Experimentation with Different Variations of the HARPOON Setup to Make Process Easier to Execute While Optimizing Quality of Results

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ABSTRACT: The HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) project is being used by students all over the nation to test the potential of mixed metal oxides as water oxidation catalysts. Although this kit may seem attractive because it is inexpensive and serviceable, the current process of the project does not always produce the most accurate and dependable results. To improve upon the methodology, many different variations and factors of the process were explored. The reference solution of Ni-Fe-Co in a 2:4:4 ratio was used as a standard to spot all the plates tested on each setup. Mainly two setups were tested, the original salad dish setup with the UV flashlight and a 3D-printed prototype holder with a variation of light sources. Each setup used the same general process of degassing the NaOH solution and taking pictures in a dim setting. The main difference in the setups were the holders and lights. The lights and the quality of mesh proved to be important factors in being able to determine the amount of oxygen produced. The 3D-printed holder used with the UV-LED flashlight proved to be easier to operate, and data processed from ImageJ confirmed that the results produced from this setup yielded more positive and consistent results than the original setup.

1. INTRODUCTION

Solar conversion provides an energy alternative[1-4] without the harmful byproducts and unsustainable nature of nonrenewable resources. Solar energy can be used to split water to produce hydrogen for chemical fuel. In order for water splitting to occur, two stable, cheap, and earth abundant catalysts are need to lower the kinetic barriers of reducing protons to hydrogen and of oxidizing water.[2]

The HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) project focuses on testing unique mixed metal oxides as catalysts for the oxygen evolution reaction (OER).[1,3,5] To do this, a mixed metal oxide combination would be drop casted on a conductive fluorine-doped tin oxide (FTO) coated glass plate. In the current and original HARPOON kit, the plate would be placed in an acrylic holder which also had the function of keeping a piece of mesh coated with dual-chromophore fast-response pressure-sensitive fluorescent paint (Innovative Scientific Solutions Incorporated, Catalog no. BUNC-12) in place with two rubber bands. The holder would be submerged in a degassed .1 M alkaline electrolyte solution (usually sodium hydroxide) inside a salad dish. Alligator clips from the power supply would then be connected to the copper tape attached to the FTO plate (anode) and also to a counter electrode graphite rod (cathode) (Figure 1).

Figure 1. Image of original setup of HARPOON kit.

Before running current through the plate, the entire setup was placed in an area without any stray light, i.e. a darkened room or preferably a box, to be able to see the fluorescence from the paint coating the mesh. The power supply would then be turned on to start electrolysis. The mesh would be illuminated by UV-LED light and results were recorded with a camera then processed with ImageJ software.

Although this kit has the potential of finding the key to great OER catalysts, it was laborious to use and had many points for possible modification. The main point for improvement with this kit was the acrylic holder, which allowed plenty of room for error. The original acrylic holder only held the mesh down on three sides, allowing for dents to easily form. A 3D-printed holder was tested in replacement of the acrylic holder and salad dish. This holder is a container and in its very nature replaces the salad dish since its only function was to hold the alkaline electrolyte. It also uses a smaller FTO plate in replacement of the graphite rod and has a mesh holder that holds the mesh on all 4 sides which would solve the problem of the mesh bending (Figure 2).

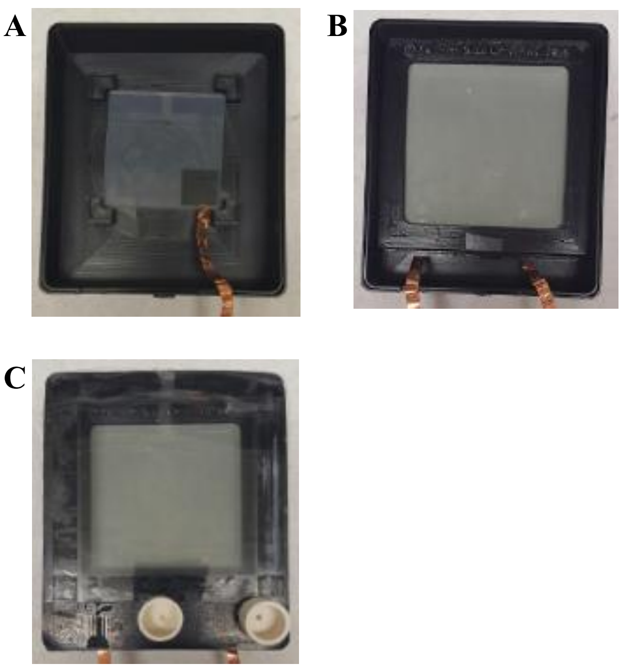

Figure 2. (A) 3D-printed holder with the smaller FTO plate. (B) 3D-printed holder with mesh holder (with the mesh) over the counter electrode and plate being tested. (C) 3D-printed holder with lid.

The 3D-printed holder consisted of attractive qualities, but was tested to see if it could yield results similar to the original kit. Other factors were also explored, such as variations in the UV light source. Positive results with experimentation will hopefully optimize this kit's abilities and make the process more convenient to handle so that the quality of results and the efforts for finding water oxidation catalysts would increase.

2. METHODS

2.1 Solution Preparation. Since experimentation was based on how to improve the kit, only the reference solution,[2,5] which is Ni-Fe-Co at a 2:4:4 ratio, was used for testing each setup. The standard solution was prepared in concentrations of .005 M, .01 M, and .05 M. Although a .005 M concentration is recommended, a variety of concentrations were still tested to see which one would work best. To make the standard solution, $Ni(NO_3)_2$, $Fe(NO_3)_3$, and $Co(NO_3)_2$ metal salts were weighed and dissolved with 25 ml of deionized water. A 50 ml Ni-Fe-Co solution was made by combining 10 ml of $Ni(NO_3)_2$ solution, 20 ml of $Fe(NO_3)_3$ solution, and 20 ml of $Co(NO_3)_2$ solution.

To prepare the alkaline electrolyte, NaOH was made at a .1 M concentration by combining 1 g of NaOH pellets with 250 ml of deionized water.

2.2 Preparing Plates. A 3” ×3” FTO plate was engraved with a diamond-tipped scribe on the top corner with a number label on the non-conductive side of the plate. The plate was cleaned with deionized water and acetone. After drying, the plate was covered with a plastic spotting template and put into an ozone cleaner. The UV in the ozone cleaner would react with oxygen to create ozone, which would eat away the impurities on the FTO plate’s surface, making the spots hydrophilic. The standard solution was dropped onto the hydrophilic spots of the FTO side of the plate using a 5 μL pipette and a spotting template. The bottom row was always left empty to leave room for the copper tape, which left a total of 54-56 testable spots. After drop casting, the plates were either air dried or left to dry on the hot plate at medium temperature. The plates were then fired in a kiln for 6 hours at 500 °C at a ramp rate of 250 °C/h, doing this not only adhered the spots to the plates but also allowed the metal salts to convert to metal oxides.

2.3 Preparation for Testing. Prior to testing a sample, 250 ml of NaOH was degassed in a glass bottle by rapidly bubbling N_2 through the solution for 15 minutes. As previously stated, both the acrylic holder and 3D-printed holder were used for testing. When using the acrylic electrode holder, a plastic salad dish was used to contain the NaOH solution and the holder (Figure 1). The box used for this holder had a hole cut through the side for the UV-LED flashlight to shine on the setup and another hole cut through the top with a piece of yellow filter taped to the underside (Figure 3).

Figure 3. Box used to for acrylic holder has hole on side for flashlight and hole on top for filter.

Data was collected by taking pictures through the yellow filter. When the 3D-printed holder was used, a different box had to be made because the walls of the holder blocked light from shining in from the sides. The only way for light to be shined onto the holder was from above, so the hole for the UV-LED flashlight was made on the top of the box, near the hole for the filter and camera (Figure 4).

Figure 4. Box used for 3D-printed holder had a hole on top for flashlight and a hole next to it for the filter.

Different lighting situations were also tested by using LED strips and a lamp with a black light bulb. The LED strips were taped along the inner top rim of the box and the hole used for the flashlight was blocked using cardboard. To test the lamp, the hole used for the flashlight was widened to fit the rim of the lamp (Figure 5).

Figure 5. A bigger hole was made on the top of the box for the 3D-printed holder to fit the rim of the lamp.

2.4 Collecting Data

After the power supply was plugged in, the camera phone took pictures every 30 seconds until the spots collided with each other. In the case that no spots appeared, only 5-6 minutes' worth of pictures were recorded. Each setup used a different method of taking pictures, depending on where the hole for the flashlight was on the box. Since the box for the acrylic holder had a hole for the light on the side, the light could only illuminate the top and bottom sides of the mesh. The box for the 3D-printed holder had a hole on top, making it easier to illuminate all corners of the mesh. When using the acrylic holder, 2 pictures were taken every 30 seconds. One picture captured the image of the light directed on the top side of the mesh while the second picture showed the light on the bottom side (Figure 6). When using the 3D-printed holder, 2-4 pictures were taken every 30 seconds. Each picture captured the image of the light on the different corners of the mesh (Figure 7). All images were then processed through ImageJ which is software that was used to quantify the amount of oxygen produced at each spot by detecting the brightness levels of each spot.

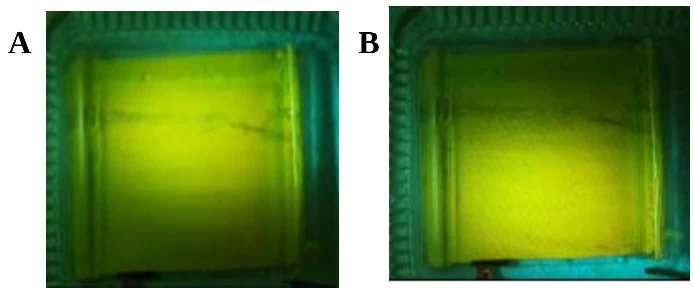

Figure 6. Images taken during electrolysis in acrylic holder. (A) Light on top side of the mesh. (B) Light on bottom side of the mesh.

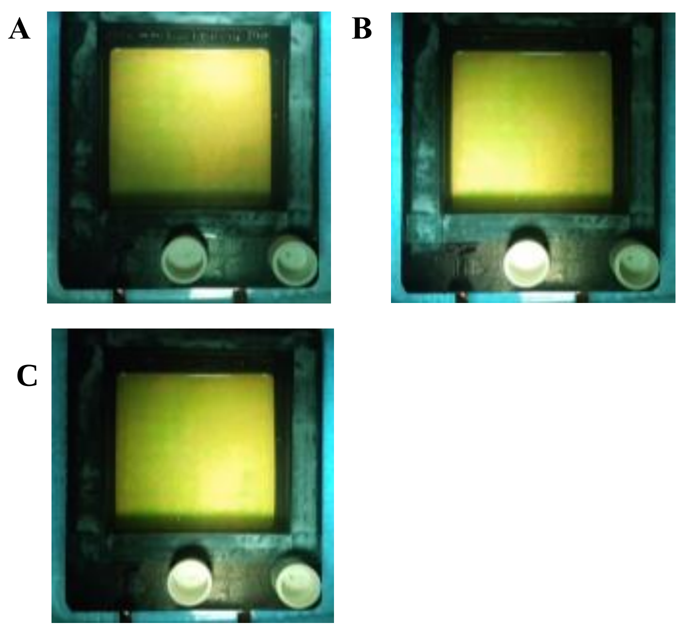

Figure 7. Images taken during electrolysis in 3D-printed holder. (A) Light on top-right corner of mesh. (B) Light on bottom-left corner of mesh. (C) Light on bottom-right corner of mesh.

Plate number	Setup Used	Concentration	Number of Spots Recorded	Value of Brightest Spots	Average Value of Spots
5	Salad dish	.05 M	14	288.0	179.2
7	Salad dish	.005 M	17	356.4	162.1
13	Salad dish	.01 M	19	154.6	125.2
17	3D holder	.01 M	21	536.8	201.3
19	3D holder	.01 M	26	433.9	218.8
20	3D holder	.01 M	27	788.6	215.4
21	3D holder	.01 M	21	393.3	171.8
22	3D holder	.01 M	39	409.6	206.8
22 (retested with different mesh placement)	3D holder	.01 M	51	658.1	382.9
24	3D holder	.01 M	46	613.7	274.5
25	3D holder	.01 M	27	339.3	211.4

Table 1. Results from plates that produced considerable amounts of oxygen. Spots were recorded based on how much oxygen they produced. Spots that did not have a brightness of at least 100, were not recorded.

3. RESULTS

3.1 Results from Different Concentrations. The spots with the .05 M concentration were almost completely black when they came out of the kiln (Figure 8A). Results processed through ImageJ showed that these spots had produced little oxygen as indicated through their dim spots (Figure 8B).

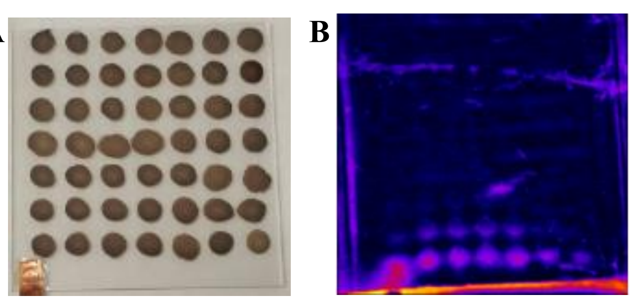

Figure 8. (A) Image of plate 5, which contained .05 M reference solution spots. (B) Result from .05 M concentration spots (Values of this plate (5) in Table 1).

The spots with the .005 M concentration were almost clear when they came out of the kiln (Figure 9A). Results collected through scans with this concentration were somewhat positive. Results from ImageJ showed that oxygen was being produced in the bottom rows of spots (Figure 9B).

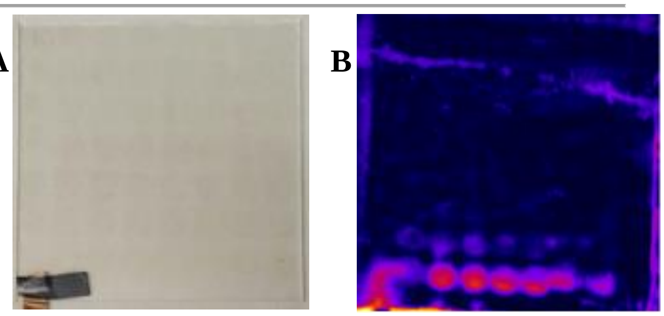

Figure 9. (A) Image of plate 7, which contained .005 M reference solution spots. (B) Result from .005 M concentration spots (Values of this plate (7) in Table 1).

The .01 M concentration looked the best out of all the spots that came out of the kiln (Figure 10A) The spots with this concentration produced the most oxygen. The brightness levels with these spots came out the highest (Figure 10B). All the concentrations were tested and the .01 M concentration ended up working the best out of all the concentrations. Since the .01 M concentration produced the best results from the three, this concentration was used for the majority of the tests.

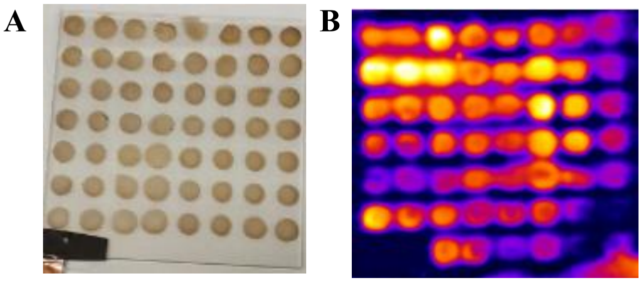

Figure 10. (A) Image of plate 22, which contained .01 M reference solution spots. (B) Result from .01 M concentration spots (Values of this plate (22 retested) in Table 1).

When these solutions were first made, they were almost a clear color with an ivory tint. As the days progressed, the solutions kept turning darker shades of orange (Figure 11). To test if there was any difference between older (made on July 7th) and newer (made on July 13th) solutions, plates with alternating columns of old and new .01 M solutions were tested. Although not many tests were run to confirm this notion, the older solution seemed to produce more oxygen than the newer solution (Figure 12).

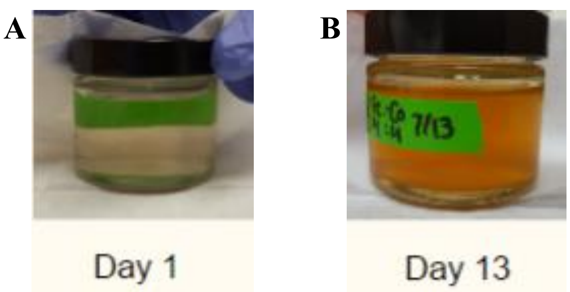

Figure 11. (A) Image of newer .01 M solution on its 1st day. (B) Image of newer .01 M solution on its 13th day.

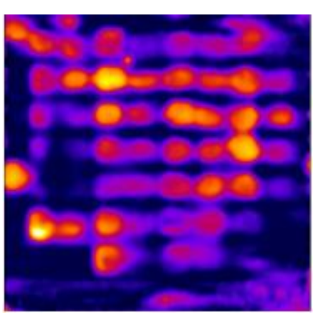

Figure 12. Older solution on 1st, 3rd, 5th, 7th columns. Newer solution on 2nd, 4th, 6th, 8th. (Values of this plate (24) on in Table 1)

Ozone cleaning the FTO plate with a template then drying the spots on a hot plate produced coffee rings on the spots after they came out of the kiln (Figure 13A). Ozone cleaning the FTO plate with a template then air drying the spots didn't produce any coffee rings on the spots (Figure 13B).

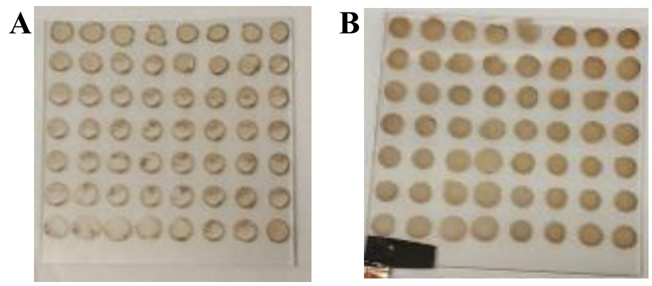

Figure 13. (A) Spots that were dried with the hot plate. (B) Spots that were air dried.

3.2 Results from Original Harpoon Kit. The best results collected with this setup only showed oxygen being produced in the bottom two or three rows at most (Table 1). This setup did not produce as positive results as the 3D-printed holder setup. This setup used approximately 300 ml of NaOH.

3.3 Results from 3D-Printed Holder. Results from this kit were more uniform; they showed that oxygen was being produced at almost all spots on the plate, not just the bottom rows (Figure 10B). The brightness levels, which quantify the amount of oxygen produced, increased by almost double when compared to the results from the original setup (Table 1). The mesh holder that was included with the setup, worked well in keeping the mesh held straight at all times. The mesh holder had the tendency to come loose, but it was easily fixed with electrical tape. Although the results from this setup came out significantly better, there was always a dull patch in most of the results. This setup used approximately 150 ml of NaOH, which is half the amount the original setup used.

3.4 Results from Different Light Sources. The UV-LED flashlight did the best job in illuminating the mesh. The adhesive LED light strips did not allow the spots on the mesh to be seen, even though oxygen was being produced (Figure 14A). The flashlight was used to illuminate the mesh right after electrolysis with the LED light strips, and the spots became visible (Figure 14B). The desk lamp with the black light bulb was too dim to illuminate the mesh.

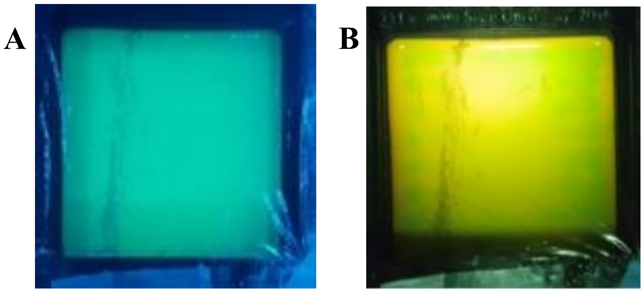

Figure 14. (A) Image of LED light strips being used during electrolysis. (B) Image of UV-LED flashlight being used right after electrolysis. Green spots are visible along the sides of the mesh.

4. DISCUSSION

4.1 Standard Solution. The .01 M concentration was chosen to test because it was thought to be a good intermediate between the .05 M and .005 M concentrations. Other intermediate concentrations have yet to be explored.

Although it was quite clear that the .01 M concentration solution produced the best results, the fact that it was tested mostly in the 3D-printed holder could have ruled in its favor. The other concentrations were tested mostly in the original setup. So the different lighting angles of each setup could have played a role in the quality of results.

It is still unknown why the standard solution darkened (solutions of all concentrations tested had darkened). Since the darkened solutions worked just as well, if not better than the lighter solutions at producing oxygen, not much concern was drawn to this phenomenon.

4.2 Why the Original Holder was Less Successful in Detecting Oxygen. The mesh of the original setup was only held down on three sides, which caused it to bend and cave in the middle. This could have led to inaccurate results since there was not an even distance between the plate and the mesh. The mesh is the most vital part of the kit, as it visually indicates oxygen production and suggest the effectiveness of the metal oxide combination at completing the OER.

The light was only shined in through the side of the box, so only the top and bottom sides of the mesh could be illuminated. Whereas the 3D-printed setup had light shining in from the top of the box, so all corner of the mesh could be illuminated, and therefore had more light distribution. The original holder was not tested with the lighting technique of the 3D-printed setup.

4.3 Important Role of Mesh. The mesh holder held the mesh on all 4 sides, which kept the mesh straight over the plate. The use of new mesh led to more uniform results among spots. The dull patch that was consistent in our results, could be because there was an uneven coat of paint on the mesh. Different mesh placements were tested by rotating the mesh. Although this speculation is inconclusive because only a few tests were run to see if this was true or not, results suggested that the mesh did play a part in causing dull patch (Figure 15). Since it is quite possible that the paint on the mesh could be uneven, it is highly recommended that different mesh placements are tested before any real scans occur. An uneven coat of paint could lead to inaccurate results.

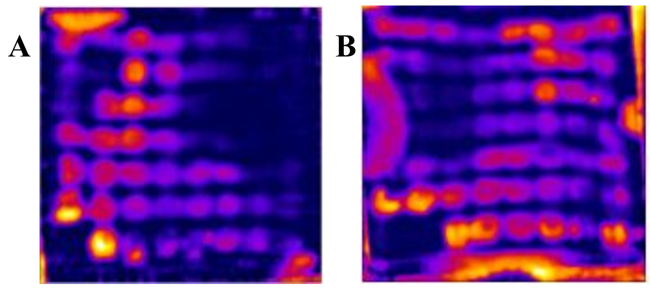

Figure 15. (A) Dull patch on top right corner (Values of this plate (21) in Table 1). (B) Mesh rotated 90° to the left and dull patch on top left corner (Values of this plate (22) in Table 1).

4.4 Why the UV-LED Flashlight Worked the Best. The LED light strips did not come with the UV black light setting necessary for illuminating the fluorescence in the mesh's paint. The wrong color was used to illuminate the mesh, in a way spots could not be seen. Not all lighting situations had been tested.

5. CONCLUSION

In an effort to maximize the potential of the HARPOON kit, different factors of the process were explored to see which ones would be best. The 3D-printed holder setup not only proved to be easier to work with but also proved to produce more accurate results. The .01 M concentration for the reference solution produced more oxygen than the recommended .005 M concentration. The combination of using the ozone cleaner and air drying the solution proved to produce the best quality spots for testing. Not all lighting situations have yet been tested, but as of the moment, the UV-LED flashlight prevailed. Hopefully future students who use the HARPOON kit can use these findings to optimize the quality of their results and find themselves making the most of their experience.

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Kiran Hamkins and Kemi Ashing-Giwa contributed equally to the creation of this work.

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ABBREVIATIONS

HARPOON, Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization; FTO, fluorine-doped tin oxide; UV, ultraviolet; LED, Light Emitting Diode

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