DESIGN OF USER-FRIENDLY ELECTRODES FOR REAL-TIME COATING CONDITION MONITORING

Submitted by:

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On my honor as a University student, I have neither given nor received unauthorized aid on this assignment as defined by the Honor Guidelines for Thesis-Related Assignments.

ADVISOR

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Design of User-Friendly Electrodes for Real-Time Coating Condition Monitoring

EXECUTIVE SUMMARY

The KARV capstone team tested multiple electrode designs in order to determine which one was most suitable for real-time analysis of corrosion protection coatings on aircrafts. This project, which was sponsored by Luna Labs, aimed to select a material and shape for an electrode that was user-friendly and compatible with three-electrode electrochemical impedance spectroscopy (EIS). The team performed EIS on brass, copper, nickel, and stainless steel to assess their corrosion resistance and measured the wettability of these materials to ensure that repeated analysis using the electrodes would remain consistent over time. Two different use cases were tested and two electrode shapes for each case were evaluated. For the general surface case, Bar and Band-Aid designs were assessed, and for the fastener case, Lunar and Scythe designs were tested. EIS was performed using the manufactured electrodes which were placed on panels that simulated the body of an aircraft.

EIS testing of the raw materials proved that nickel was the most corrosion resistant. Stainless was shown to be the most wettable as received, while nickel was the most consistent in its wettability. The team was able to produce electrodes using all of the materials except for stainless steel, which was incompatible with the manufacturing process. During panel testing, the nickel electrodes that were of the Band-Aid design worked the best for defect detection on the flat surface of the panel, while both nickel electrode designs for testing around fasteners, Lunar and Scythe, worked equally well. However due to increased ease of manufacturing, the nickel Scythe design was ultimately recommended.

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INTRODUCTION

Aluminum and steel are commonly used structural materials for several applications, but one problem that must always be accounted for is corrosion. Corrosion impacts the performance, safety, and cost of any equipment or system that uses metals. As a specific example, each year approximately 25% of the US Air Force’s yearly maintenance budget goes towards research and prevention of corrosion (GAO, 2003). To improve vehicle lifespans, many vehicles such as the HH-60W Combat Rescue Helicopter (CRH) are coated with corrosion-resistant paint. These corrosion-resistant coatings are usually made up of three layers: an external barrier, an inhibitor layer, and a third sacrificial layer. Each layer works to keep the base metal away from the corrosive agent, and any small defect in the coating could lead to corrosion damage, which means that they must be regularly inspected. However, testing the health of such coatings has only ever been done destructively, meaning that the coating cannot be used after it is tested. Coatings are also only tested for potential damage over regular intervals, meaning that some damage could be detected late. Furthermore, many current coatings use chromium as a corrosion inhibitor. However, this material is highly carcinogenic. Different coatings are being explored with the goal of maximizing material performance without compromising operator health. Our capstone group aimed to aid the construction of a real-time, non-destructive procedure to test coating integrity. If this technology continues to develop, it could facilitate the transition away from chromium coatings without compromising safety, as well as improve the corrosion damage assessment process.

PROBLEM STATEMENT

In order to improve this testing technology, new electrode designs are needed for improved coating testing. The electrodes would be attached to the outside of the CRH on any general surface panel or around fasteners, as these are hotbeds for corrosion damage. The electrodes placed around fasteners would be circular in order to detect defects around the fastener heads, while the general surface electrodes would be relatively rectangular in shape. The electrodes must withstand harsh environments, potentially over long periods of time, and give reliable data even after significant saltwater exposure. This makes corrosion resistance and material wettability important factors. Electrode durability is also necessary to assess so the electrodes can survive any accidental impacts during use as well as resist any unnecessary deformations during application. Furthermore, important aspects of this project are the assessment of manufacturability and user experience. Manufacturability is relevant since these electrodes are meant to be mass produced for general use, so the manufacturing process must be simple and quick. User experience is of importance to make sure that any untrained individual would be able to easily learn how to apply the electrodes and run the necessary tests. User experience also comes into play by making sure that these electrodes are easy to use, ensuring that they are not too fragile when handled. These requirements, as well as cost and availability, influenced the materials chosen and the final geometries that were explored.

RESEARCH

The objective of this research was to find the optimal material and shapes for electrodes used for electrochemical impedance spectroscopy (EIS) on a coated aluminum panel. After considering the previously discussed design constraints, four candidate materials were selected and tested: nickel, copper, brass, and stainless steel. Two geometries were designed for each use case. For the fastener, the designs were called Lunar and Scythe, and for the panels, they were called Bar and Band-Aid.

MATERIAL SELECTION

The materials were assessed for their properties, cost, and availability. To find corrosion-resistant materials, ANSYS Granta was used to generate a preliminary list of materials. This software provided not only corrosion properties but also yield strengths and hardness values which informed our durability evaluation. Next, the KARV team determined what materials were available from the distributor McMaster-Carr in an 0.001 inch thickness. Some materials such as gold and titanium were eliminated due to high cost and/or lack of availability. Due to these factors, the four materials selected were 110 copper, 316 stainless steel, 260 brass, and 200 nickel. These four materials provided a range of costs, durabilities, and corrosion resistances which are listed in Table I.

Table I. Material properties of the four selected materials.

Material	**Yield Strength (MPa)**	**Hardness**	**Cost (USD/in^2)**
110 Copper	50	42 HV	8.91
316 Stainless Steel	205	88 HRB	8.51
260 Brass	110	63 HV	19.48
200 Nickel	80	42 HRB	2.62

ELECTRODE GEOMETRY

As previously discussed, different electrode shapes were considered to see how, or if, the geometry affected testing procedure and results. Different shapes were also needed for testing different areas that could potentially be affected by corrosion damage: a general flat surface and the area around a fastener head. The KARV team, in collaboration with Luna Labs, designed four shapes in total, two for the general surface case and two for the fastener head case. The general surface designs were named Bar and Band-Aid, shown in Figure 1, and the fastener head designs were named Lunar and Scythe, shown in Figure 2 (note that the fastener head is also displayed in the figure to show electrode placement). The Bar and Lunar designs were previously conceived by Luna Labs, and previous testing had been done with these. The Band-Aid and Scythe designs were designed with reference to the Bar and Lunar, and they were created in an attempt to decrease the amount of material used per electrode and to make the manufacturing process easier. The Band-Aid is the same length as the Bar (38.00 mm), but has curved edges instead of sharp corners. The Scythe design was made by moving the curved parts of the Lunar design such that there was one continuous side instead of two. Once designed, the areas and perimeters of each pair of electrodes was calculated, as shown in Table II. The goal was to minimize perimeter and area used. Minimizing area decreased material used and cost of manufacturing, and minimizing perimeter means that theoretically it will be faster to manufacture for the Silhouette cutter due to a shorter path. As the results show, the Band-Aid has a smaller area and perimeter than the Bar, and the Scythe has a slightly smaller area but a larger perimeter. Though the Scythe has a larger perimeter, the team suspected that it would actually be easier for the Silhouette cutter to cut the Scythe design than the Lunar design because of the path the Silhouette cutter takes during its cutting process. It must be stated that though one design has a smaller area than another, the differences are on the order of square millimeters. These are not major changes overall, but it is still beneficial to use less material if possible.

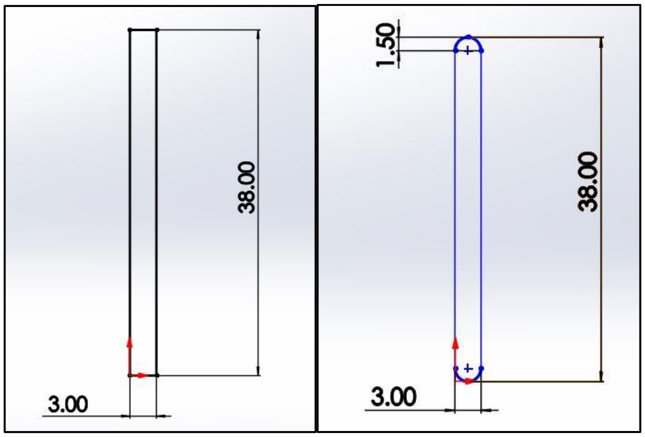

Figure 1. Electrode schematics for Bar (left) and Band-Aid (right) designs.

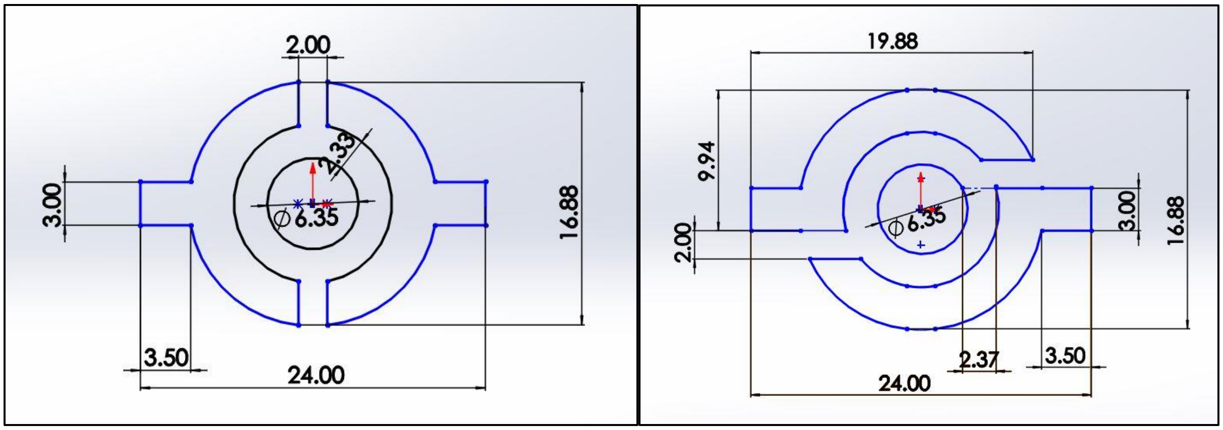

Figure 2. Electrode schematics for Lunar (left) and Scythe (right) designs.

Table II. Electrode design dimensions.

Design	Area (mm^2) for pair	Perimeter (mm) for pair
Bar	228.00	164.00
Band-Aid	224.14	158.86
Lunar	144.68	106.60
Scythe	143.33	107.39

RESULTS AND DISCUSSION

RAW MATERIAL TESTING

To assess the corrosion resistance of the four materials selected for testing, the KARV team performed three-electrode electrochemical impedance spectroscopy (EIS) on the metals as they were received from McMaster-Carr. The team performed each measurement in a beaker as shown in Figure 3, with an Ag/AgCl reference electrode, platinum mesh counter electrode, and a 1 cm^2 sample of the chosen material as the working electrode. The electrodes were connected to a BioLogic potentiostat and placed in 0.6M NaCl solution. Every sample was subject to a 30 minute open circuit voltage (OCV) measurement to ensure that the cell was at a steady state followed by an EIS measurement over a frequency range of 100 kHz to 10 mHz. The BioLogic EC-Lab software automatically plotted the impedance data onto Nyquist and Bode plots, which are shown for nickel in Figure 4. The charge transfer resistance of each material was estimated by calculating the difference between the impedance value measured at 10 mHz and the impedance measured at 100 kHz. Table III displays these values, and since the nickel sample provided the highest charge transfer resistance it was determined to be the most corrosion resistant.

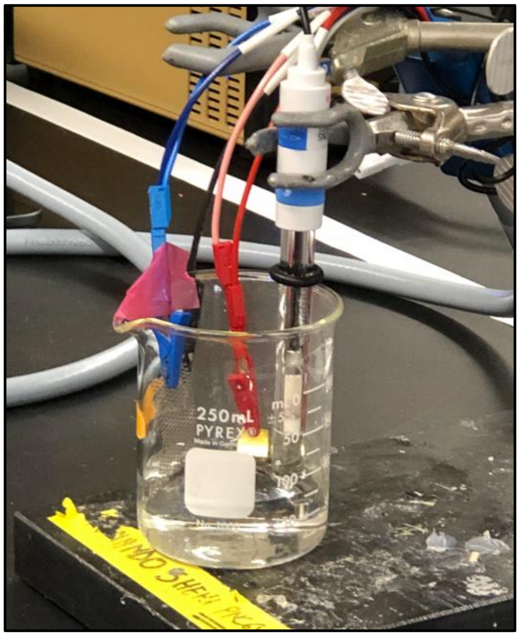

Figure 3. Electrode EIS setup (brass sample shown).

Table III. Estimated current transfer resistance values.	
Material	**Estimated R_{ct} (Ω-cm^2)**
Copper	4.94×10^3
Stainless Steel	3.34×10^5
Brass	1.27×10^3
Nickel	6.01×10^5

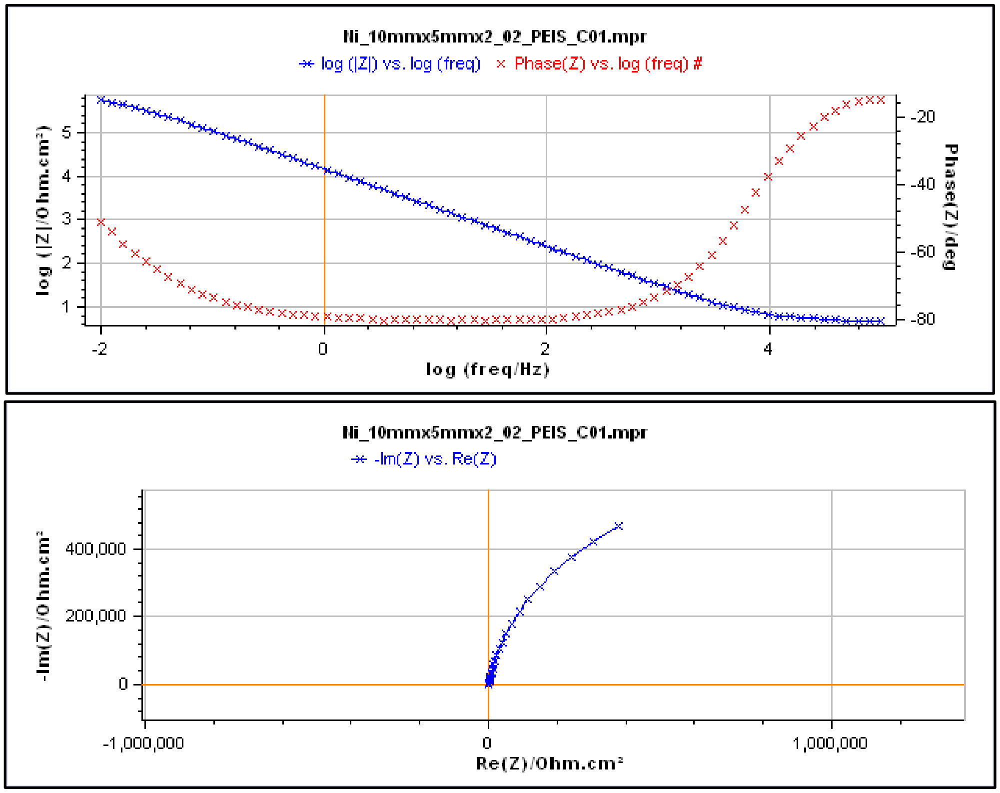

Figure 4. Bode impedance (top) and Nyquist impedance (bottom) plots for nickel.

ELECTRODE PRODUCTION

To make the electrodes, the sheets of material were first cut into large rectangular shapes and covered in 3M 467MP adhesive tape on one side. These sheets were then placed and centered in a Silhouette Cameo cutter, a commercial desktop cutting machine, with the desired electrode geometry to be cut out loaded via a .dxf file. The Silhouette cutter then cut out the imported designs, and would sometimes cut straight through both the sheet and the adhesive or just the metal sheet. If the adhesive was not cut through, the excess metal sheet was peeled off to leave only the desired electrode material on the adhesive backing. Once the electrode shapes were cut out, wires were then soldered onto one side with lead solder, and then marine sealant was applied to the electrode to cover the exposed wire and the solder. Results of the manufacturing process used are shown in Figure 5.

The process detailed above was implemented for all materials chosen, but there were significant difficulties when attempting to manufacture stainless steel electrodes. The main issue encountered was when the team tried to use the Silhouette cutter on the steel sheets. The blade was not able to cut completely through the material and adhesive, and after cutting for a few seconds the blade was severely damaged to the point where it was functionally unusable. Attempts were made to increase the blade length and blade force, but no progress was made and so no steel electrodes were produced this way. Since the Bar and Band-Aid designs were relatively simple, an attempt was made to manufacture these designs by simply cutting them out from the steel sheets using scissors. It was soon discovered that the lead solder being used for the other materials was not compatible with steel, as it was not forming a usable bond with the material. In a final attempt to make steel electrodes, the wires were attached via copper tape, with the idea that this would be strong enough to hold the electrode together and then be marine sealed. It was then discovered that the bond between the steel and adhesive was not very strong, and during the application of copper tape all of the steel electrodes fell off of their adhesive backings. In the end, no panel testing was conducted with steel electrodes. Technical outreach was performed with various departments at the University of Virginia in order to find a new processing method for steel, but a solution was not identified due a lack of available time, the material being too thin, or the electrode design being too small and detailed.

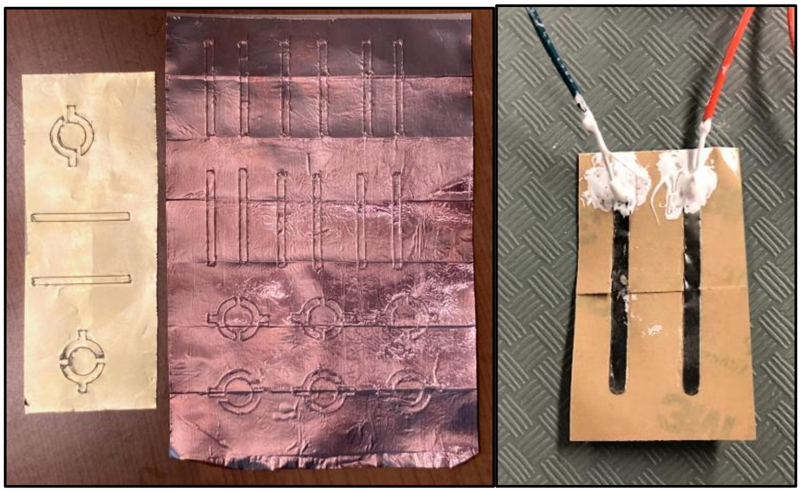

Figure 5. Examples of results of cutting process (left) and finished electrodes (right).

PANEL TESTING

In order to determine the defect detection ability of each shape and material combination, the electrodes were tested on panels that simulated the surface of an aircraft. These panels, which were created and provided by Luna Labs, were Al 7075 sheets with two fasteners riveted into them. The panels and fasteners were then coated in a trichrome surface pretreatment, an epoxy primer containing a non-chrome corrosion inhibitor, and a polyurethane topcoat. Lastly, one fastener on each panel was covered in a protective sealant. Two examples of finished panels are shown in Figure 6.

Figure 6. Panels for electrode testing.

To perform a panel test, one electrode pair would be placed on a panel such that the electrodes were 2 mm apart from each other. For the Bar and Band-Aid designs the electrodes were placed parallel, and for the Lunar and Scythe designs the electrodes were placed around a fastener such that each electrode was also 2 mm away from it. For each geometry and material combination, a test was performed with and without a defect. Defects were added to a panel by scratching a line through the coating 2 mm away from one Bar or Band-Aid electrode, or by testing the Lunar or Scythe electrodes around a fastener that was not covered in sealant. A paint test cell was secured over the electrodes and the defect if one was present. The electrodes were then connected to a Gamry potentiostat for a three-electrode EIS test, with the panel as the working electrode, one electrode as the reference electrode, and the other as the counter electrode. When performing defect testing with a Bar or Band-Aid shaped electrode, the electrode that was closest to the defect was set as the reference. A 0.6 M NaCl solution was poured into the cell, and an EIS test was performed over a frequency range of 100 kHz to 0.2 Hz. The panel testing configurations for the general surface electrodes and the fastener electrodes are displayed in Figure 7. Bode plots were generated from the data collected and these were used to do further analysis (example plots shown in Figures 8 and 9).

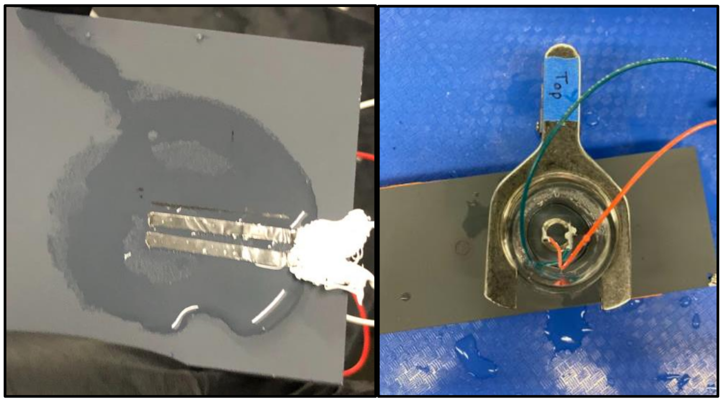

Figure 7. Panel testing electrode attachment (left) and full test setup (right).

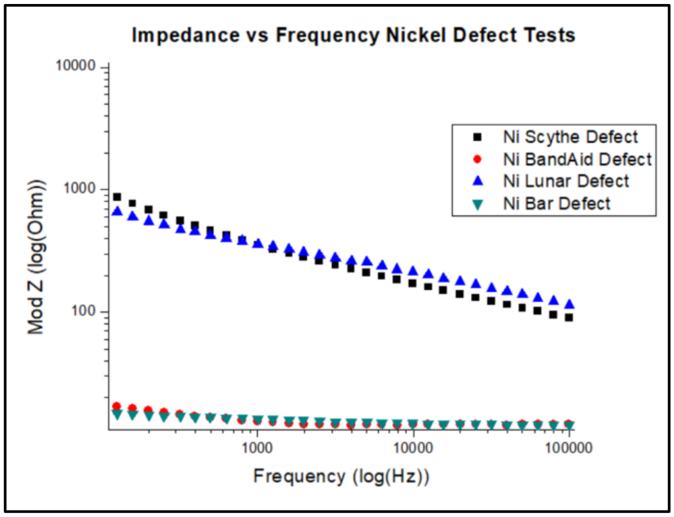

Figure 8. Bode plots for nickel defect tests.

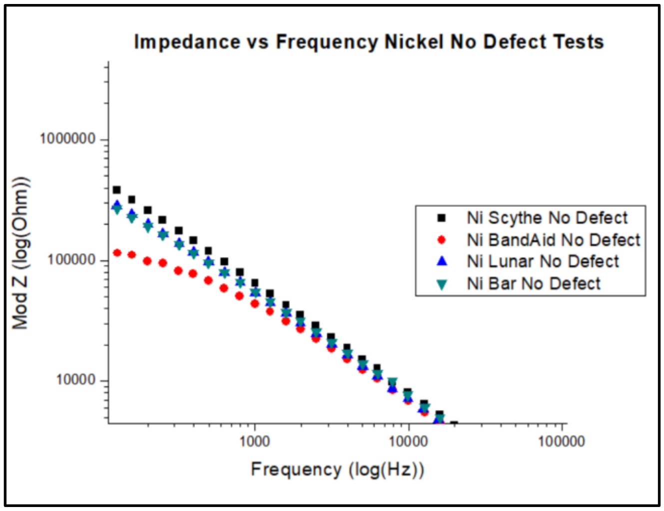

Figure 9. Bode Plots for nickel non-defect tests.

Analysis of the panel testing was performed by calculating ratios between the impedance measured during a defect test and the impedance measured during a non-defect test for each shape and material combination. These ratios were calculated at two frequencies, the coating conducting frequency of 10 Hz and the solution frequency of 25 kHz. A higher ratio indicated that the electrode was more sensitive to a defect, indicating superior performance. The data grouped by geometry at each frequency is shown below in Figure 10.

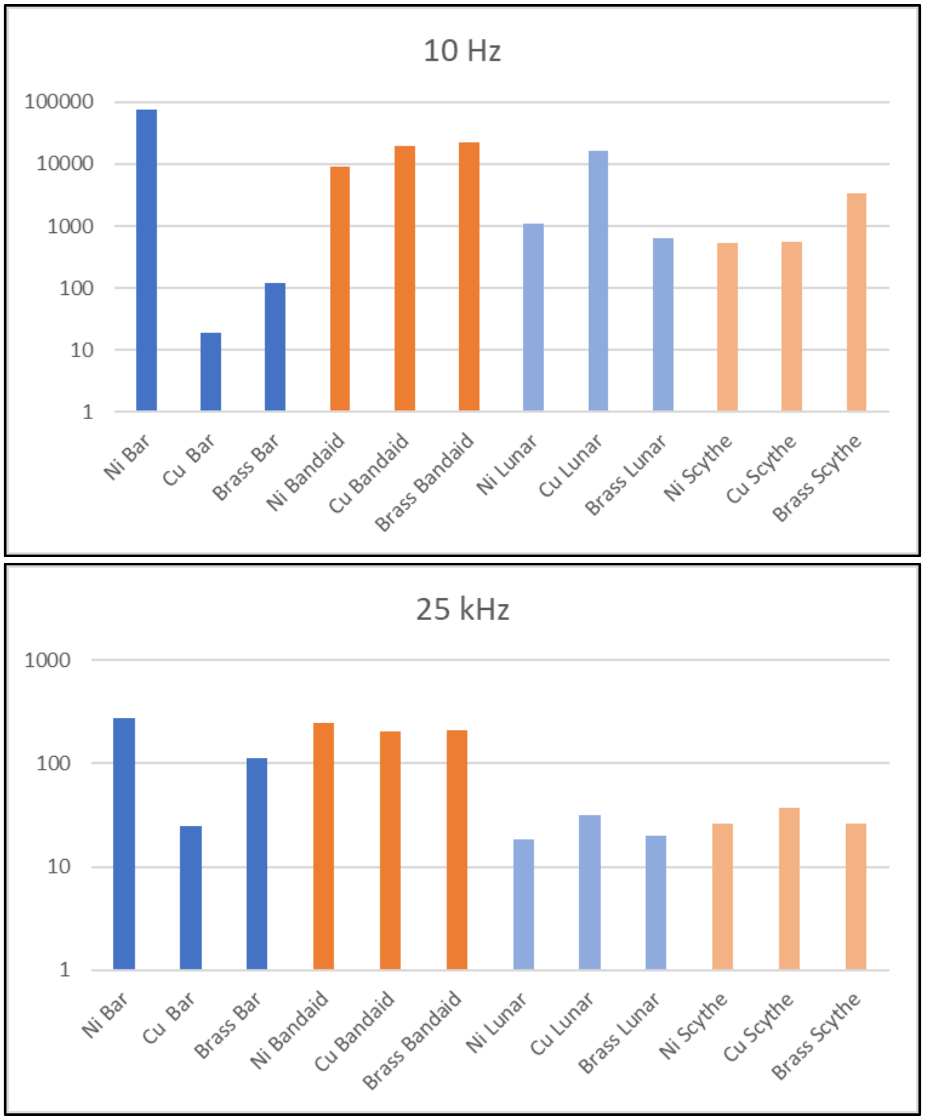

Figure 10. Impedance ratios sorted by geometries, separated frequencies 10 Hz (top) and 25kHz (bottom).

Nickel performed consistently well across geometries and frequencies. Copper also performed quite well, with ratios comparable to nickel in all but the Bar category, which may be an outlier. Interestingly, both the brass and copper Bar performed worse than their Band-Aid counterparts, while the opposite was true for nickel. However, given that nickel has the most advantageous material properties this data supports the assertion that manufacturing defects or damage around the edges of panel electrodes would not affect results significantly. Within the fastener category, the Lunar and Scythe designs performed similarly both within material and geometries comparisons, with copper slightly outperforming the other materials in the Lunar category. It is of note that some of the Bar and Band-Aid defect tests experienced bubbling within the paint cell during testing, and so values given in our analysis may not be exact.

However, overall behavior should not have been affected; this bubbling was attributed to improper sealing of the wires and solder or oxide layer formation, but results were still comparable to expected performance.

WETTABILITY TESTING

As stated above, wettability is an important aspect to take into account for tests such as EIS. Data inaccuracies could be caused by the material rejecting or interacting negatively with the electrolyte. In this case, ensuring that the salt water spread well on the electrode surface was necessary. Change in wettability over time was also relevant to determine the accuracy of an electrode over multiple tests. To analyze wettability, a small square of each material was cut out and then taped onto a flat surface. A micropipette was utilized to place a 6 microliter droplet of salt water onto the surface of the material. An iPhone camera with an attached 20X magnification lens was then used to take a picture of the droplet on the material. To study wettability changes, square pieces of each material were submerged in salt water for two different immersion times, one for 5 minutes and another for 2 days and 16 hours. The same droplet and picture process was done for these samples. An ImageJ Contact Angle plugin was then used to analyze the images taken and calculate the contact angle. The software required the user to define the interface between the droplet and the surface, and then place five points along the curvature of the droplet to allow the software to do the calculation. Figure 11 shows the experimental setup and example of a droplet image. The results of the contact angle measurements for all experiments are shown in Table IV. The percent change shown in both columns are referring to the change from the dry material contact angle.

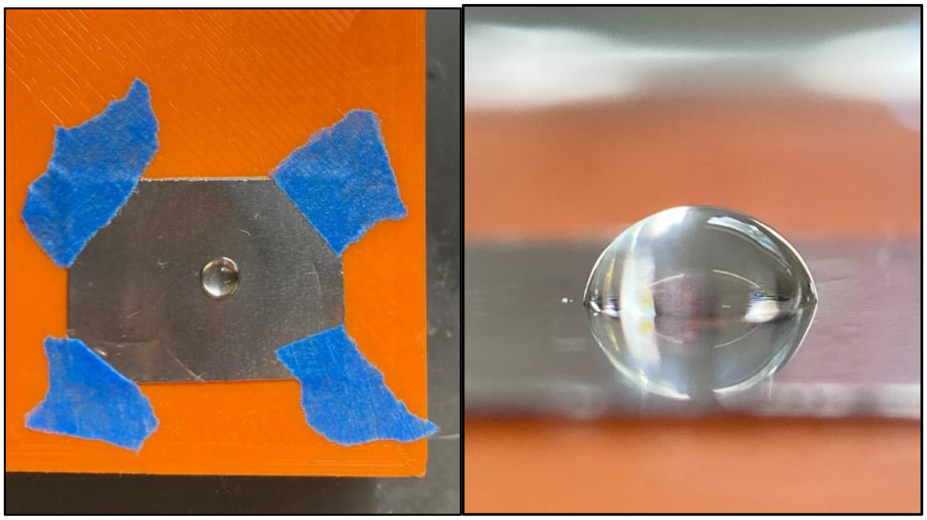

Figure 11. Wettability testing, setup (left) and droplet example on steel (right).

Table IV. Contact angle results.

	Dry	5 minutes	2 days 16 hours
Material	**Original Contact Angle**	**Contact Angle % Change**	**Contact Angle % Change**
Copper	96.70	-4.73	-35.95
Brass	89.25	6.86	-60.07
Nickel	87.10	2.84	-1.15
Stainless Steel	79.83	7.08	9.91

As seen in the results, copper had the highest original contact angle, and therefore worst wettability, and stainless steel had the lowest original contact angle, and therefore the best wettability. This result was interesting as it suggested that stainless steel would have been an effective electrode material if it were manufacturable using the chosen process, but the later tests would prove otherwise. After being submerged in salt water for 5 minutes, all materials had slight increases in contact angle except copper, which decreased. This means that in this short amount of time, the wettability decreased in three of the four materials, which was not a good sign for longer term testing. The final set, which was submerged for a couple of days, yielded even greater differences in contact angles. Copper and brass had drastically decreased contact angles, and during the tests the drops spread across the surfaces. Stainless steel, though it was incredibly promising in the beginning, continued to have an incremental contact angle. The most interesting result of all was the nickel contact angles. It had a reasonable contact angle originally which increased slightly over five minutes and then decreased slightly over the weekend immersion. This implies that the nickel wettability overall does not change significantly over multiple days, which would help nickel electrodes give consistent measurements for longer periods of time than the other three materials. In terms of only wettability effects, nickel would be the best material to use according to these results. It would be worth exploring the wettability changes over even longer periods of time, to see if there exists a lifetime for nickel in this application.

CONCLUSIONS

This project was conducted in order to gain a deeper understanding into what material and geometry would be best for use as EIS electrodes on different areas susceptible to corrosion. Research was first done on cost and availability of possible materials. Once these materials were purchased, EIS was performed on samples of nickel, brass, copper, and stainless steel to determine their resistance to corrosion in salt water, in order to mimic their eventual real world application. Electrodes were then manufactured with these materials from earlier LunaLabs designs and new designs made by the team. EIS panel testing was performed with the new electrodes on coated Al-7075 panels to test the ability of each electrode geometry and material combination to detect surface defects. The impedances at certain frequencies allowed the team to calculate ratios between defect and no defect tests that determined the accuracy of each electrode material and geometry combination. Wettability of the electrodes was quantified by using ImageJ software to measure the contact angle between the sodium chloride electrolyte and each material of interest. The contact angle was measured prior to and following submersion in a salt water solution to determine any change in wettability.

Based on this research, several major conclusions could be made. Nickel was found to have the highest corrosion resistance of the materials tested. Band-Aid geometries were found to perform better than Bar designs, while Lunar and Scythe designs performed similarly in most tests. Nickel was found to have the most consistent contact angle and wettability over time, with minimal changes over the course of a couple of days. Though the Scythe and Lunar designs performed to a similar degree, the Scythe design was found to be easier to manufacture using the Silhouette cutter and easier to handle during panel testing application. Though nickel was not the hardest material tested, it had a decent reported yield strength and was the cheapest material per square millimeter that was used. The overall testing procedure, specifically the handling and application of electrodes onto the panels, was straightforward and easy to follow, leading to a positive user experience. Given the design constraints of corrosion resistance, durability, wettability, cost, availability, and manufacturability, it is recommended that Luna Labs continues their research using nickel material and Band-Aid and Scythe geometries.

RECOMMENDATIONS

Some manufacturing details could be improved for future use. The designs that used sharp edges were more difficult to accurately cut with the Silhouette cutter, notably in the Bar design. Introducing designs with more curved edges decreased the possibility of a design being morphed during cutting. In addition, the Bar and Band-Aid designs could be placed 2 mm apart directly on the material sheet when cut, which could make the overall panel testing process quicker, rather than the current method of indiscrete distances used between the electrodes when cutting. Finally, if the Silhouette cutter is deemed the best manufacturing method, the optimal blade depth and force must be determined in order to standardize future manufacturing.

The eventual application for these electrodes may require them to be in use for several days, weeks, or months. Longer-terms testing with these electrodes would be beneficial to understand how the electrodes, and their measurements, are affected if used over longer periods of time. The longest experiment the team performed was the wettability test over a couple of days, which was not long enough to truly assess the viability of the electrodes in long term use. This goes along with assessing the reusability of the electrodes, since once they are adhered to the panel they cannot be removed and reapplied, as their shape is destroyed when peeled off in the current setup.

Micro-electrical discharge machining may be a viable manufacturing method for producing the electrode designs desired. The cutting method used in this project was inadequate for producing electrode designs from the stainless steel material. The cutting method utilized a physical blade that was damaged repeatedly upon use with the stainless steel material. The stainless steel had a hardness value of 88 HRB, which was much higher than the hardness values of the copper, nickel, and brass alloys. Stainless steel and titanium could be examined as potential electrode materials, if available and not too expensive in sheet form. There is evidence that stainless steel and titanium have comparable/better corrosion resistance and mechanical properties than any of the materials that were fully tested. However, stainless steel and titanium would only be viable if a different cutting method is used instead of the Silhouette cutter. Another consideration is that stainless steel, and possibly titanium, would require more expensive silver solder, since lead solder was not compatible with the steel when attempted during this project.

The effects of different coating materials on the different electrode materials should also be investigated with the intention of further increasing the service time of the electrodes. In addition, a different adhesive could prove to be a better option than the current one, if a new adhesive can be found that is better at avoiding unwanted peeling before electrode application.

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