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Effectiveness of Different Materials as Catalysts for Alkaline Water Electrolysis

Lance T. Bartol
Macalester College, lbartol@macalester.edu

James Doyle
doyle@macalester.edu

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Effectiveness of Different Materials as Catalysts for Alkaline Water Electrolysis

Abstract

We tested the catalytic properties of various nickel and molybdenum electrodes as potential replacements for platinum for usage in alkaline water electrolysis. After initial tests found molybdenum-based electrodes to be significantly more effective than nickel electrodes, we moved to calculate overpotentials. We found nickel electrode overpotentials at ± 10 mA current to be 939 and -960 mV. Conversely, molybdenum electrode overpotentials at the same currents were 244 and -681 mV respectively. While still significantly higher than overpotentials for platinum, these results indicate that, with more testing, molybdenum-based electrodes could eventually emerge as a cheaper, more abundant alternative to platinum electrodes.

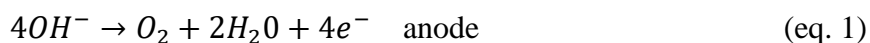
Keywords

Renewable Energy, Water Electrolysis, Electrolysis

I. Introduction

To deal with climate change, renewable energy technologies, such as solar and wind, are being developed to replace fossil fuels due to their much lower greenhouse gas emissions. However, wind and solar are not “reliable” forms of energy in that humans cannot directly control when they produce their energy. As such, to enable widespread adoption of these technologies, long-term energy storage must be utilized. One of these methods of long-term energy storage is hydrogen. By using electricity produced by renewable energy, hydrogen can be produced with no additional greenhouse gas emissions via electrolysis of water.

Electrolysis is the process of splitting water into oxygen and hydrogen gas. This chemical reaction is an example of a reduction-oxidation (redox) reaction as it involves the transfer of electrons between parts of the water molecule. While electrolysis can be performed in a wide range of pH values, this project only focuses on electrolysis in alkaline (low pH) solution. In alkaline solution, the reactions are as follows:



To create the alkaline solution, a salt, such as NaOH, is added to water, which dissolves the salt into Na^+ and OH^- ions (the OH^- ions are what makes the solution alkaline). However, this isn't sufficient to create electrolysis. The reactions will only take place at a catalyst (typically some kind of metal). The catalyst that forms oxygen gas is called the anode and the catalyst that forms hydrogen gas is called the cathode. Collectively, the anode and the cathode are the electrodes of the reaction, which is how they will be referred to in the remainder of this paper.

Currently, for industrial processes, platinum is used as the catalyst as it gives the highest efficiencies of any known electrodes (roughly 70%) [1]. However, due to its relative scarcity, the cost of manufacturing platinum electrodes for use in electrolysis is too high to justify its use to produce hydrogen when compared to using fossil fuels [2]. As such, there is currently much research focused on developing more abundant and cheaper catalysts, which was the focus of this research. Most of the literature is focused on molybdenum-based compounds, such as a paper by Kuang et al (2017) that found NiS₂/MoS₂ hybrid nanowires to have performance nearly as effective as platinum [3]. However, the starting point of this project was a paper by Han et al (2021) that found that nickel electrodes produced by DC sputtering were highly effective as catalysts [4].

Sputtering is a form of Physical Vapor Deposition that takes place in a vacuum chamber (typical pressures are on the order of 10⁻¹⁰ atm). Argon gas is then pumped into the chamber and a voltage is applied to ignite the Argon into a plasma. Argon ions then strike the target (made of what is being sputtered – nickel for this project) and eject target atoms. These ejected atoms then land on the opposite side of the chamber, where a substrate is located. Over time, enough atoms are ejected to form a thin film of the desired substance.

II. Methodology

A. Preparation of Electrodes

The first electrodes made were all nickel based. For a baseline, nickel sheet metal was polished with steel wool. Three sputtered films were then made. NI02 was deposited onto unaltered 304 stainless steel (304 stainless steel was chosen as the substrate due to its compatibility with alkaline solutions, from now on stainless steel refers to 304 stainless steel) at a chamber pressure of 20 mTorr of Argon for a total of 10 minutes. NI03 was deposited onto stainless steel that had been

polished using a metal polishing cream until it was possible to see reflections in (to decrease surface roughness). The sputtering parameters were the same as for NI02. NI04 was nickel deposited onto stainless steel that had been etched with ferric chloride for 1 minute (to increase surface roughness). To increase the ability of the film to stick to the substrate, for the first 5 minutes of deposition, the chamber was at 3.3 mTorr, then for the remaining 15 minutes, the pressure was increased to 20.7 mTorr. Scanning Electron Microscope (SEM) images of all the sputtered films before and after deposition are shown below in Figures 1-3. As these figures show, the surface properties of the sputtered nickel films are very similar to the surface properties of their substrate.

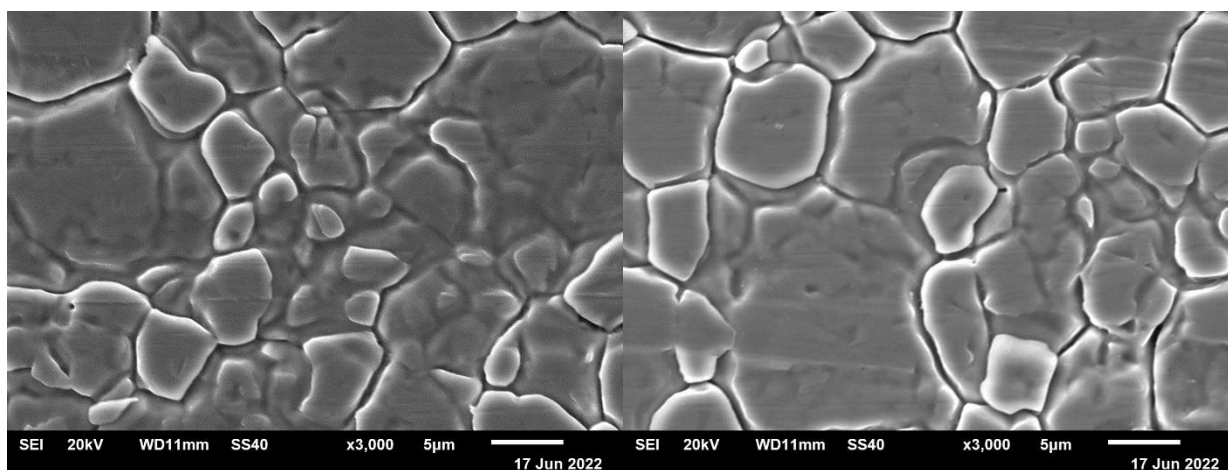


Figure 1. SEM images of film NI02 (Nickel deposited onto unaltered 304 stainless steel). Left: Stainless Steel (no sputtering) Right: Nickel (sputtered)

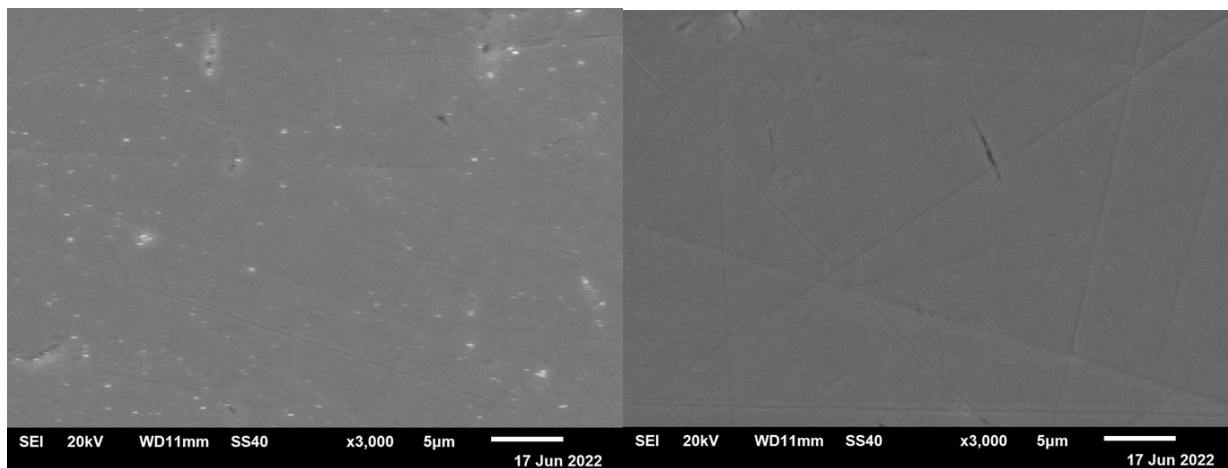


Figure 2. SEM images of film NI03 (Nickel deposited onto polished 304 stainless steel). Left: Stainless Steel (no sputtering) Right: Nickel (sputtered)

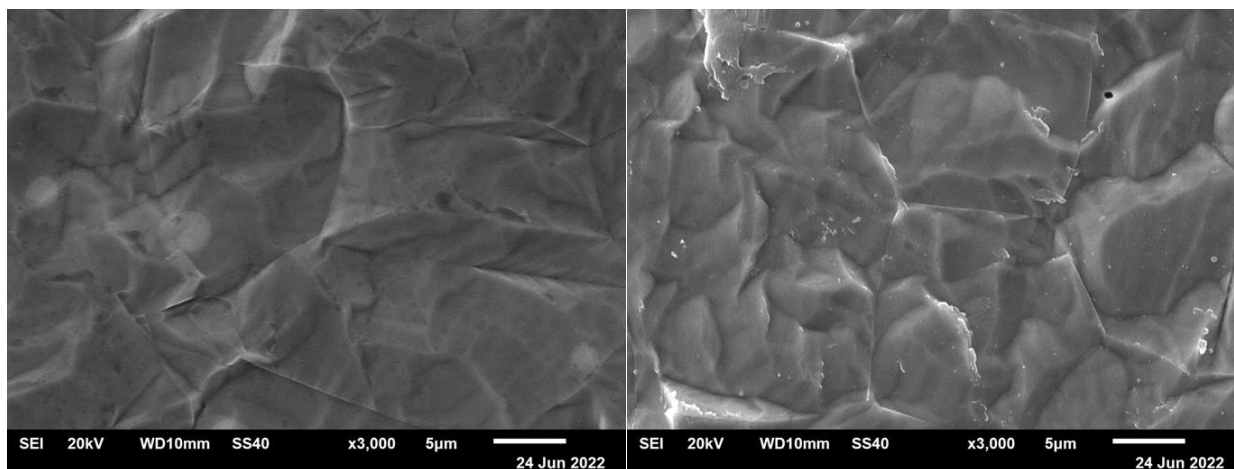


Figure 3. SEM images of film NI04 (Nickel deposited onto 304 stainless steel etched with Ferric Chloride). Left: Stainless Steel (no sputtering) Right: Nickel (sputtered)

After the results of the tests of the nickel electrodes, we moved to looking at other materials. As a baseline, we used stainless steel electrodes. Before being used for tests, both electrodes were washed with Alconox, then rinsed with de-ionized water. This became the standard procedure for all electrodes from this point onward. As molybdenum is another promising material mentioned in the literature, we used molybdenum sheet metal electrodes, treated as described for stainless steel.

Following the results of the molybdenum tests, molybdenum electrodes became the focus of this project. First, using the same cleaning procedure as described above, we tested a molybdenum anode and stainless steel cathode and a stainless steel anode and a molybdenum cathode. Next, we pre-oxidized two molybdenum electrodes by thoroughly cleaning them with a 50% HCL 50% H₂O solution before heating them in a tube furnace at 500°C for 2.5 hours. As much of the literature worked with molybdenum disulfide, we similarly cleaned two molybdenum electrodes with the same solution as for molybdenum oxide, then heated them in a tube furnace in the presence of sulfur at 600°C until all the sulfur had been used (26 m 50s). Additionally, we tested a combination of a molybdenum anode and a molybdenum disulfide cathode.

B. Electrolysis Tests

To test the effectiveness of the different electrodes, we had to develop methods of testing. First, we developed the IV Curve test. A diagram of the electrical circuit for this test is shown below in Figure 4. By writing a LabVIEW program that varies V_{out} over a user specified range, the current and voltage of the electrolysis cell can be found by circuit analysis. The voltage across the cell is simply V_2 , while the current across the cell is given by Ohm's Law:

$$I_{\text{cell}} = (V_1 - V_2)/R \quad (\text{eq. 4})$$

Then, a plot of current vs voltage can be constructed. For an electrolysis cell, the current will be 0 until the required voltage is reached. At that point, the current begins to curve upward until it becomes a linear relationship between current and voltage. The result of this test is the x-intercept of a linear fit of the linear part of the graph. Theoretically, better materials will have smaller intercepts. To keep the electrodes in place throughout the test, we developed a plastic holder that sits on the side of the container of the solution (for this test 3.0 M NaOH) that provides a low-resistance gold contact between the electrodes and the wire going to the rest of the circuit. This holder allowed us to fix the available surface area of the electrodes to 1 cm^2 . Additionally, we used stands to clamp glass bottles directly above both electrodes that hold the oxygen and hydrogen gas generated during electrolysis. The LabVIEW program allowed for variation of the wait time between voltage increments, magnitude of voltage increments, starting voltage, and final voltage. All tests used wait time = 60 sec and $\Delta V = 0.1 \text{ V}$. Nickel and stainless steel tests took place over a voltage range of 2 – 5 V. The stainless steel anode, molybdenum cathode test used voltage of 1 – 5 V. All other tests used a voltage range of 1 – 4 V. These ranges were chosen to give a couple data points at 0 current and allowing the current to increase to at least 50 mA.

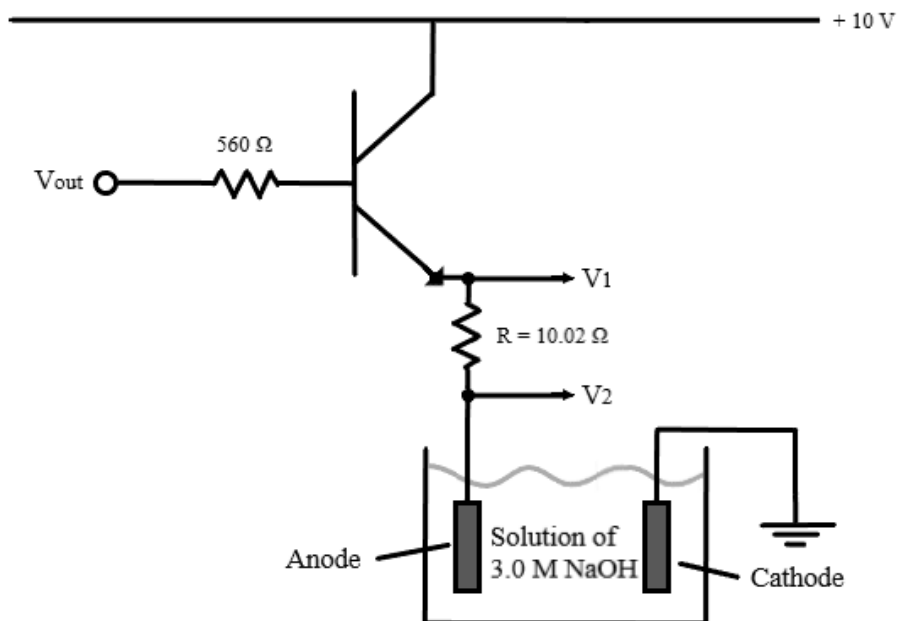


Figure 4. A circuit diagram of the circuit used for the IV Curve test. The circle located at V_{out} indicates it is the voltage sent from the computer via the LabVIEW program. The arrows pointing out of V_1 and V_2 indicate that the LabVIEW program measures those voltages every time it takes a measurement.

The second test we developed early on was the average voltage test. A diagram of the circuit used is shown below in Figure 5. We used a programmable current source that allowed us to choose the current through the electrolysis cell. The LabVIEW program for this test simply records the voltage across the cell at a specified time interval. By averaging the voltage measurements, we can find the average voltage of the cell. Theoretically, better materials will require a lower voltage given identical currents. This test used the same set-up as the IV Curve test (only the circuit and LabVIEW program differs between the tests). The parameters for the tests were time between measurements of 10 sec and data recorded until 8.0 mL of hydrogen gas is formed in glass bottle above cathode. For all materials, runs were done at both low current (10 mA) and high current (50 mA).

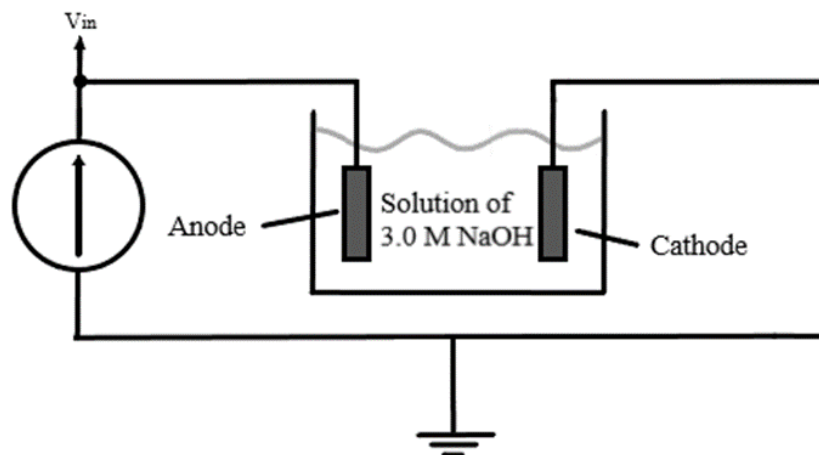


Figure 5. A circuit diagram of the circuit used for the average voltage test. The arrow located at V_{in} indicates that the LabVIEW program measures that voltage every time it takes a measurement. The current source in the circuit is a programmable current source that lets the user pick the current sent from it.

The final test we developed was the Tafel Plot test. A circuit diagram for the circuit used is shown below in Figure 6. This test is more in-line with the typical tests done in the literature. In Figure 6, the working electrode is the electrode that is being tested (by applying both positive and negative voltages at V_{out} from LabVIEW, the working electrode acts as both an anode and a cathode). The reference electrode allows the effect of the working electrode to be accurately measured. We used a Pb/PbSO₄ reference electrode in this test (1.0 M KOH was used as solution for this test to maintain compatibility with the reference electrode). The counter electrode is what allows current to flow throughout the circuit. We used a stainless steel counter electrode with a total area of 3 in² (larger area provides more consistent results). The LabVIEW program for this test sends out a voltage at V_{out} , then measures the voltages at V_{WE} , V_{RE} , and V_I . The voltage that is relevant in this circuit is $V_{WE} - V_{RE}$, which from now on, will be referred to as ΔV . The current across the cell is given by applying Ohm's Law across the resistor: $I_{cell} = V_I/R$. The parameters for all tests were: voltage increment = 0.005 V, wait time = 3 sec, averaging delay = 1 ms, averaging number = 100. The averaging takes 100 data samples in quick succession and averages them, reducing the effect of noise significantly. The voltage ranges for V_{out} were different for each material, to try to get

data for a maximum current (both positive and negative) of 20-25 mA (our Operational Amplifiers could only accept up to 25 mA of current). For stainless steel, this range was -2.2 to 2.2 V, for nickel, it was -2.0 to 2.0 V and for molybdenum and molybdenum disulfide, it was -1.5 to 1.25 V. The results that we obtained from this test are described in detail in the results section.

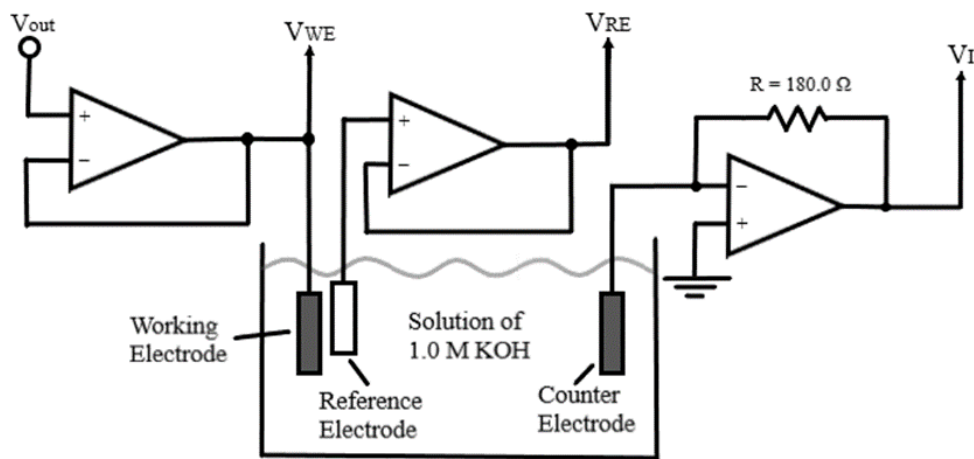


Figure 6. A circuit diagram of the circuit used for the Tafel Plot test. The circle at V_{out} indicates it is the voltage sent from the LabVIEW program. The arrows located at V_{WE} , V_{RE} , and V_I indicate that the LabVIEW program measures those voltages every time it takes a measurement. The relative placement of the different electrodes in solution is accurate. 4 Tests were done with varying the working electrode between stainless steel, nickel, molybdenum, and molybdenum disulfide. The reference electrode was a Pb/PBSO₄ reference electrode. The counter electrode was stainless steel with a total area of 3 in².

III. Results and Discussion

Using the IV curve and average voltage tests, we were able to successfully generate initial characterizations of all the materials described in Section II A. A plot of the IV Curve generated for molybdenum is shown below in Figure 7.

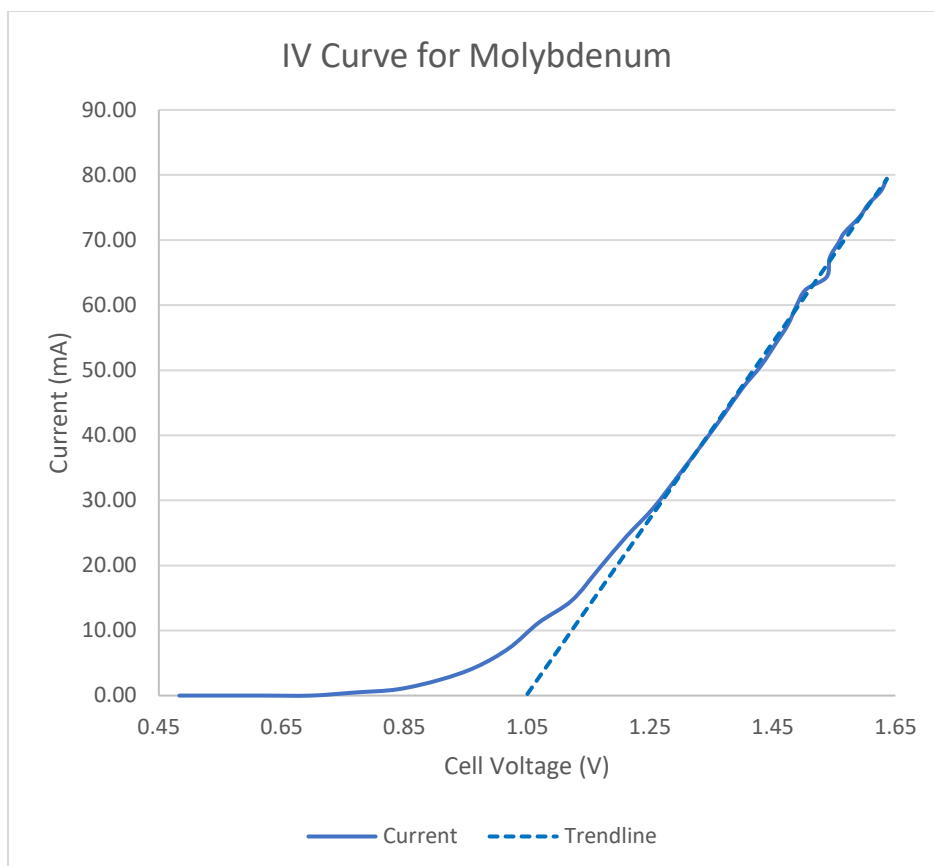


Figure 7. A plot showing the result from the IV Curve test for molybdenum electrodes. A trendline generated from just the “straight” section of the graph is included.

This is the expected shape. There is no current until about 0.7 V, from which point the current then begins to increase. At a voltage of 0.9 V (corresponding to a current of 2.4 mA), bubbles indicating electrolysis is occurring first begin to appear. Eventually, at 1.25 V, the relationship between current and voltage becomes linear. Extrapolating this linear portion yields an x-intercept of 1.05 V. All tests gave results that qualitatively looked very similar to this, with the main difference being the voltage at which the current begins to increase. Plots showing the results from the average voltage test for molybdenum electrodes are shown below in Figure 8.

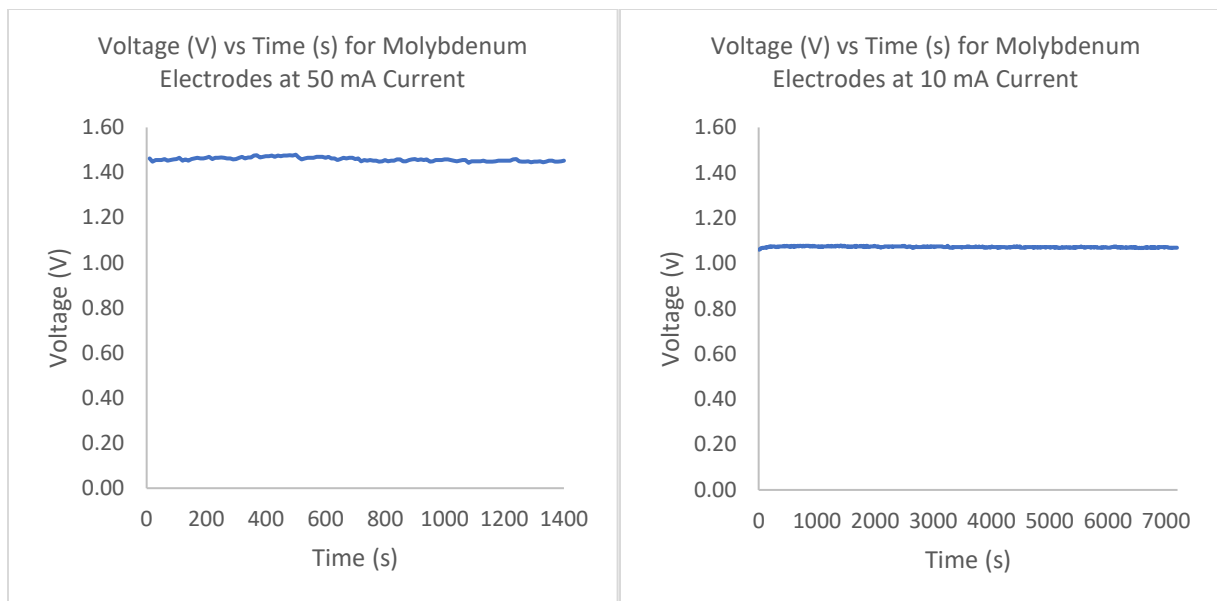


Figure 8. Plots showing the results from the average voltage test for molybdenum electrodes at both high (50 mA) and low (10 mA) current. The tests were ran until 8.0 mL of hydrogen gas was generated. For high current, the average voltage was 1.47 V, while for low current, it was 1.07 V.

From these plots, it can be seen that the voltage is mostly constant as a function of time with relatively small fluctuations. This suggests that the catalytic capabilities of the electrodes are consistent over time. The average voltage is noticeably higher for larger current with the average voltage at high current being 1.47 V versus 1.07 V for low current. It is worth noting that the low current test takes about 5 times longer than the high current test, which suggests that the rate of hydrogen generation is directly proportional to current. A table showing the results for all electrodes is shown below in Table 1. First, looking at the results for the nickel electrodes, we see that overall, NI03 had the worst performance, which was expected, given its low surface area. Secondly, NI04 was the best performing sputtered film, which again was expected given its higher surface area. However, none of the films were any better than nickel sheet metal and the overall variations in performance are rather small. An unexpected result was that for all the nickel tests, the cathodes experienced discoloration by the end of the tests. SEM images of the nickel sheet metal electrodes before and after testing are shown below in Figure 9.

| Electrodes | IV Curve (Intercept) | Low Current Average Voltage | High Current Average Voltage |
|------------------------------------|-------------------------|--------------------------------|---------------------------------|
| Nickel | 1.83 V | 2.01 V | 2.41 V |
| NI02 | 1.95 V | 2.09 V | 2.64 V |
| NI03 | 2.01 V | 2.20 V | 2.61 V |
| NI04 | 1.82 V | 2.01 V | 2.61 V |
| 304 Stainless Steel | 1.98 V | 2.07 V | 2.67 V |
| Molybdenum | 1.05 V | 1.07 V | 1.47 V |
| SS Anode, Mo Cathode | 1.98 V | 2.10 V | 3.11 V |
| Mo Anode, SS Cathode | 1.06 V | 1.14 V | 1.73 V |
| Molybdenum Oxide | 1.07 V | 1.12 V | 1.76 V |
| Molybdenum Disulfide | 0.98 V | 1.19 V | 1.87 V |
| Mo Anode, MoS ₂ Cathode | 0.96 V | 1.21 V | 1.83 V |

Table 1. A table showing the results from the IV Curve and average voltage tests for the listed electrodes. The IV Curve result is the x-intercept of a line fitted from the straight part of the IV Curve, the Average Voltage results are the average voltage over the entire test (low current is 10 mA, high current is 50 mA). More effective materials would receive smaller voltages for all of these results when compared to less effective materials. For tests with different electrodes as anode and cathode, molybdenum is abbreviated Mo, 304 stainless steel is abbreviated SS, and molybdenum disulfide is abbreviated MoS₂.

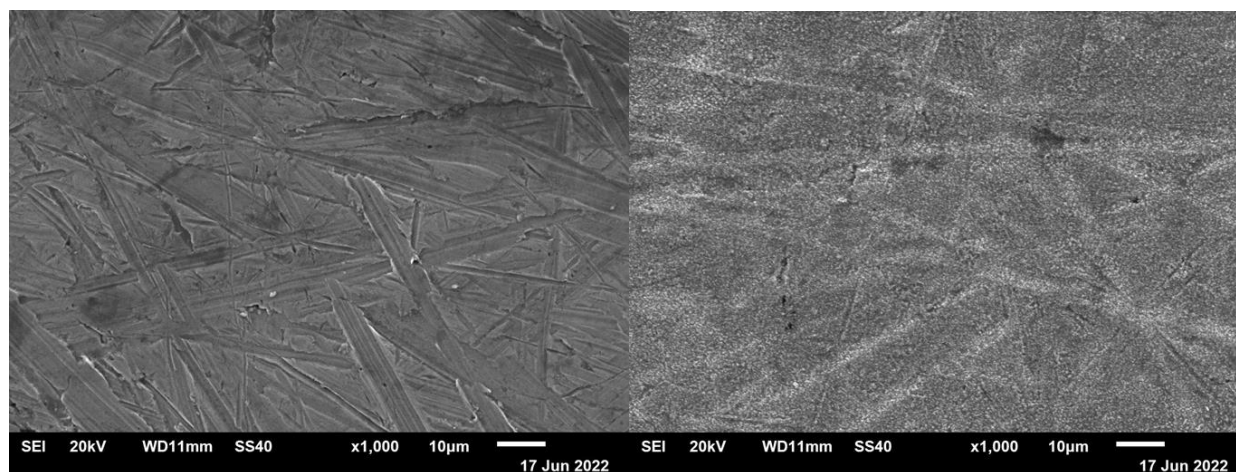


Figure 9. SEM images of nickel sheet metal electrodes before (left image) and after (right image) usage in the IV Curve and average voltage electrolysis tests.

What we see from these SEM images is that some kind of paste is forming on top of the cathode. We do not have any explanation of what this is, but it does not seem to affect the results significantly given the stability of the average voltage tests. Next, we looked at stainless steel and molybdenum electrodes. From Table 1, stainless steel has very similar results to nickel, particularly when comparing to NI02, the nickel film with the same surface properties as stainless steel. molybdenum, however, is clearly much more effective than either nickel or stainless steel

with results for all tests 50 - 60 % of the results for nickel. Because of this, we moved to focus more on molybdenum electrodes at this point and performed the remainder of the tests shown in Table 1. The half stainless steel -half molybdenum tests show that molybdenum is much more effective as an anode than as a cathode. The IV Curve result for Mo Anode-SS Cathode is 1.06 V, nearly identical to the molybdenum result of 1.05 V. Flipping the anode and cathode gives a result of 1.98 V, identical to the stainless steel result. None of the tests where molybdenum was the anode formed any oxygen gas, so we theorized that the molybdenum was being oxidized. Therefore, we performed tests on pre-oxidized molybdenum, but found no significant deviations in results. Similarly, molybdenum disulfide tests gave similar results to regular molybdenum. For all molybdenum electrodes, the anode appeared blackened after testing and the cathode also experienced some discoloration. We then imaged molybdenum electrodes before and after being used in electrolysis using the SEM, these images are shown below in Figure 10. These images show that the cathode is having a similar paste forming to the nickel cathodes. However, the anode appears to be oxidizing and/or slowly dissolving. This proposes a serious issue for molybdenum electrodes as an alternative to platinum, as needing to constantly replace electrodes would substantially increase costs, even if performance isn't immediately impacted by dissolution.

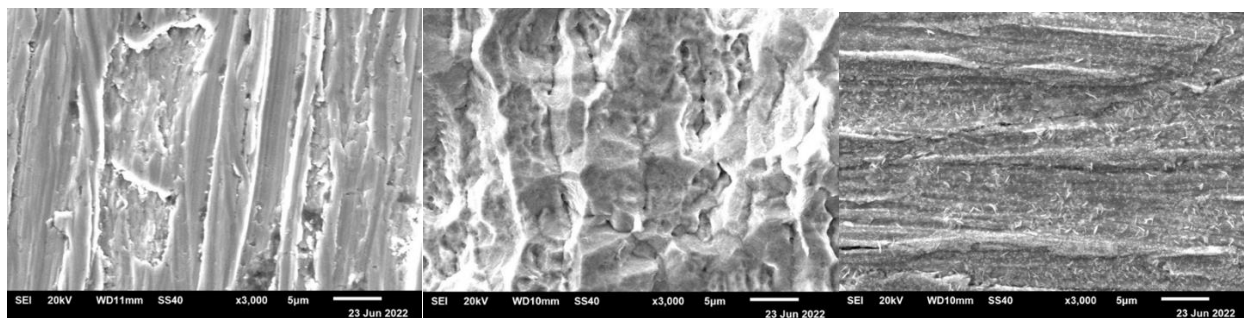


Figure 10. SEM images of molybdenum electrodes before and after being used in electrolysis. Molybdenum before electrolysis: Left image. Anode after electrolysis: Center image. Cathode after electrolysis: Right image. In the middle image, the structure of the molybdenum is dissolving. In the left image, a paste of small particles appears on top of the structure of the molybdenum. Both of these effects are noticeable by eye as the molybdenum electrodes are discolored relative to before electrolysis.

To get results more comparable across studies, we developed and used the Tafel Plot test as described above for nickel, stainless steel, molybdenum, and molybdenum disulfide. The first result we can draw from these tests is a polarization plot. This is a plot of ΔV vs I . The polarization plots are shown below in Figure 11.

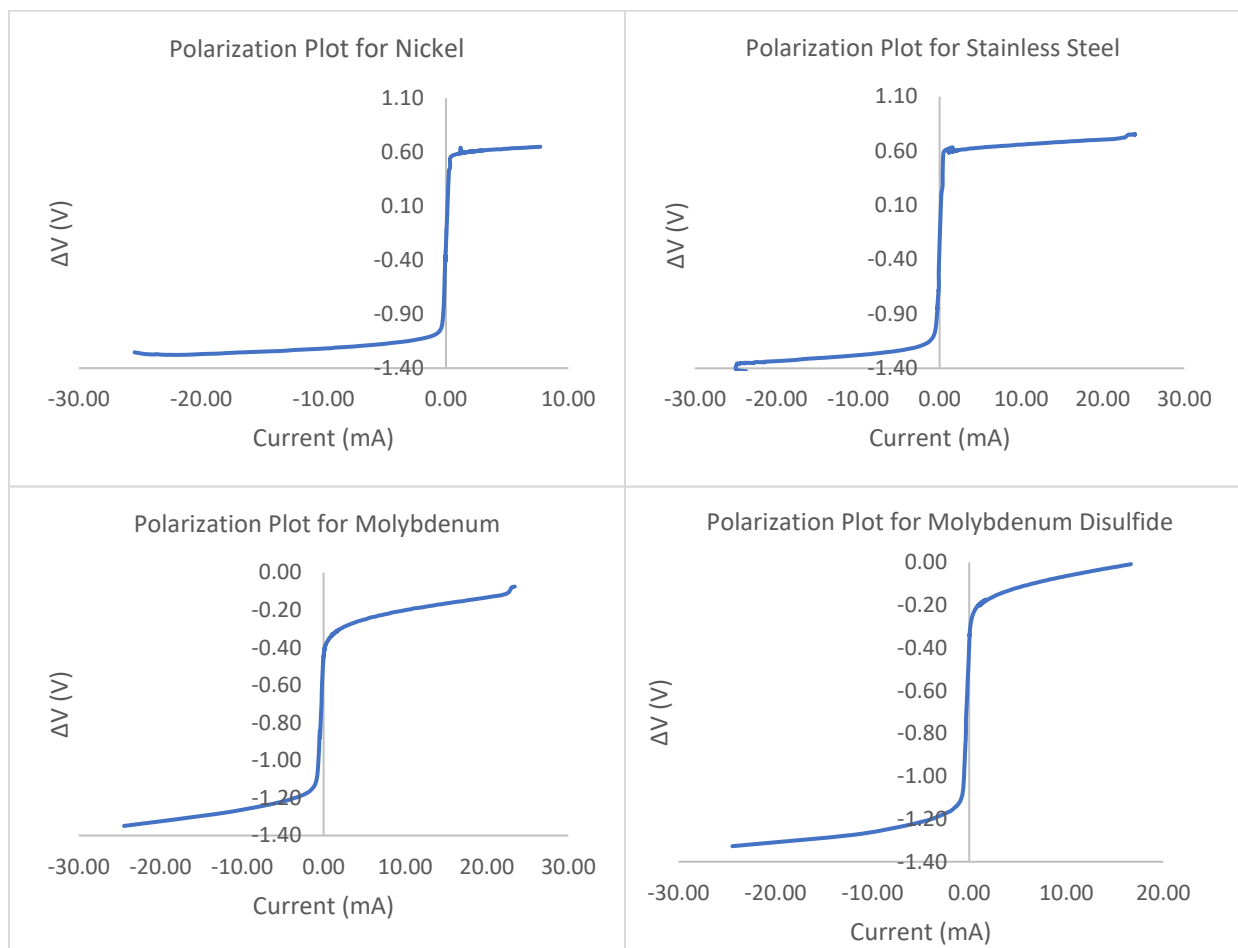


Figure 11. Polarization plots for nickel, 304 stainless steel, molybdenum, and molybdenum disulfide working electrodes using the Tafel Plot test.

These plots show more conclusively the relative effectiveness of nickel, stainless steel, and molybdenum. nickel and stainless steel have very similar plots and molybdenum and molybdenum disulfide have very similar plots. Additionally, the range of voltages is smaller for molybdenum based electrodes than for nickel and stainless steel, which suggests that the molybdenum based electrodes are more effective. Next, using this data, we can calculate overpotentials. The

overpotential (at a given current) gives the additional voltage you must apply above the theoretical minimum. Thus, better materials will have lower overpotentials. As such, it is the most common metric for comparing the effectiveness of different catalysts. We calculated the following overpotentials:

$$\eta_{10mA} = \Delta V_{10mA} - \Delta V_{eq} \quad \text{anodic overpotential} \quad (\text{eq. 5})$$

$$\eta_{-10mA} = \Delta V_{-10mA} - \Delta V_{eq} \quad \text{cathodic overpotential} \quad (\text{eq. 6})$$

Where ΔV_{eq} is ΔV at 0 mA current. By subtracting the two overpotentials, we can get a result for the cell voltage at 10 mA (analogous to the voltage measurements for previous tests). According to Fang et al, current state of the art platinum electrodes have overpotentials at 10 mA of magnitude 34 mV [5]. Table 2, shown below, shows our results for overpotentials.

| Electrodes | η_{10mA} | η_{-10mA} | ΔV_{eq} | V_{cell} |
|----------------------|---------------|----------------|-----------------|------------|
| 304 Stainless Steel | 906 mV | -1032 mV | -248 mV | 1.938 V |
| Nickel | 939 mV | -960 mV | -262 mV | 1.899 V |
| Molybdenum | 244 mV | -681 mV | -446 mV | 0.925 V |
| Molybdenum Disulfide | 316 mV | -744 mV | -377 mV | 1.060 V |

Table 2. A table showing the results from the Tafel Plot test for 304 stainless steel, nickel, molybdenum, and molybdenum disulfide working electrodes. Anodic overpotentials (η_{10mA}) are calculated by equation 5. Cathodic overpotentials (η_{-10mA}) are calculated by equation 6. Equilibrium Voltage (ΔV_{eq}) is given by y-intercept of corresponding polarization plot. Cell voltage (V_{cell}) is calculated by subtracting cathodic overpotential from anodic overpotential.

As with the polarization plots, the overpotentials show that nickel and stainless steel are much less effective than molybdenum and molybdenum disulfide. The overpotentials also show that molybdenum is more effective as anode than a cathode, given that the anodic overpotential was 244 mV for plain Mo and 316 mV for MoS₂, much lower in magnitude than the -681 mV and -744 mV, respectively for cathodic overpotentials. Finally, while molybdenum is more effective than nickel or stainless steel, it doesn't quite measure up to the results for platinum (less than 34 mV). The final data we can extract from the Tafel Plot test is to make a Tafel Plot (plot of ΔV vs $\log_{10}(I)$)

and calculate the Tafel Slope. This analysis was only done for molybdenum, as it is considered to be our baseline material. The Tafel Plot for molybdenum is shown below, in Figure 12.

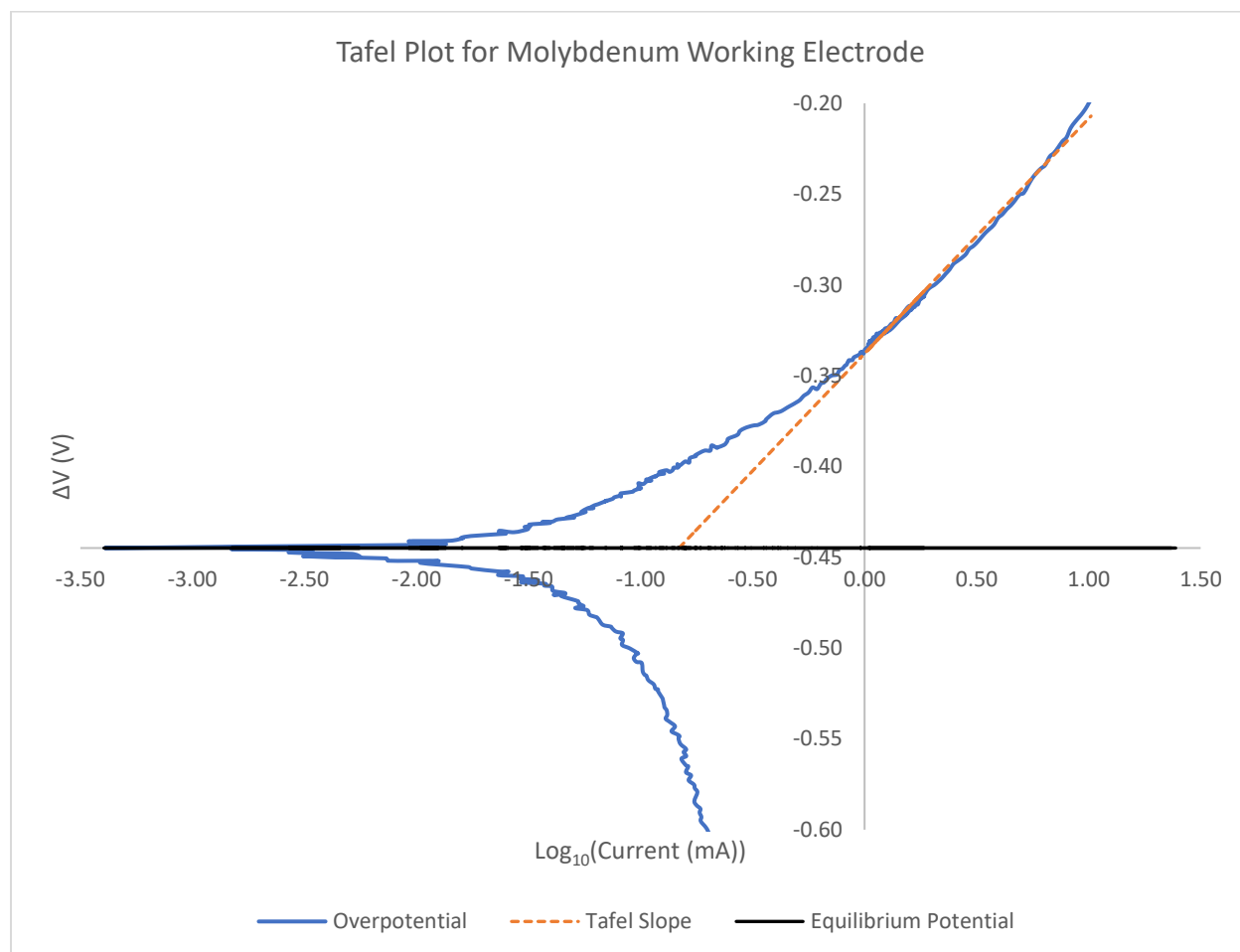


Figure 12. A plot showing the Tafel Plot for a molybdenum working electrode. The data is shown in blue. The Tafel slope is shown in orange (slope of 129 mV/dec). The equilibrium potential ($\Delta V = -446$ mV) is shown in black.

The Tafel Slope is found in a similar process to the intercept for the IV Curve test. Once the relationship between ΔV and $\log_{10}(I)$ becomes linear, the slope of that relationship is calculated, which is the Tafel Slope. We determined this to be 129 mV/dec. This means that when the current is increased by a factor of 10, the overpotential increases by 129 mV. This is somewhat larger than other reported results for molybdenum-based electrodes [3] but given that these electrodes are just unaltered molybdenum sheet metal, without any complicated fabrication techniques, this is an acceptable result.

IV. Summary and Conclusions

In summary, we tested the catalytic properties of various nickel and molybdenum electrodes for alkaline water electrolysis. After initial tests found that molybdenum based electrodes were significantly more effective as catalysts than nickel and thin nickel films, we then moved to calculate proper overpotentials of these materials. We found nickel overpotentials at ± 10 mA of current to be 939 and -960 mV respectively, similar to overpotentials for stainless steel of 906 and -1032 mV. This suggests that nickel by itself is not an effective catalyst for electrolysis of water. Our overpotentials for molybdenum were much more encouraging, with overpotentials of 244 and -681 mV for plain molybdenum and overpotentials of 316 and -744 mV for molybdenum disulfide. While this is much higher than the near zero overpotentials of platinum, this suggests that with more development, molybdenum-based electrodes could become a cheap alternative to platinum in the future. Additionally, we calculated the Tafel Slope for molybdenum, and found it to be 129 mV/dec. Future work on this project includes developing molybdenum-nickel alloy electrodes, employing techniques such as chemical etching to increase the surface area of electrodes, experimenting with sputter deposited molybdenum films, and investigating the cause of the discoloration of the molybdenum electrodes.

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