Improving HARPOON Kit Components for Oxygen Overpotential Reaction

Kemi Ashing-Giwa[†], Christina Sim[†], Kiran Hamkins[†]

[†] SEAL Summer Outreach Program, Beckman Institute, California Institute of Technology, Pasadena, California 91125, United States

Abstract: The focus of the experiments conducted throughout the duration of this project was on potential modifications to be made to the HARPOON (Heterogeneous Anodes Rapidly Perused for Oxygen Overpotential Neutralization) kit. A second target of investigation concerned the identification of an ideal molar concentration for the Ni-Fe-Co (2:4:4 ratio) standard solution. The HARPOON kit utilizes Earth-abundant metal oxides as catalysts for OER (Oxygen Evolution Reaction(s)) in order to cause water-splitting, potentially in a solar fuel generator.[1-3] In order to measure the ability of a metal oxide solution to catalyze water oxidation, current is applied to an FTO (fluorine-doped, tin oxide-coated) glass plate containing a sample. The HARPOON kit then quantifies the amount of oxygen evolution. Two models were utilized, the original version and a new 3D-printed prototype, while various molar concentrations ranging from 0.005 to 0.05 M, spotting techniques involving ozone treatment, and various lighting methods were tested on both kits. The results of the experiment made clear the advantages of the 3D-printed variant, and several prospective modifications to increase its positive attributes have been hypothesized.

1. INTRODUCTION

The severity of the negative effects of carbon emissions on the environment and the rapid depletion of fossil fuels has spurred the search for renewable clean energy resources. In high schools and colleges across the country, the HARPOON kit has been implemented as a powerful research tool. Utilizing the kit, students evaluate the viability of oxides containing earth-abundant metals as catalysts which could split water in a photoelectochemical cell (Scheme 1). Metal nitrate samples are drop casted onto an FTO-coated glass plate, and after being converted into oxides during annealing, the sample is submerged in an aqueous solution of NaOH. By testing samples under an applied potential, the HARPOON kit measures the amount of oxygen gas released from OER occurring at a specific location on the FTO plate via mesh painted with oxygen-sensitive fluorescent material.[5] The successful catalysts found while experimenting with the HARPOON kit could be implemented in future solar fuel generators to power water-splitting in which the separated hydrogen gas would be stored as a power source.[1,2]

In this study, the majority of the research that was conducted had the explicit intention of improving the HARPOON kit. Several complications arose during preliminary tests, most concerning the large quantity of NaOH necessary, the large, often cumbersome components, and the arrangement of the painted mesh. In order to address these complications and obtain viable solutions, tests were conducted on a 3D-printed kit. The compact, efficient structure of the new model eliminated many of the issues first encountered, and several further potential modifications were hypothesized in order to increase the kit's success. Additional research concerned the molar concentration of the Ni-Fe-Co standard (which contains nitrate variants of the metals in a respective ratio of 2:4:4). Traditionally, a solution with a concentration of 0.005 M is prepared; however, the results produced by using 0.005 M concentrations of the standard solution were limited. To improve results, higher concentrations (0.05 M and 0.01 M) of the standard solution were used.

2. EXPERIMENTAL PROCEDURES

2.1. Solutions

Deionized water was used to prepare the 25 mL aqueous solutions of nickel (II) nitrate hexahydrate ($N_2NiO_6 * 6H_2O$), cobalt (II) acetate tetrahydrate ($Co(C_2H_3O_2)_2 * 4H_2O$), and iron (III) nitrate nonahydrate ($Fe(NO_3)_3 * 9H_2O$), all of which possessed concentrations of 0.05 M. To create the suggested reference solution, 10 mL of Ni and 20 mL quantities of both Fe and Co were combined to produce 50 mL of solution in a respective 2:4:4 ratio. The second collection of solutions prepared consisted of $Ni(NO_3)_2$, $Fe(NO_3)_3$, and $Co(NO_3)_2$ with molar concentrations of 0.005 and in quantities identical to the first solutions. The molarities of both groups of solutions were deemed to be either too high or too low, and so a third set was made in order to find a more suitable range of molar concentrations. A molar concentration of 0.01 was selected, and both the variety of metal nitrates and the ratio was preserved as 2:4:4 for all of the standard solutions. When preparing the 0.1 M sodium hydroxide solution, 250 mL of deionized water was combined with 1 g of NaOH pellets.

2.2. Metal Oxide Samples

When preparing metal nitrate samples, a diamond-tipped scribe was used to engrave the plate number on the nonconductive side of a three inch by three inch square FTO plate. After the plate had been labelled, it was cleaned with both deionized water and isopropyl alcohol. The plate was then treated in an ozone cleaner for 10 minutes before the metal nitrate solution was applied. Using a 10 µl micropipette, the desired solution was then drop-casted onto the plate according to an LED spotting array, such that there were 54 aliquots pipetted onto each plate, with the last row left blank as a control. The plate was then annealed in a kiln for 6 hours at 500°C to convert the metal nitrate salts into mixed metal oxide material.
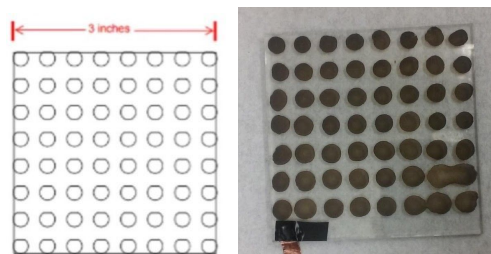

Figure 1. Aliquot Template and Completed Plate

## 2.3 Testing Via The HARPOON Kit

2.3.1. Original Kit

The original kit contained an acrylic holder in which an FTO plate containing a metal oxide sample was placed beneath a square of mesh coated with fluorescent paint.[1,5] The holder was then placed into a polyethylene dish. Copper tape, acting as an electrode, was attached to to the FTO plate with electrical tape. A graphite rod, the counter-electrode, was fastened at the edge of the dish.[1] A 300 mL solution of 0.1 M sodium hydroxide (NaOH) was then carefully poured over the holder, while ensuring that the mesh was entirely submerged. Nitrogen gas was used to purge the sodium hydroxide solution of oxygen. In order to guarantee that the system was thoroughly degassed, nitrogen was bubbled through the solution first for fifteen minutes in a glass bottle, then again for five minutes in the polyethylene container. To begin electrolysis, 5 mA of current were sent through the FTO plate via the electrodes, which were attached to leads from a constant-current power supply. An ultraviolet 395 nm flashlight was inserted into a slot in the side of the darkroom box constructed while a camera phone was placed on top of a yellow filter. Pictures were taken at regular 30 second intervals for

5-7 minutes with the flashlight oriented at different angles to provide a complete view of the mesh in the holder below. The collected pictures were then downloaded onto a computer and analyzed with ImageJ software.

A.
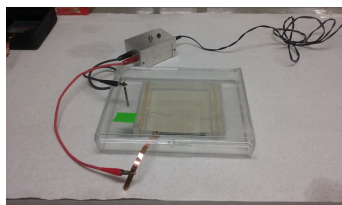
B.

Figure 2. (A) The entire assembly of the HARPOON kit, shown with flashlight positioned at the top of the darkroom box. (B) The original acrylic holder in the shallow dish with the graphite rod functioning as the counter-electrode.

2.3.2. 3D-printed Model

The new 3D-printed model was made of black ABS polyethylene to minimize the reflection of light, which could tamper with results obtained while testing. The graphite rod utilized in the original kit as a counter-electrode was replaced with a small FTO plate with copper tape attached. The oxygen-sensitive mesh was secured by two 3D printed components that slid together in order to ensure that the surface of the mesh was as even as possible. A cover with holes designed to fit 14/20 septa allowed for more efficient and secure purging, and a clear sheet of polyethylene made it possible to view the entire painted mesh during testing. Besides these modifications, the 3D-printed holder functioned almost identically to the original model, as depicted in Figure 3.

Figure 3. The assembled 3D-printed kit with the original polyethylene dish
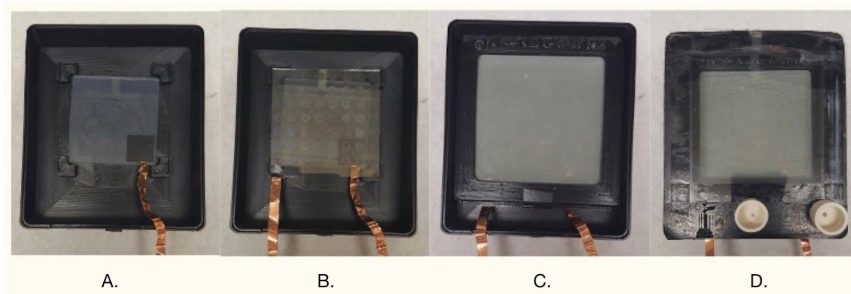

| A. | B. | C. | D. |

Figure 4. (A) The FTO plate serving as the counter-electrode. (B) The spotted and annealed sample plate. (C) The mesh painted with oxygen-sensitive fluorescent material. (D) The 3D printed cover with septa.

2.3.3. Modified Kit

A new darkroom box was made with the intention of further complementing the 3D-printed holder and an LED light strip was attached around the inside of the box to supplement the flashlight. While maintaining the placement of the yellow filter, the location of the flashlight slot was shifted to the top, rather than the side of the box. This alteration allowed light to be evenly distributed across the mesh by altering the angle of the flashlight during testing, as opposed to restricted to a single point over the holder. However, the angle of the light caused a significant portion of the mesh to be obstructed by shadow, and as a result, tests were not as successful as had been anticipated. A second alteration to the original kit was made; a blacklight lamp was procured and angled over an opening at the top of a new darkroom box. However, the light did not illuminate the inside of the box well, even when supplemented with the LED light strips. Therefore, the use of the these modified darkroom boxes was limited. An alteration that was implemented for the majority of the study was the replacement of the original dish by a deeper version that not only allowed for more efficient purging but also reduced the amount of sodium hydroxide that spattered onto the cover of the dish during degassing.

Figure 5. Darkroom box with blacklight lamp

3. RESULTS

3.1. Kit Modifications

In the darkroom box prototype with LEDs, no positive results were recorded in tests. However, when the light strip was utilized within the first 1-2 minutes of a test and then replaced with the UV flashlight, several plates proved to be successful. The holder in the 3D-printed model straightened the mesh so that results were more accurate, as the distance between the plate and the oxygen-sensitive material was equal for all spots. Further, the compact structure of the prototype allowed for more efficient purging, as the needle could reach all areas of sodium hydroxide. However, pockets of air were often trapped between the plate and the mesh during testing, often hampering results by obstructing large sections of the metal oxide spots on the sample plate.

3.2. Catalyst Adhesion To The FTO Plate

Although the photocorrosion that often occurs with the SEAL kit is avoided with the HARPOON model, metal oxide spots often dissolved, in varying amounts, into the sodium hydroxide solution. FTO plates that had been treated in the ozone cleaner exhibited less corrosion during testing, and results improved significantly, as the "coffee ring" effect was also eliminated. "Coffee rings" observed after annealing sample plates formed where the metal oxide was unequally deposited within the aliquots so that a greater concentration of solution was present near the periphery of a spot.

3.3. Variations In Molar Concentration

Standard solutions contained nickel (II), iron (III), and cobalt (II) nitrates in a 2:4:4 ratio and were made in increasing molar concentrations of 0.005, 0.01, and 0.05. The 0.05 M solution possessed too high of a concentration, while the 0.005 M, which was recommended by the HARPOON Experiment Procedure guide,[2] did not produce desired values when the images were processed using ImageJ software. Although the 0.005 M and 0.05 M solutions proved unsuccessful, the 0.01 M solution consistently yielded very positive results.

3.4. Alterations In Solution Coloration

Over a short period of time, the standard solutions darkened significantly, from a transparent, pale yellow to an opaque, dark orange. This alteration was hypothesized to be caused by contamination, and although extra measures were taken when preparing new solutions, color changes were still observed. However, this change was not necessarily negative, as results improved greatly as the solutions darkened (Table 1 and Figure 8). The brightness values of the last plates tested were almost twice as high as those of the ones spotted even a few days prior. To document this change, images of the most recently produced Ni-Fe-Co standard were taken daily.
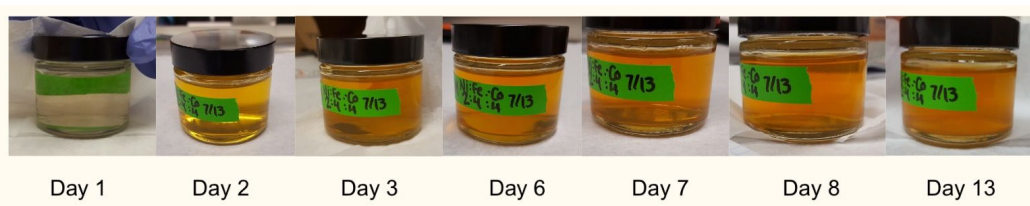

Figure 6. Solution Coloration Changes Over Time

3.5. Significant Plates

Plate Number	Average Brightness Value (approximate)	Day (since new 0.01 M solution was prepared)	Details*
13	122.1	0	Third plate made with the new 0.01 M solution, did not undergo ozone treatment.
14	147.3	1	The spots with the highest brightness values were located around the edges of the plate.
17	197.1	5	Most areas of water-splitting were within the bottom two rows of the sample plate.
19	218.8	7	Made with the old 0.01 M solution on the left side and the new 0.01 M solution on the right; the older solution seemed to perform better.
20	220.6	8	The highest spot possessed a brightness value of 788.6.
22 (Figure 7)	387.7	12	Alternating rows of new and old 0.01 M standard solutions, results were from a retest in which the mesh was rotated 90°.

*All plates were air-dried, underwent ozone treatment, and were prepared with only the new solution unless otherwise noted.

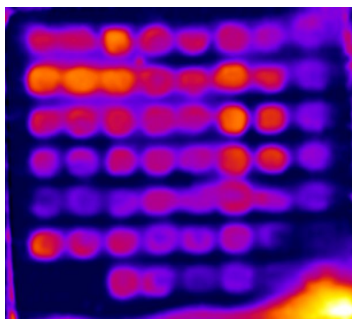**Table 1.** Average Brightness Value and Day of Plate Preparation

Figure 7. Final processed image of plate 22, which contained the new and old 0.01 M standard solutions. The spots were made after the use of the ozone cleaner, and this picture was taken after the kilning process.
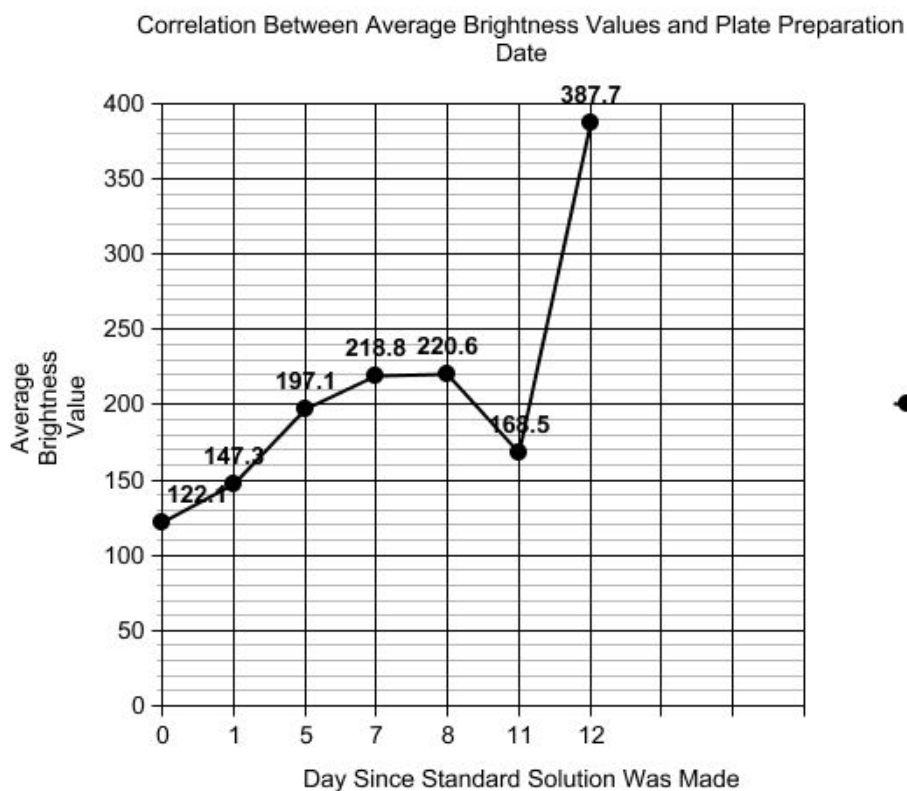

Figure 8. Correlation between brightness values and plate preparation date

4. Discussion

4.1. Original kit and holder

After first testing several plates with the original holder and kit, several points of potential modifications were identified. The kit itself was quite large, and a significant amount of sodium hydroxide was needed in order to submerge the holder in its entirety. The shallow, wide dish used in the original kit made purging and disposal of the sodium hydroxide a challenge. Degassing the sodium hydroxide was difficult, as solution often splattered onto the topmost inner surface of the container. In addition, the oxygen-sensitive mesh often grew concave during tests. Both issues often contributed to interference with data when processed with ImageJ. In order to purge all of the sodium hydroxide completely, a flexible, extended needle was bent at various angles to reach all areas of the dish.

Overall, very positive results were obtained from the use of the original kit. The arrangement of the clear acrylic holder was such that the entire sample plate was visible during testing, and no pockets of air were trapped between the mesh and the plate, an issue which later proved to yield negative results on samples tested with other kits.

4.2. New 3D-printed holder

The alterations to the first kit apparent in the design of the 3D-printed prototype addressed many of the points of modification found with the original. The newer kit was much more compact, such that approximately half of the sodium hydroxide needed to completely submerge the oxygen-sensitive mesh in the first kit was needed in this variant (150 mL in comparison to slightly over 300 mL). Further, the straightened mesh allowed for not only significantly more accurate, but consistently positive results. However, on several occasions, pockets of air were caught between the oxygen-sensitive mesh and the plate, leading to erroneous results and potentially disguised data that could easily be misinterpreted. In addition, a shadow cast over the mesh from the holder often obstructed several metal oxide spots from view.

Prospective alterations to the holder might include slanted walls and an enlarged window in the cover to avoid impeding shadows. A further possible change could be an added distance between the mesh and the holder walls so that it would be less likely for pockets of air from purging to be forced above the sample plate. The most positive results obtained were done so through this kit.

4.3. Solutions

Plates spotted with aqueous metal nitrate solutions with a concentration of 0.01 M generated the highest results. Two 0.01 M Ni-Fe-Co standard solutions possessing a 2:4:4 ratio between the respective metals were prepared at different times (on July 7th and on July 13th); several sample plates were tested in order to determine a definitive higher-performing mixture. The most recent results suggested that the older solution was favored. However, as that particular solution had had more time to darken (a strongly positive correlation was identified

between the darkness of the solution and the success of the plates made with it), it is possible that the disparity in results was not truly as great as it appeared to be. Conversely, the plate with the highest results was made entirely of the new solution, although human error may be held accountable for this discrepancy.

5. Conclusions and Future Work

Highly positive results can be obtained through the use of the Ni-Fe-Co standard (in a 2:4:4 ratio) by utilizing a 0.01 M solution of nitrates and annealing the sample plate for 6 hours at a temperature of 500°C. Purging via nitrogen gas should be for 15 minutes in a silicon dioxide jar and then for 5 minutes in the polyethylene dish. Light from an ultraviolet 395 nm flashlight should be cast over the holder during testing; shining the flashlight directly on the oxygen-sensitive mesh should be avoided. Future studies could work towards discovering the cause of color alteration in the standard solution over time, involve the testing of various metal oxides and nitrates, and the investigation of catalyst adhesion to the FTO plate.

Author Information
Correspondence
kemigiwa@gmail.com

Stoichiometry of Solutions
0.05 M

- 25 mL, 0.363 g of nickel (II) nitrate hexahydrate ($N_2NiO_6 * 6H_2O$)
- 20 mL, 0.249 g of cobalt (II) acetate tetrahydrate ($Co(C_2H_3O_2)_2 * 4H_2O$)
- 20 mL, 0.404 g of iron (III) nitrate nonahydrate ($Fe(NO_3)_3 * 9H_2O$)

0.005 M, 10 mL

- 0.015 g of nickel (II) nitrate hexahydrate ($N_2NiO_6 * 6H_2O$)
- 0.015 g of cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 * 6H_2O$)
- 0.020 g of iron (III) nitrate nonahydrate ($Fe(NO_3)_3 * 9H_2O$)

0.01 M, 25 mL

- 0.073 g of nickel (II) nitrate hexahydrate ($N_2NiO_6 * 6H_2O$)
- 0.073 g of cobalt (II) nitrate ($Co(NO_3)_2 * 6H_2O$)
- 0.101 g of iron (III) nitrate ($Fe(NO_3)_3 * 9H_2O$)

Abbreviations
HARPOON, Heterogeneous Anodes Rapidly Perused
for Oxygen Overpotential Neutralization; FTO,
fluorine-doped, tin oxide-coated glass; OER, oxygen
evolution reaction.

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