GNG5140 - Engineering Design

Finalized Report

Submitted by

[3D Electroprinter]

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Abstract

The investigations from the previous report have led to a minimal viable prototype (MVP) that can perform simple movements with an attached electroplating system and potentiostat. There are several issues, among which are; Gcode modification, Integration of Systems, and lack of validation testing, that still need to be performed. That being said, there are several future recommendations given through the research of the team, and these can work as a basis for future projects. The future teams must look into the modification of the Gcode to be more consistent with the stepping of the motor, as well as properly integrating the printer UI and potentiostat UI. Lastly a current density profile must be acquired to show validation of a working model, though any further validation will require extensive modification of the Gcode through a 3rd software.

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List of Acronyms

Acronym	Definition
FDM	Fused Deposition Modeling
HBT	Hydrogen Bubble Templating
SLA	Stereolithography
PLA	Polylactic Acid
UI	User Interface
MOBO	Motherboard
DAC	Digital to Analog Convertor
CVC	Current to Voltage Convertor

1 Introduction

While there are few changes made to the design as of the writing of the previous report there are a few things to touch on as capstones to the project. It's important to note that the project itself is in an ever changing state due to the nature of this project. There are several smaller changes, chiefly to the anode holder, Gcode, and potentiostat design that can be covered, as well as some scalability concerns that can not be addressed in the current iteration. Most importantly this report will serve as a basis for future projects, due to the extensive future works that can be done on this project. While the design goal of this project was met, and a 3D Printer that can move through an electroplating solution was produced, there is still quite a bit of testing and modification to be done. This will be spoken of more in further sections, but the two systems that were cut, pumping and heating, will be important to include. Not only cut systems, but also testing and validation that has not yet been completed, as well as quality control measures (such as more consistent cathode holders) will need to be introduced for any reasonable testing to be confirmed. All of these future recommendations, as well as the current state of the prototype show that this project has a journey ahead of it.

2 Revised Global Solution and Final System Concept

The largest component of this project is a Crealty Ender 3 3D printer that has the anode and cathode of the electrochemical system mounted on the print head and print plate, respectively. No filament is fed to the printer but at this stage the machinery responsible for conventional FDM 3D printing has not been removed. The electrochemical prints are interpreted by the printer as a conventional print with a single layer, and through following those printing instructions it moves the anode over the cathode to create the desired shape.

The electrochemical reactions taking place in this system are regulated with an Aruduino-based potentiostat that is an extensively simplified and modified version of an open source design published in 2016 [1]. The PWM signal from an arduino is smoothed to a true analog signal using a 2 microfarad capacitor, and fed to an op-amp capable of supplying over 140 mA. This op-amp output is wired to the anode of the electroplating system. The opposite electrode, the cathode, is wired to a simple current to voltage converter (CVC) that measures the voltage across a grounded 10 ohm resistor. Another op-amp relays this voltage (proportional to the current through the cell) to the analog input of the arduino. A schematic of the potentiostat circuitry and images of the assembled design are shown in figure 1.

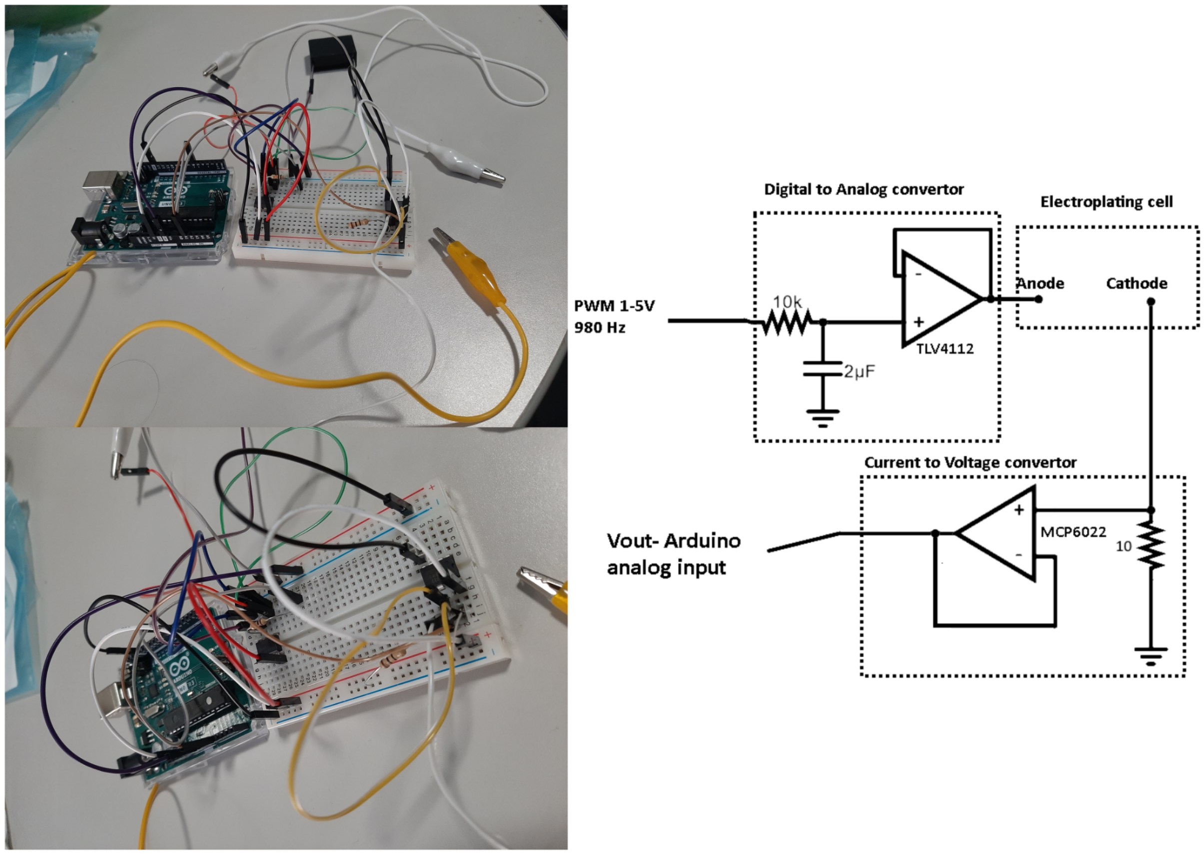

Figure 1: photographs and schematic of potentiostat

The coding, or “Sketch” run on the arduino uses a simple incremental search algorithm to change the voltage until a desired current (currently, the target current must be set calculated manually by the user from desired current density) is achieved. Since the required voltage to achieve a target current fluctuates over time (due to anode movement and varying occlusion of its surface by bubbles) a fast algorithm like the bisection method cannot be used due to it relaying on continually narrowing bounds. This code is shown in appendix 1.

The cathode is a flat copper plate that lies in the plating basin, attached to the system through a stripped wire duct-taped onto one corner. This tape is waterproofed with candle wax. It lies flat on the bottom of a glass dish that serves as the electrochemical bath. At the current prototyping stage only relatively inert baking soda solution is used in the bath, with electrolysis of it serving to test the printer's electrochemical systems.

The anode is a long needle adapted from one intended for clearing 3D printer extruders. It is mounted in a plastic holder screwed to the printer's hot end, and is positioned a vertical distance of about 4 mm above the cathode. The hot end has been stripped of its casing and fans as they are not needed, but the filament extruder has not been removed in order to avoid the printer's software thinking an error has occurred.

Due to lack of software experience in the team, there is currently no integration between printer and potentiostat software/UI. The arduino sketch controlling the potentiostat must be manually activated through an attached computer with the Arduino IDE installed when printing begins. The IDE's serial monitor serves as the potentiostat's information output to the user, as shown in figure 2

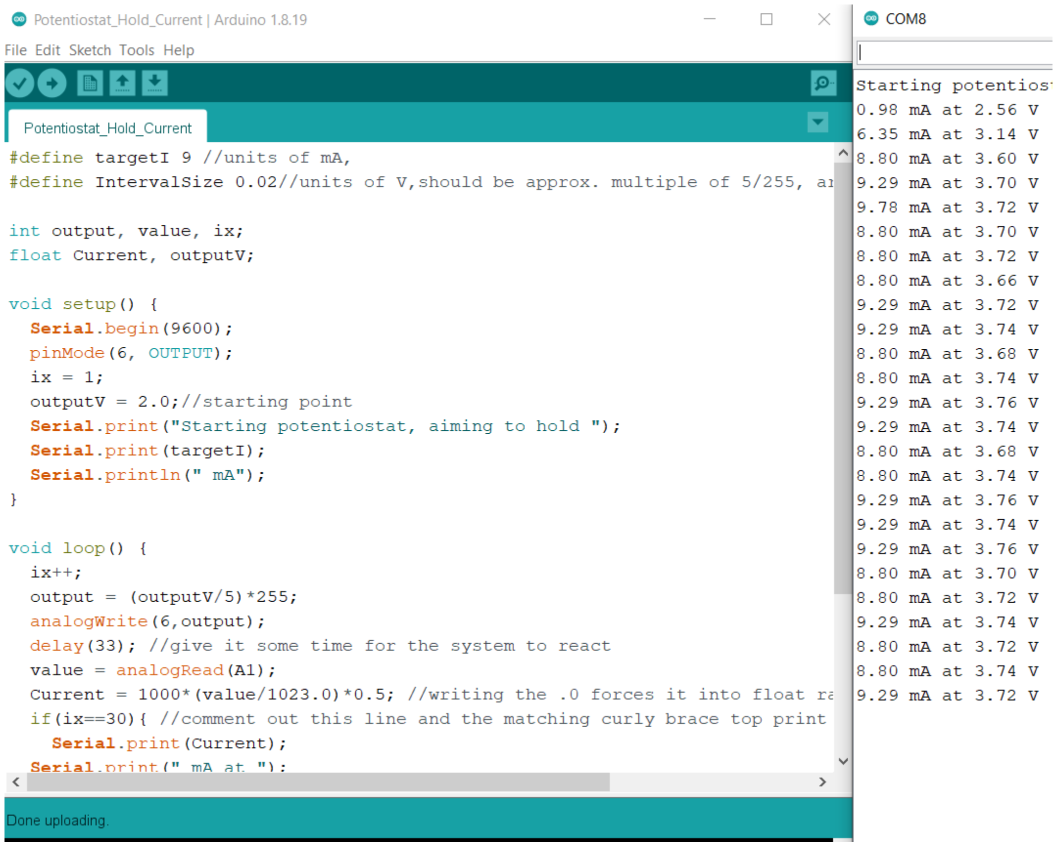

Figure 2: Arduino IDE, serving as potentiostat UI

Beyond the work done on the electrochemical side of things, there is also the movement system which is from a heavily modified version of an Ender 3, with the hot-end shroud, filament removed, and the Gcode heavily modified. The brunt of the work to utilize this movement will be covered in the remaining section under the Gcode modification, as this is where a majority of the work was done to modify the printer.

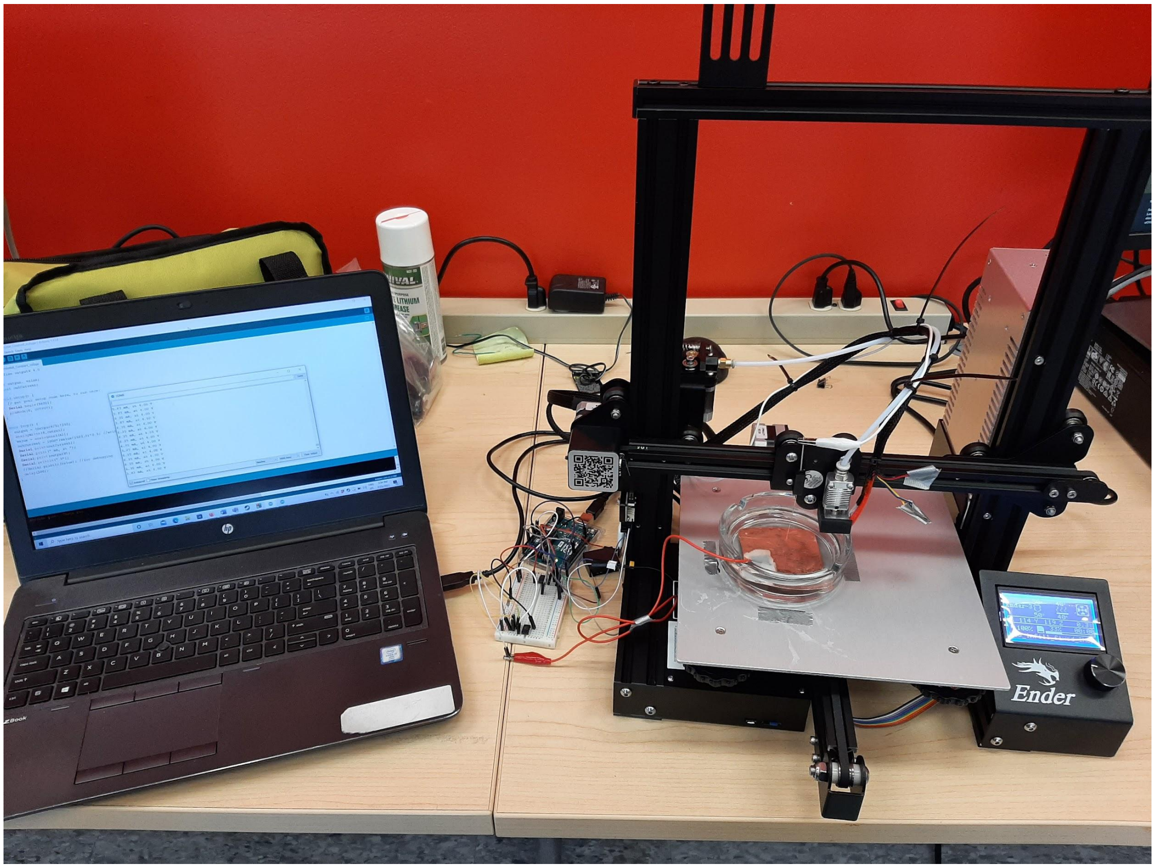

Figure 3: Final Prototype Picture

Lastly, the bill of materials that this project has used has also been kept up to date, with one new purchase since our last report, specifically Kapton Tape which will be utilized after the end of this project to do further testing. This testing will be used as a stepping stone in further reports to show viability of the product.

Item #	Name	System	Price	Shipping	Tax	Lead Time	Received ?
1	Creality Ender 3D Printer	Movement	$ 329.99			1 week	Y
2	Arduino Uno R3	potentiostat	$31.48	$8.00	$4.74	3 days	Y
3	op amp TLV4110IP	potentiostat	$3.85			3 days	Y
4	op-amp MCP6022-E/P	potentiostat	$2.51			3 days	Y
5	Cables w/alligator clips	potentiostat	$3.44			3 days	Y
6	2 uF capacitor	potentiostat	$2.73			3 days	Y
7	breadboard	potentiostat	$7.33			3 days	Y
8	1Ω resistor	potentiostat	$0.15			3 days	Y
9	10kΩ resistor	potentiostat	$0.14			3 days	Y
10	1kΩ resistor	potentiostat	$0.14			3 days	Y
11	9kΩ resistor	potentiostat	$0.14			3 days	Y
12	20Ω resistor for testing	potentiostat	$0.14			3 days	Y
13	jumper cables x10	potentiostat	$4.13			3 days	Y
14	jumper cables x30	potentiostat	$3.44	$8.00	$3.66	3 days	Y
15	op amp 2-circuit TLV4112IP	potentiostat	$8.21	$8.00	$0.86	3 days	Y
16	1 Roll of Kapton Tape	Testing	$3.30		$2.71	1 week	N

Table 1: BOM of Final Prototype

3 Sustainability, Scalability, and Quality

Currently only baking soda solution is used, but the long-term goal is to use this device for plating nickel and other metals. As a project that involves solutions of heavy metals, this project has inherent sustainability concerns. Spillage of nickel plating solution would be hazardous so in the future more work will need to be done on containment, and it will be heavily recommended that the printer be operated in some sort of secondary containment to minimize risks. On the flip side, one of the intended uses for the 3D electroplating printer is to allow Hydrogen Bubble Templating of nickel electrodes. These can be used to electrolyze water at substantially lower overpotentials than standard electrodes [2]. This is important for any move towards using hydrogen as a storage medium, which would greatly expand the practicality of intermittent sources of renewable energy. Aside from that, as with normal 3D printers this project would provide a new method of rapid prototyping and small-scale local manufacturing, which would promote economic growth and innovation in areas too underdeveloped to host larger industrial metal plating facilities.

Scalability-wise a few things could be improved. Using a purpose-built chassis rather than modifying an existing 3D printer model would have substantial up-front costs but would streamline mass production as it would remove the need to afterwards modify each units with the changes needed to incorporate the plating system. The potentiostat could be made as a one-piece printed circuit board, which requires advanced equipment but would simplify the manufacturing process. It would also increase reliability by avoiding the issues with unstable contacts that often plague breadboard projects.

As a project this 3D electroplating printer is in an extremely early stage of technological development and the current prototype is not close to being suitable for mass production. Consequently application of strategies for optimizing production like Kaizen or 6 Sigma are largely premature. However with the context of Six Sigma one prominent failure mode was identified: Multiple times during testing the cathode lead wire came un-taped from the cathode, indicating the current combination of duct tape and wax is not a durable solution. A more enduring sealant is needed.

4 Prototype Modifications

4.1 Counter-electrode Holder

The need to attach the anode to the printer pushed us to design the holder that can easily be fixed to the printer Figure 4. The main role of this is to hold the anode at a desired position as it undergoes the plating process. This part was 3D printed using an Ender 5 printer. 3D technology offers services relatively affordable compared to other technologies that we would have used to get this part done. This design is limited to the current cross-section of the anode being used; any change of the anode's diameter may result in change of the holder. Also, in presence of volatile chemicals such as electroplating solution, this attachment may weaken with time. There is a need to take into consideration the variation of the anode's section in the next design and replace this part with a corrosion resistant material.

Figure 4: Counter electrode Holder

4.2 Gcode and Slicer

The backbone of the testing protocol was in the Gcode, which has not been modified heavily from previous versions, but new discoveries have been made about it. First and foremost the Gcode itself has been correctly stopping, waiting, and moving in the way that is expected and has kept a consistent distance from the cathode at all times. What has changed from the writing of the previous report is the removal of the fans, and as such, the removal of the Gcode that controls the fans, as they are now set to permanently be off. This is a hot-fix and should not be intended as a permanent fix, as they are still likely drawing power from the power supply, but they are just shorted. It has also come to the team's attention that there is a limitation in the slicer that was not found previously, there is a minimum time for the printing of a Gcode file, which means that if the slicer determines that not enough time will pass for a print to go through it will show an error and not render any slicing, even if the step distance is short enough to account for it. The issue seems to be hard-wired into the Slicing software (Ultimaker), and as thus if an STL were fed into another slicing program this may be able to be circumvented.

4.3 Wiring

The anode and cathode are connected to the potentiostat by alligator clip leads. Currently, the potentiostat's arduino and breadboard simply sit next to the printer chassis without being directly attached. The cathode lead is partly bundled together to reduce its effective length but is otherwise allowed to lie loose over the printer bed. The anode lead requires more careful management to remove the risk of it becoming caught in the printer's moving parts. To ensure this the anode wire was run along the existing bundle of cables linking the hot end to the body of the printer, secured in place using zip ties. A close-up of the way the anode wire is attached is shown in figure 5.

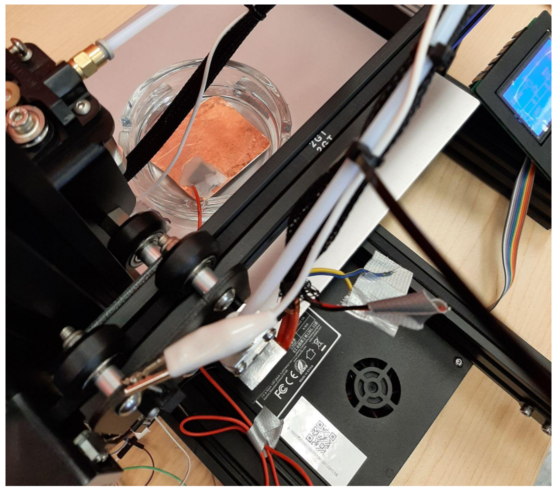

figure 5: Anode wire management

5 Future Plans

5.1 Electroplating

An unfortunate discovery in the late stage of testing was that the electric field spreads out greatly. Consequently the cathode reaction is spread out over a large area (>1 cm^2) of the cathode rather than being localized to the area directly below the anode. This is a problem because 1) it means the desired current densities cannot be achieved without very high current and 2) it prevents printing with any real precision. This is believed to occur because current flows to the solution through the entire anode surface rather than just the tip. This could be solved by insulating the sides of the anode. Figure 6 sums up the problem and the proposed solution. The choice of insulating material will be important as it must be compatible with the electroplating solution in the future.

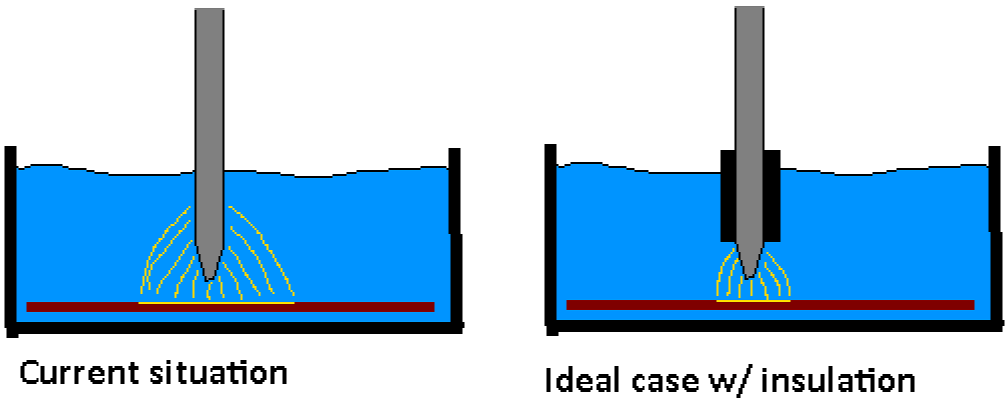

Figure 6: Anode insulation issues: Overly wide electric field spread in current prototype (left) and proposed solution (right).

Another task will be finding a more permanent and durable approach to securing the writing on the cathode. The current approach of duct tape and candle wax sealant can break off relatively easily, and even when not breaking off often sees the contact between wires and cathode degrade over time. The most important task that a future team must undertake is implementing actual electroplating, as thus far the team was only able to prototype with baking soda electrolysis. This entails at minimum filling the basin with a solution of nickel chloride and using it to plate nickel on the cathode. A further goal is also adding ammonium chloride to the solution to facilitate the Hydrogen Bubble Templating procedure and allow highly hydrophilic surfaces to be created on the cathode [2]. As electroplating would use hazardous ammonium and heavy metal chlorides rather than relatively harmless sodium bicarbonate, the safety and environmental concerns are much greater. This requires that such experiments be carried out in a wet lab with facilities to handle aqueous waste, so obtaining access to such space will be essential.

5.2 Movement Testing

The majority of changes needed in the movement section can be summed up through the use of the Gcode. Currently there is a lot of hand-modification of Gcode to add stops in, and while this is manageable on the square test strips that have been printed thus far, it could become unwieldy very quickly in complex designs. Additionally, it has shown that the printer only does movement commands and each point is not rastered individually. To alleviate this, additional points could be added through linear interpolation between the two endpoints given by the Gcode. This would require the Gcode file to be run through a Matlab program that does several things; First it would need to add additional points between the start and end point until the (X_1-X_2) point would be equal to 0.06 mm (but not less), next it would need to add M0 Sx where x is equal to the amount of seconds that it would need to plate the given area, and then afterwards it would need to add a stop command at the beginning and end of the code to add time to add and remove the plating component. This code could be done in C or MatLab but the team has not started this as of yet, though it is in the future plans. Additionally there needs to be an integration between the movement system and potentiostat to read the distance between the cathode and anode as a differential of voltage and then move the Z-axis to accommodate any issues with leveling. This would move into the need for an integrated system of both software but this is far outside the skillsets of the current team.

5.3 Heating

The current heating system used is not sufficient to aid the plating process. Only the resistive heater of the Ender 3 is utilized, this gives no control over the temperature being generated by the heater. The transport of ions in the electrolyte is much better when heated and maintained at the desired temperature. This speeds up the plating process speed and improves the quality of the plating. To increase the efficiency of the plating, it would be better to consider in the future the implementation of a heating system that would take into consideration the generative electrolyte solution heating and control the temperature of the plating bath.

5.4 Pumping

No pumping system is being used for this prototype. This makes the disposal of the circulating fluid a bit harder and uncontrollable and reduces the efficiency of the plating process. A pumping system should be looked at in the future for its advantages to the process, this system should be able to provide a regular and clean flow of electrolyte solution into the plating process. Before disposing the electrolyte residue to the environment, the pumping system must wash out the substrate and ensure that the used electrolyte is safe to be disposed of to the environment; in preference it should be subjected to the recycling process, this will reduce the cost of the electrolyte. Implementing the heating and pumping systems will increase the efficiency of the electroplating process and provide a preheated electrolyte solution to be put into the system to maintain a constant bath temperature.

6 Conclusions

This project has delivered on the promise of an electrode that can move through a plating solution, and to stop at given points. There are certainly shortcomings that need to be addressed such as;

- Inconsistent Z-axis level, due to machine screw flex, this leads to inconsistent current between the anode and cathode due to variable distance. This can be alleviated through a capping mechanism on the top of the screw which would keep it from flexing at the top of the printer.
- Insufficient stopping points in Gcode which would lead to inconsistent plating time over the surface. This can be alleviated through the introduction of linear interpolation using a 3rd program, though this would cause increased tracing in a project and would add an additional language that the user would have to be aware of.
- Heating and Pumping solutions have not been found; These two systems were cut early into the project's lifecycle and future projects would have to look at ways to integrate them into the system. To assure scalability and environmental sustainability it is crucial to look into the pump and heating system solutions.
- Prototype Anode Holder (non-adjustable). While the current anode holder can be slotted in at a fixed distance, it makes it very difficult to modify the overall Z-axis without moving the entire print head. Furthermore the anode holder does not include insulation for the anode, and as previously discussed this leads to a larger plating area and poor current density.

- Lack of validation testing, which due to the Z-axis inconsistency is hard to procure. Currently the current density profile has not been completed, but this is to be completed before any further reports are given on the subject. This hinges on the improvement of the Gcode through a third party program to ensure proper movement by the printer.
- Poor wire connection with the cathode; the current solution of taping stripped wire down and sealing it with was has proven unreliable. This arrangement has limited effectiveness proofing the tape against the solution, and often sees the wires come loose from the anode. A more durable solution is needed, likely some sort of epoxy. Whatever is used will need to be compatible with a basic environment.

Overall these shortcomings can lead into further projects under this design, as these are all actionable problems. Further teams will have to focus specifically on the Z-axis level, Gcode, Integration of the systems, as well as the testing that needs to be done. With these problems being addressed then the heating and pumping systems can then be solved. Additionally a quick fix to the anode holder would be adding a proper plastic sheath that can be 3D ABS printed, though it requires an acetone vapor bath which the team does not have access to. Overall, the project met the expected deliverables, but there is still much more work to be done to get this to a viable point.

7 Bibliography

[1] Meloni, Gabriel N. “Building a Microcontroller Based Potentiostat: A Inexpensive and Versatile Platform for Teaching Electrochemistry and Instrumentation.” Journal of Chemical Education, vol. 93, no. 7, 26 Apr. 2016, pp. 1320–1322, 10.1021/acs.jchemed.5b00961.

[2] Hao, M., et al. “Hydrogen Bubble Templating of Fractal Ni Catalysts for Water Oxidation in Alkaline Media.” ACS Applied Energy Materials, vol. 2, no. 8, 30 July 2019, pp. 5734–5743, 10.1021/acsaem.9b00860

APPENDICES

1. Arduino code

Primary potentiostat code: Potentiostat_Hold_Current.ino

```
#define targetI 30 //units of mA,
#define IntervalSize 0.02//units of V,should be approx. multiple
of 5/255 ~0.02

int output, value, ix;
float Current, outputV;

void setup() {
  Serial.begin(9600);
  pinMode(6, OUTPUT);
  ix = 1;
  outputV = 2.0;//starting point
  Serial.print("Starting potentiostat, aiming to hold ");
  Serial.print(targetI);
  Serial.println(" mA");
}

void loop() {
  ix++;
  output = (outputV/5)*255;
  analogWrite(6,output);
  delay(33); //give it some time for the system to react
  value = analogRead(A1);
  Current = 1000*(value/1023.0)*0.5; //writing the .0 forces it
into float rather than integer division
  if(ix==30){ //comment out this line and the matchin curly
brace top print every loop
     Serial.print(Current);
  Serial.print(" mA at ");
  Serial.print(outputV);
  Serial.println(" V");
  ix = 1;//only print every 30 delays = ~every 1000 ms
   }
```

```
  if((Current<targetI)&&(outputV+IntervalSize<5.0))//will not
increase if doing so would exceed 5V
     outputV = outputV+IntervalSize;
  if((Current>targetI)&&(outputV-IntervalSize>0))//will not
decrement if that would go below zero
     outputV = outputV-IntervalSize; //not likely but better
safe than sorry

}
```

<u>Current stability investigation</u>: potentiostat_Constant_voltage.ino

```
#define outputV 3.5 //set to whatever you want from 0 to 5

int output, value;
float outCurrent;

void setup() {
  // put your setup code here, to run once:
  Serial.begin(9600);
  pinMode(6, OUTPUT);
}

void loop() {
  output = (outputV/5)*255;
  analogWrite(6,output);
  value = analogRead(A1);
  outCurrent = 1000*(value/1023.0)*0.5; //writing the .0 forces
it into float rather than integer division
  Serial.print(outCurrent);
  Serial.print(" mA, at ");
  Serial.print(outputV);
  Serial.println(" V");
  //Serial.println(value); //for debugging
  delay(500);
}
```

<u>Polarization Curve Generation</u>: Potentiostat_generate_polarization_curve.ino

```
#define outputPin 6

float volts, outCurrent;
int output, input;
void setup() {
  // put your setup code here, to run once:
  Serial.begin(9600);
```

```
  pinMode(outputPin, OUTPUT);
  Serial.println("potential(V);current(A)");
}

void loop() {
  // put your main code here, to run repeatedly:
  for(volts = 0; volts <5; volts=volts+0.1)
     {output = (volts/5)*255;
     analogWrite(outputPin,output);
     delay(100);
     input = analogRead(A1);
     outCurrent =(input/1023.0)*0.5; //writing the .0 forces it
into float rather than integer division
     Serial.print(volts);
     Serial.print(";"); //allows printout to be pasted into a
separate file and interpreted as semicolon-separated by Excel
     Serial.println(outCurrent,5); //print to 5 decimal places
     }
     //repeat in reverse, to get 2nd data point for each
voltage, get idea of variance (or hysterisis, god forbid)
     for(volts = 5.0; volts >0; volts=volts-0.1)
     {output = (volts/5)*255;
     analogWrite(outputPin,output);
     delay(100);
     input = analogRead(A1);
     outCurrent =(input/1023.0)*0.5; //writing the .0 forces it
into float rather than integer division
     Serial.print(volts);
     Serial.print(";");
     Serial.println(outCurrent,5); //print to 5 decimal places
     }
     Serial.println("end");
     delay(50000); //gives time to stop and unplug
}
```

Gcode

M190 S40.000000

M109 S50.000000

```
;Sliced at: Fri 25-03-2022 15:37:19
;Basic settings: Layer height: 0.06 Walls: 1.2 Fill: 100
;Print time: 1 minutes
;Filament used: 0.003m 0.0g
;Filament cost: None
;M190 S40 ;Uncomment to add your own bed temperature line
;M109 S50 ;Uncomment to add your own temperature line
G21        ;metric values
G90        ;absolute positioning
M82        ;set extruder to absolute mode
M107       ;start with the fan off
G28 X0 Y0  ;move X/Y to min endstops
G28 Z0     ;move Z to min endstops
G1 Z15.0 F6000 ;move the platform down 15mm
G92 E0                ;zero the extruded length
G1 F200 E3            ;extrude 3mm of feed stock
G92 E0                ;zero the extruded length again
G1 F6000
;Put printing message on LCD screen
M117 Printing...


;Layer count: 1
```

;LAYER:0

G1 F4800 E-6.00000

G0 F6000 X108.500 Y108.500 Z50.00 ;Additional Raising Gives Time to Set Up Electroplating

M0 Click to continue ;Only Click after Electroplating has been set up.

G0 F6000 X108.500 Y108.500 Z0.300

;TYPE:WALL-INNER

G1 F4800 E0.00000

G1 F60 X111.500 Y108.500 E0.14967

M0 [S5]

G1 X111.500 Y111.500 E0.29934

M0 [S5]

G1 X108.500 Y111.500 E0.44901

M0 [S5]

G1 X108.500 Y108.500 E0.59868

M0 [S5]

G0 F6000 X108.100 Y108.100

G1 F60 X111.900 Y108.100 E0.78827

M0 [S5]

G1 X111.900 Y111.900 E0.97785

M0 [S5]

G1 X108.100 Y111.900 E1.16743

```
M0 [S5]
G1 X108.100 Y108.100 E1.35701
M0 [S5]
G0 F6000 X107.700 Y107.700
;TYPE:WALL-OUTER
G1 F60 X112.300 Y107.700 E1.58651
M0 [S5]
G1 X112.300 Y112.300 E1.81600
M0 [S5]
G1 X107.700 Y112.300 E2.04550
M0 [S5]
G1 X107.700 Y107.700 E2.27499
M0 [S5]
G0 F6000 X108.000 Y107.910
G0 X108.639 Y108.922
;TYPE:SKIN
G1 F60 X111.076 Y111.359 E2.44694
M0 [S5]
G0 F6000 X111.359 Y111.076
G1 F60 X108.922 Y108.639 E2.61888
M0 [S5]
G0 F6000 X109.488 Y108.639
```

```
G1 F60 X111.359 Y110.510 E2.75089

M0 [S5]

G0 F6000 X111.359 Y109.945

G1 F60 X110.054 Y108.639 E2.84300

M0 [S5]

G0 F6000 X110.619 Y108.639

G1 F60 X111.359 Y109.379 E2.89521

M0 [S5]

G0 F6000 X111.359 Y108.813

G1 F60 X111.185 Y108.639 E2.90749

M0 [S5]

G0 F6000 X108.639 Y109.488

G1 F60 X110.510 Y111.359 E3.03950

M0 [S5]

G0 F6000 X109.945 Y111.359

G1 F60 X108.639 Y110.054 E3.13161

M0 [S5]

G0 F6000 X108.639 Y110.619

G1 F60 X109.379 Y111.359 E3.18382

M0 [S5]

G0 F6000 X108.813 Y111.359

G1 F60 X108.639 Y111.185 E3.19609
```

M0 [S5]

M107

G1 F4800 E-2.80391

G0 F6000 X108.639 Y111.185 Z5.270

;End GCode

M104 S0 ;extruder heater off

M140 S0 ;heated bed heater off (if you have it)

G91 ;relative positioning

G1 E-1 F300 ;retract the filament a bit before lifting the nozzle, to release some of the pressure

G1 Z+50 E-5 X-20 Y-20 F6000 ;move Z up a bit and retract filament even more

M0 Click to continue ;Remove Specimen During this time

G28 X0 Y0 ;move X/Y to min endstops, so the head is out of the way

M84 ;steppers off

G90 ;absolute positioning

M81