe(NO_3)_3$, and 0.005 M $Co(NO_3)_2$ were made. Then, 10 mL of the 0.005 M $Ni(NO_3)_2$ was combined with 20 mL of the 0.005 M $Fe(NO_3)_3$ and 20 mL of the 0.005 M $Co(NO_3)_2$ solution. This created a 0.005 M solution of nickel, iron, and cobalt in a 2:4:4 ratio, as desired. However, after a plate made using this solution was annealed, the metal oxide spots were almost invisible, demonstrating that this concentration might have been too weak (Figure 4).

In pursuit of a metal oxide solution that gave positive results and had the desired appearance of light brown spots after being annealed, a 0.01 M solution of nickel, iron, and cobalt was created. 25 mL solutions of each metal nitrate ($Ni(NO_3)_2$, $Fe(NO_3)_3$, and $Co(NO_3)_2$) were prepared in 0.01 M concentrations. Then, 10 mL of the 0.01 M $Ni(NO_3)_2$ was combined with 20 mL of the 0.01 M $Fe(NO_3)_3$ and 20 mL of the 0.01 M $Co(NO_3)_2$ solution. The resulting solution was once again Ni:Fe:Co in a 2:4:4 ratio, but twice as concentrated as the previous solution had been. When the 0.01 M solution was drop casted on an FTO plate and annealed, the spots turned the expected shade of brown (Figure 5).

One phenomenon that was observed, particularly with the 0.01 M Ni:Fe:Co solution, was that the solution seemed to become darker day by day, especially after the first day. In order to document this change and make sure it was not due to contamination of the solution, a new 0.01 M Ni:Fe:Co solution was made in the same way as before. Some plates were also spotted using both of the 0.01 M solutions in order to compare them and see which one yielded better results.

### 2.3. UV/Ozone Cleaning to Reduce the Coffee Ring Effect

One problem that was commonly observed when FTO plates were spotted with metal oxides was the coffee ring effect. The coffee ring effect occurred when the edges of a drop of solution became pinned to the glass plate, and the suspended particles within the spot traveled to the outside of the spot during evaporation.[6] This created a “coffee ring” shape, or a higher concentration of solution on the outside of the drop. The faster the metal nitrate dried, the more enhanced the effect was, so drying FTO plates on a hot plate as opposed to air drying them made the coffee ring effect worse. To fix this problem, a homemade ozone cleaner, developed and loaned to us by the SEAL team at Oakwood School, was used to clean the plates before the metal oxides were deposited onto them. The cleaner worked by using an ultraviolet lamp to emit UV light, which caused the contaminants on the FTO plate to be excited or dissociated.[7] At the same time, oxygen ($O_2$) was dissociated by the UV light waves, producing ozone. The ozone was dissociated by the UV light again, creating atomic oxygen. The molecules of contaminant that had been excited and dissociated reacted with the atomic oxygen to form simpler molecules such as carbon dioxide ($CO_2$) and water ($H_2O$).[7] This process produced an ultraclean surface on the top of the glass FTO plate. A template with the spotting pattern was

placed over the plate to restrict the cleaning to the areas that were intended to contain solution. After the plate was cleaned in the UV ozone cleaner for 10 minutes, the glass became hydrophilic and the metal nitrate solution adhered to it well. The coffee ring effect was virtually eliminated and the spots dried in a uniform pattern.

### 2.4. Containers for the Sodium Hydroxide and FTO plate

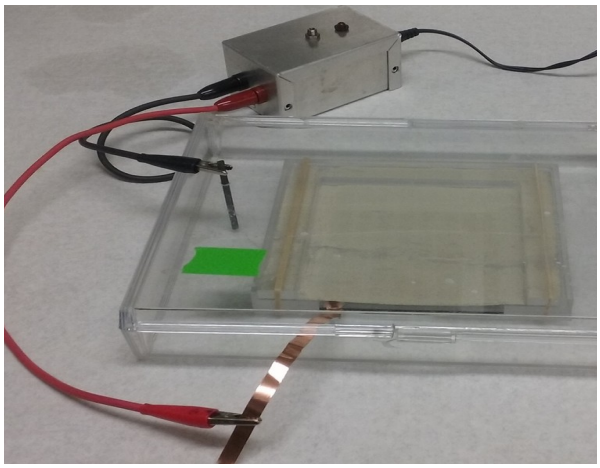

**Figure 6.** HARPOON setup with original dish.

#### 2.4.1. Original Container

The original HARPOON setup involved using a shallow plastic dish to contain the sodium hydroxide, FTO plate, and mesh (Figure 6). Two FTO plates were tested using this container, and multiple issues were noted during the process. For instance, the sodium hydroxide solution had to fill the container almost to its top in order for it to cover the mesh as necessary. Having the sodium hydroxide level so high meant that the dish could not be tilted at all, making it difficult to remove any bubbles that may appear between the mesh and the FTO plate. Additionally, cleaning up the sodium hydroxide after running a scan was a messy process when the container had such little depth. Furthermore, the system had to be degassed with the nitrogen tank for at least 5 minutes while it was in the container. Because the dish was so shallow, even gentle degassing created bubbles which hit the lid of the container. This splashing was a problem because pictures needed to be taken through the top of the dish, and they became distorted when solution appeared on the lid. Another issue was the width of the container. Although the container was shallow, it was also wide, which meant that a large amount of sodium hydroxide, about 300 mL, must be used to fill it. A narrower container would reduce the amount of sodium hydroxide necessary.

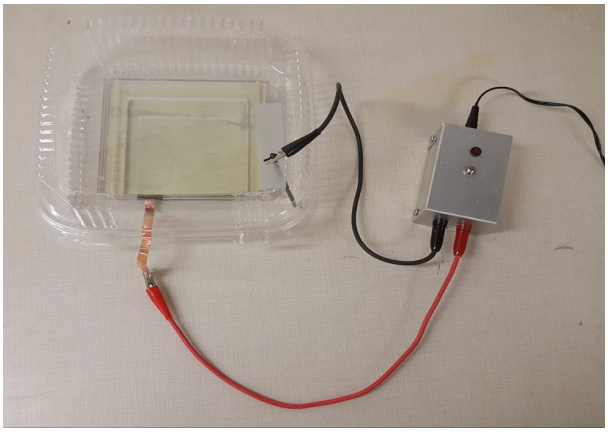

**Figure 7.** HARPOON setup with salad dish.

#### 2.4.2. Salad Dish

The next container that was tested was a plastic salad to-go box (Figure 7). This dish was significantly deeper than the previously used one, which allowed it to be tilted back and forth in order to remove bubbles from under the mesh. However, it also had a similar width to the original container, meaning that just as much sodium hydroxide solution had to be used per scan as before. The salad dish was also not as airtight as it should have been, because even though the container does not have to be completely airtight, the sides of the salad dish had unwanted gaps where the lid met the bottom. Moreover, due to the size of the salad box, the sodium hydroxide solution had to be degassed in more than one corner of the box in order for it to be completely purged of oxygen. This setup was easier to use than the previous container, and did not result in as much of a mess to clean up.

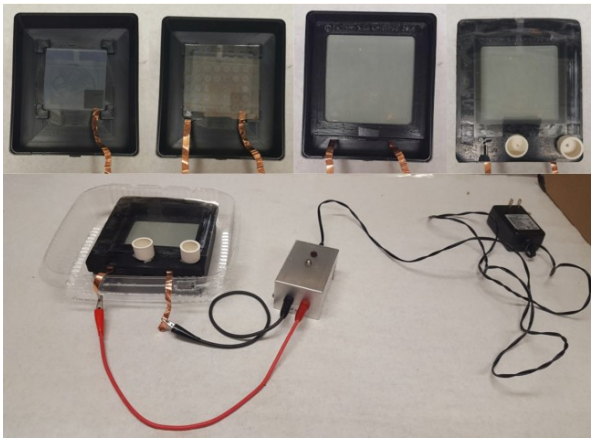

**Figure 8.** Top (from left to right): 3-D printed holder with FTO plate counter-electrode; FTO plate spotted with metal oxides; mesh secured by mesh holder; holder lid with window and septa. Bottom: Full 3-D printed holder setup.

### 2.4.3. 3-D Printed Holder

The final container that was tested was a 3-D printed prototype holder made out of black plastic (Figure 8), which was developed by our mentor Allison Moore at Fairmont State University in West Virginia. The main container was a rectangular box with two tiers on the bottom. The bottom tier held a small, conductive FTO plate that served as the counter electrode in place of the graphite rod. The second tier held the FTO plate with the metal oxides on it. The piece that was placed over the spotted FTO plate was the mesh holder. It consisted of two interlocking pieces that fit together to secure the mesh on four sides, and held it in position a few millimeters above the plate. The last piece was the lid, which fit loosely over the top of the container. It had a large window in it, so as to observe the FTO plate and mesh. It also had two holes near the bottom for septa to be inserted and used to degas within the holder.

During preliminary testing, cling wrap was stretched over the window and attached using double-sided tape, and the degassing holes were covered with parafilm. However, the cling wrap tended to stretch and create wrinkles which were difficult to see through. The cling wrap was replaced by a hard, thin piece of plastic cut from the material of a to-go box, and was secured by double-sided tape. This plastic did not have to be replaced and was easy to see through. The parafilm was eventually replaced by septa, which were easier to use and more permanent.

## 2.5. Lighting Systems

**Figure 9.** UV flashlight shining into cardboard box.

### 2.5.1. UV Esco-Lite LED Flashlight

The first lighting system tested was the UV flashlight, which was part of the original kit (Figure 9). With the original container and the salad dish, the flashlight was used to cast light over the mesh by illuminating the sodium hydroxide through a hole cut in the side of a cardboard box. The flashlight was moved back and forth when taking pictures of the scan in order to illuminate the entire plate, as the beam was not wide enough to light up the whole piece of mesh from one position. However, when used in conjunction with the 3-D printed holder, the light beam could not be cast from the side, due to the height of the holder and the fact that the holder was black, not clear like the other two dishes. A new cardboard box was constructed, with an opening in the top for the light to illuminate the mesh from above. The flashlight had to be maneuvered back and forth while capturing pictures in order to ensure that the entire mesh was lit up, and that no single part of the mesh was exposed to a concentrated beam of light for an extended period of time, as this would prevent oxygen from being detected.

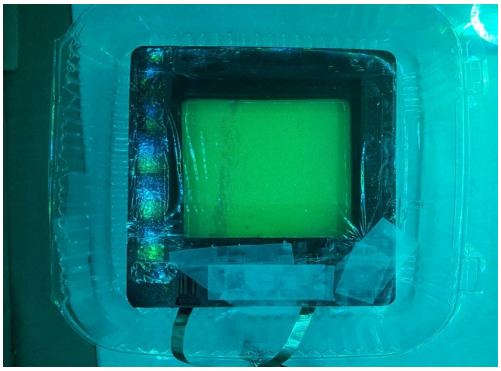

**Figure 10.** Inside of cardboard box illuminated with LED light strip.

### 2.5.2. Color Changing Adhesive LED Light Strip

The next attempted lighting system involved eliminating the flashlight from the testing procedure. In an effort to develop a lighting method in which the lights did not have to be manually adjusted throughout the scan, an adhesive LED light strip was obtained, with the intent of lighting up the inside of the cardboard box evenly (Figure 10). The light strip was run around all four sides of the box in its top corners, and then run down the side of the box, and out through a small hole where it could be connected to a computer. An additional incentive for using the LED light strip as opposed to a flashlight was that having light arriving from several angles, instead of just one, would eliminate any shadows that the lid of the 3-D printed holder cast onto the mesh.

**Figure 11.** Lamp with blacklight bulb held over top of cardboard box.

### 2.5.3. Lamp With Blacklight Bulb

The third lighting method that was tested was a desk lamp that had a blacklight bulb instead of a normal one. This light was tested in the hopes that it would illuminate the entire box, and cast enough light on the mesh so that it could be clearly seen. Because the head of the lamp was much larger than any of the previous lights that had been used, a large circle, slightly smaller than the lamp head, was cut in the top of the cardboard box to accommodate it. The head of the lamp rested over the hole from which the blacklight illuminated the box (Figure 11).

## 3. RESULTS

### 3.1. Results of the Mixed Metal Oxide Solution with Nickel, Iron, and Cobalt.

The first solution made was intended to be a 0.005 M solution of Ni:Fe:Co in a 2:4:4 ratio, but was likely too concentrated due to miscalculations. FTO plates tested using this solution received minimal results, as the one plate that did give results (Plate 5) yielded few oxygen spots, which were extremely dim and gave relatively low brightness values (Table 1). They also only appeared on the bottom two rows of the plate and nowhere else. Additionally, the spots on the plates turned completely black after being annealed, which reinforced suspicions that the solution might have been too concentrated.

In light of these results, the second Ni:Fe:Co solution was made in a 2:4:4 ratio. This solution, which was 0.005 M, produced clear spots that were almost invisible after being annealed. The first plate spotted with this solution (Plate 7) yielded encouraging results when tested: its highest value was 356.4, which was the highest brightness observed so far. Once again, the oxygen production was restricted to the bottom area of the plate. However, no other FTO plates tested using this solution yielded any results. This led to the conclusion that the previously tested plate may have been a fluke, and the light color of the annealed metal oxide spots indicated that a more concentrated solution may prove more effective.

| Oxygen Producing Scans | | | | | |
|---|---|---|---|---|---|
| Plate Number | Solution Concentration and Date Solution Made | Container Used | Highest Spot Brightness | Average Spot Brightness | Number of Oxygen-Evident Spots |
| 5 | 0.005 M (6/21) | Salad Dish | 288.0 | 179.2 | 14 |
| 7 | 0.005 M (6/28) | Salad Dish | 356.4 | 162.1 | 17 |
| 13 | 0.01 M(7/07) | Salad Dish | 302.5 | 125.2 | 19 |
| 14 | 0.01 M (7/07) | 3-D Printed Holder | 422.9 | 138.6 | 14 |
| 16 | 0.01 M (7/07) | 3-D Printed Holder | 393.4 | 229.0 | 16 |
| 17 | 0.01 M (7/07) | 3-D Printed Holder | 536.8 | 201.3 | 21 |
| 19 | 0.01 M (7/07 & 7/13) | 3-D Printed Holder | 433.9 | 218.8 | 26 |
| 20 | 0.01 M (7/13) | 3-D Printed Holder | 788.6 | 215.4 | 27 |
| 21 | 0.01 M (7/07 & 7/13) | 3-D Printed Holder | 392.3 | 168.5 | 22 |
| 22 | 0.01 M (7/07 & 7/13) | 3-D Printed Holder | 409.6 | 205.5 | 39 |
| 22 | 0.01 M (7/07 & 7/13) | 3-D Printed Holder | 658.1 | 382.9 | 51 |
| 24 | 0.01 M (7/07 & 7/13) | 3-D Printed Holder | 513.0 | 272.3 | 46 |
| 25 | 0.01 M (7/07) | 3-D Printed Holder | 339.2 | 211.2 | 27 |

**Table 1.** Brightness values of oxygen producing scans. Spots were only recorded if brightness value was greater than 100.

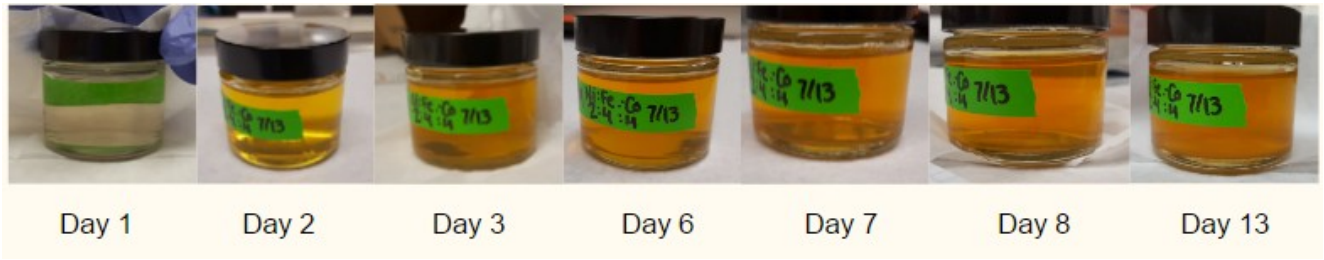


**Figure 12.** Darkening of 0.01 M Ni:Fe:Co solution over time.

Next, a 0.01 M solution of Ni:Fe:Co was made, and metal oxide spots appeared light brown after annealing. Results using this solution were increasingly positive. The first scan that was run using a plate made with this solution (Plate 13) peaked at 302.5 with an average brightness of 125.2 (Table 1). However, results were once more only appearing on the bottom few rows of the plate. Three more plates were successfully tested using this solution (Plates 14, 16, and 17), and they seemed to improve overall brightness values as time went on, though the oxygen spots were still restricted to the bottom portion of the plate. It was hypothesized that this might have been due to the mesh that was used, which was old and scratched up in some places.

In order to replicate the 0.01 M solution that had begun to give good results, a new 0.01 M solution of Ni:Fe:Co was made, again in a 2:4:4 ratio. Immediately after this solution was made, it appeared light in color, nearly clear. However, the next day, the solution had darkened significantly, and it continued to do so little by little each day after that (Figure 12). Though no reason for this phenomenon has been discovered yet, the darkening does not seem to be a negative change as far as results are concerned. In fact, the brightness values increased at first, then maintained a steady level. The highest brightness level detected with this solution was 788.6, which was significantly higher than any of the results found using either of the 0.005 M solutions.

Testing was also performed to determine which 0.01 M solution gave better results. The first plate that was tested (Plate 19) was spotted with the newest solution on the left half, and the older 0.01 M solution on the right. The results showed that the left half of the plate seemed to produce more oxygen, but other factors, such as the light angle could have contributed to this. The next plate (Plate 21) was made with the older 0.01 M solution on the left, and the new one on the right. This time, the left half of the plate again produced more oxygen. In an attempt to receive conclusive results, two more FTO plates (Plates 22 and 24) were made with alternating columns of the new and old 0.01 M solutions. The results from Plate 22 were highly positive, but did not demonstrate any notable difference between the two 0.01 M solutions. A final test was run with Plate 24, and this scan showed conclusively that the old solution performed visibly better than the new one (Figure 13).

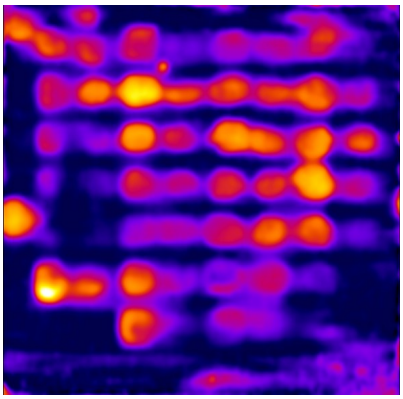

**Figure 13.** Processed scan of Plate 24.
Columns 1,3,5,7: old 0.01 M solution
Columns 2,4,6,8: new 0.01 M solution

### 3.2. Results for Different Containers

#### 3.2.1. Original Container

Preliminary testing was done using this container, but it was soon found to be imperfect. Only two plates were tested using this shallow dish, and neither one of them produced results. However, this was likely due to several factors, not just the dish itself. Even so, the difficulties encountered when using it demonstrated its weaknesses, and prompted ideas for how the next model would have to differ from this one. For example, the next dish would have to be deeper than this one, because the bubbles produced by degassing the sodium hydroxide solution within the container caused splashing on the lid. This interfered with the pictures that were taken of the results. Furthermore, this container was difficult to use because it was so shallow, and hard to clean up without spilling the sodium hydroxide. The lid also had scratches on it, further obscuring the view of the mesh.

#### 3.2.2. Salad Dish

Scans run in this container did show more results, and this container was easier to work with. The main issue with the original container was that it was too shallow, and the salad dish solved this problem, allowing the sodium hydroxide solution to be easily degassed without splashing on the lid. However, gaps between the bottom of the box and the lid made the salad dish less airtight than preferred, meaning that the solution had to be degassed longer than would otherwise be necessary. This dish, like the original one, used about 300 mL of sodium hydroxide per scan. When plates were tested in this container, results were usually produced, giving values that averaged in the 100s. The places where oxygen was produced was restricted to the bottom two or three rows for the majority of these scans. This is most likely because the piece of mesh that was used in the acrylic holder was scratched up and painted unevenly.

#### 3.2.3. 3-D Printed Holder

The container that was used for the majority of testing was the 3-D printed holder, which produced positive results for most of the scans run in it. This container seemed to produce more consistent results as well. The first plate tested with this holder did not produce any oxygen whatsoever, but this was most likely because of the dilute 0.005 M solution used to make the plate. Later on, the results from the holder became increasingly positive. Oxygen spots were consistently observed in the scans, some brightness levels reaching into the 500s. However, the places where oxygen was produced stayed isolated to the bottom half of the plate until the last few scans, which were run using a different piece of mesh. Once a new piece of mesh with oxygen sensitive paint was acquired, oxygen spots began to appear over the entire plate, indicating that the mesh which had previously been used was the reason for our results only showing oxygen appearing at the bottom of the plate. The new piece of mesh displayed oxygen spots over the entire FTO plate, indicating that it was evenly coated with the oxygen sensitive paint.

Using the 3-D printed holder was easier and more effective than using any of the other dishes. The holder was smaller, so it used about half as much sodium hydroxide as the salad dish, and it also took less time to fully degas the container. The holder also had septa for degassing the solution as opposed to a small hole covered in parafilm, which made it easier to degas. Furthermore, the FTO plate and mesh were secured in a set position that could not be altered. This made testing more uniform, and reduced the number of variables involved when running scans. The mesh was held on four sides as opposed to three, as it was in the previous containers, so it lay flatter and at a uniform distance from the FTO plate for each scan.

### 3.3. Results for Different Lighting Systems

#### 3.3.1. Results From UV LED Flashlight

The UV flashlight was used for most of the scans that were run. It was able to cast light from the side over the original container and the salad dish, where it would be moved back and forth from side

to side in order to illuminate the entire mesh. However, when it was used to illuminate a plate from above, as was necessary with the 3-D printed holder, the direct beam cast by the light was too intense in one area to allow oxygen to be detected, and too narrow to light up the rest of the mesh without being moved around (Figure 14a). Because the flashlight had to be manually moved around during the scan, it was difficult to be consistent with the lighting levels from scan to scan. Additionally, the light only came from one angle, so it cast a shadow over a small part of the mesh, partially obstructing the view of the bottom row of spots. Nevertheless, the light produced by this flashlight was capable of revealing oxygen spots.

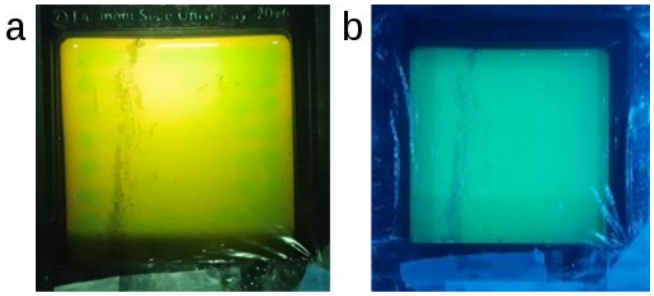


**Figure 14.** (a) Mesh when UV flashlight is shined from above. (b) Mesh when LED light strip is shined.

### 3.3.2. Results From Color Changing Adhesive LED Light Strip

The LED light strip was much easier to use than the UV flashlight. Since it did not have to be held or moved around, it was simply plugged in at the beginning of the scan, and steadily lit up the mesh from every direction, reducing the shadows cast on the mesh. The entire piece of mesh could be clearly seen (Figure 14b). The LED strip color was set on blue, as this was the closest color to the light given off by the flashlight. However, when the scan was run, no change in mesh color could be seen. After the scan, the mesh was illuminated using the UV flashlight, and oxygen spots could clearly be seen. This demonstrated that the blue light emitted from the light strip was not the right color, and would not work.

### 3.3.3. Results From Lamp With a Blacklight Bulb

The blacklight bulb lamp was placed over the top of the cardboard box in the hopes that it would light up the entire box with the correct color light. The blacklight may have been the correct color, but the bulb was too weak to fully illuminate the mesh. In addition, the light had to be balanced carefully in order for it to block out any external light and shine down on the holder properly. The lamp also heated up very quickly, making it dangerous to have turned on for extended periods of time.

### 4.1. Effectivity of Mixed Metal Oxide Solutions

The first metal oxide solution that was created, which was intended to be a 0.005 M solution of nickel, iron, and cobalt in a 2:4:4 ratio, did not produce oxygen well. This was most likely because of miscalculations that caused the solution to be overly concentrated. The second 0.005 M solution produced negative results as well, most likely because the solution was too dilute. The third solution of Ni:Fe:Co in a 2:4:4 ratio, which was created with a concentration of 0.01 M, produced positive results, but it unexpectedly turned darker day by day. Another 0.01 M solution of the same metals was created to study this effect and make sure it was not due to contamination. The second 0.01 M solution exhibited the same effects and produced positive results when running scans. Both 0.01 M solutions seemed to increase in oxygen production over time. When tested against one another, the first 0.01 M solution performed slightly better than the second one, which supports this hypothesis. A reason for the darkening of the solutions has not yet been discovered.

### 4.2. Effect of UV/Ozone Cleaning

The first four plates that were made were spotted without using an ozone cleaner first, and they exhibited signs of the coffee ring effect, even when they were air dried. By placing FTO plates in the ozone cleaner for about 10 minutes before drop casting the solution onto them, the coffee

ring effect was completely eliminated when the plate was air dried.

### 4.3. Effectivity of Containers for Sodium Hydroxide and FTO Plate

Three containers were tested with HARPOON. The original container had the most issues, as the shallowness of the container and the scratches on the lid prevented HARPOON from being used to its maximum potential. The salad dish was superior because it was deeper, and so provided more space for the sodium hydroxide. The 3-D holder was preferable to either of the other two dishes. It held the mesh evenly over the FTO plate, and kept the mesh flat by securing it on all four sides. It was also smaller than the other two containers and required half as much sodium hydroxide for testing. The holder had holes where septa could be inserted and used for degassing instead of parafilm, which was more convenient. However, unlike in the salad dish, the lid of the holder cast a shadow over a small part of the mesh, preventing oxygen from being detected there.

Some modifications to the 3-D printed holder might render it even better, but several factors must be taken into consideration, and a balance must be found between them. For instance, making the window on the lid wider would solve the shadow problem, but making the holder wider would mean that more sodium hydroxide must be used. An alternative to this may be to move the top inside edges of the window further back, and keep the bottom edges in the same place, so that the sides slant outward from the window. This would reduce the amount of shadow on the mesh without increasing the volume of the holder. Furthermore, the mesh holder was only held together on one side, so it was difficult to ensure that it stayed together throughout the scan. The mesh holder could be improved by modifying it so that it is held together on opposite sides. Another possible change would be to make the holder more airtight by putting an insulator around the top of the lid. In addition, the bottom of the holder developed a leak which increased as testing went on. The leakage could have been caused by the holder material degrading over time. Future work could also include investigating different 3-D printing materials to find one that maintains its solidity throughout numerous scans.

### 4.4. Effectivity of Different Lighting Systems

The UV LED flashlight was the only light source capable of detecting oxygen spots on the mesh. However, the LED light strip was the best at lighting up the entire mesh evenly all at once. The blacklight lamp was completely ineffective. Ideally, an LED light strip with UV light bulbs would be used to light up the box instead of the flashlight. If the light came from multiple angles, it would reduce the intensity of the shadows that are cast over the mesh. A light source such as this might eliminate the need to change the 3-D printed holder design.

## 5. CONCLUSION

The HARPOON experiment was tested with three different containers and three different lighting systems in order to improve the kit. Several versions of the HARPOON standard solution were made for testing, and it was found that a 0.01 M solution of Ni:Fe:Co in a 2:4:4 ratio yielded the most positive results. The 3-D printed holder was found to be the easiest to use and the least trouble to clean up. The UV flashlight was found to be the most effective at detecting oxygen. This container and lighting system were used together to run the HARPOON experiment the most effectively, and with the few identified modifications to the 3-D printed holder and the lighting system, HARPOON may be made even more straightforward and simple to use in the future.

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**ABBREVIATIONS**

HARPOON, Heterogenous Anodes Rapidly Perused for Oxygen Overpotential Neutralization; OER, oxygen evolution reaction; FTO, fluorine-doped tin oxide; UV, ultraviolet

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