Establishment of Modern Chemical Techniques for Analytical Chemistry and Fundamental Research

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Abstract: The mixture of common molecule ferrocene in the solvent of astronitrile and supporting electrolyte tetrabutylammonium hexafluorophosphate was studied heavily throughout the entire semester. Electron transfer at applied potential or a running potential were monitored closely and analyzed to the best of our ability. With plots that were determined by the electrochemical analyzer, I was able to obtain different types of parameters and achieve more once the plot was transferred to Microsoft excel. Also I was able to find out some sort of secondary reaction happens when the solution is at rest.

Introduction: I started off my research getting introduced to the CV-50W electrochemical analyzer to understand the fundamentals of electrochemistry, more specifically, cyclic voltammetry. My first cyclic voltammetry reaction consisted of 0.003g of ferrocene, 10mL of astronitrile, and 0.3874g of tetrabutylammonium hexafluorophosphate (supporting electrolyte) and it took a while to obtain the correct reading on the plot. Once I was able to obtain it, I transferred my work onto the BASi Epsilon Eclipse electrochemical analyzer, a more complex and more efficient analyzer. I practiced getting more cyclic voltammetry readings and once I was comfortable reading the plot, I transitioned into a new technique that would help me obtained better readings under different circumstances. The controlled potential coulometry technique sets a potential at a certain millivolt and will do either an oxidation reaction or a reduction reaction. The type of the reaction is determined by the potential set from the oxidation or reduction peaks from a cyclic voltammetry plot. Once the reaction was going we noticed a color change and we decided to test a hypothesis. The hypothesis was to indirectly getting the charge using the beers law and Nernst equations. We would use a UV-VIS spectrophotometer to obtain a plot and with the plot, obtain absorbance and use that and insert the variable into the equations for charge. This hypothesis failed due to plot issues but we plan on continuing using this spectrum to obtain other parameters that will later be learned into my research.

Equipments and Materials: As said earlier, I used the CV-50W and BASi epsilon eclipse electrochemical analyzer.

For cyclic voltammetry, I used this cell that has 3 electrodes. We use this cell to obtain a cyclic voltammetric plot to get different parameters. To set up a typical CV experiment, you have to purge inert nitrogen or any inert gas to keep oxygen at the bay throughout the operation using a two small tubes, one is to purge through the experimental solution and the other on is to be kept at the top of the solution to blanket the surface of the solution while CV measurement were been take.
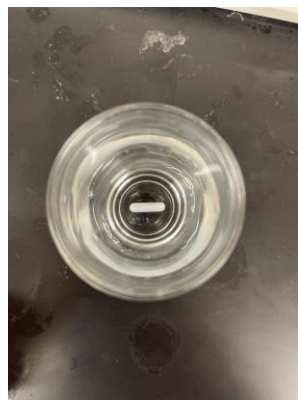

For controlled potential coulometry I used a 3 electrode cell as well The potential of the working electrode is applied minimum 200 mv passed to the $E_{1/2}$ value of the redox system, that was determined through Cyclic voltammetry measurement to ensure completes electrolysis of the desired species. The auxiliary electrode is a spring like electrode that goes in its own chamber. In that chamber, a reduction reaction occurs while oxidation happens inside the cell. In this chamber, there is a solution of the same solvent and supporting electrolyte only. About 3-5 mL fit in it. The reference electrode is the same thing as the cyclic voltammetry reference electrode and does the same thing as it as well.
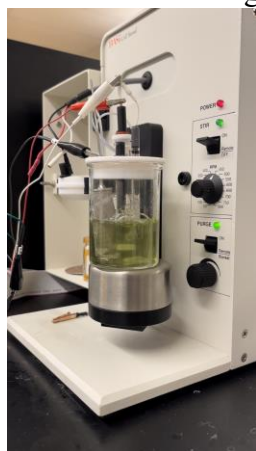

For our hypothesis, we used a spectroelectrochemical cell that is designed to monitor cell reactions spectrophotometrically (using UV-Vis instrument) while quantitative electron transfer is taking place at the platinum flag electrode. This set up was only tried once without putting the

cell on Uv-Vis spectrophotometer. I need to spend more time on it to explore the set up in the future.
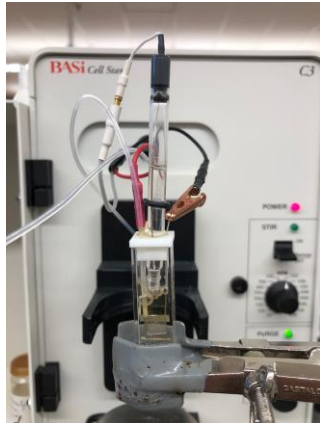
Once I couldn't get the cell going, I went back to the traditional way of spectroelectro chemistry and used a quartz cell that perfectly fits into the UV-VIS spectrophotometer.
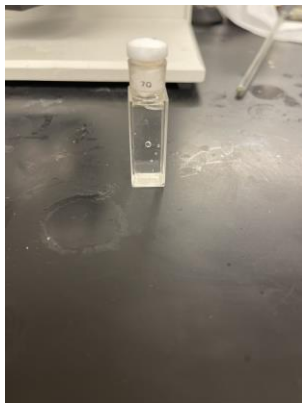
This is the spectrophotometer I used to get the absorbance verse wave length plot. This helped get the concentration while using the beers law equation even though at the end of it all, our hypothesis was inconclusive.
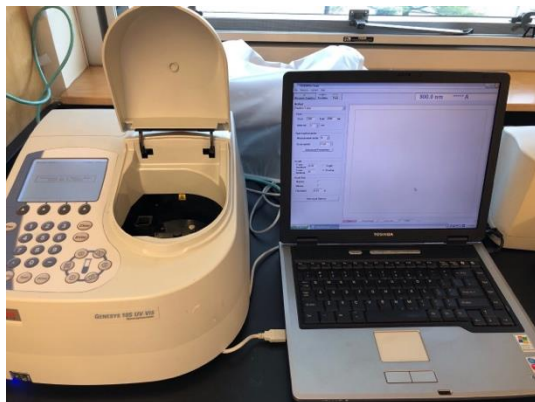
Results: My first completed graph of cyclic voltammetry, it didn't come out how we expected it to be. I would get different peaks in spots it wasn't suppose to be in. I realize after some long consideration, I didn't purge in enough nitrogen to remove the oxygen from the system. Once I purged in nitrogen for a significant amount of time, the graph came out to look like the one shown below.
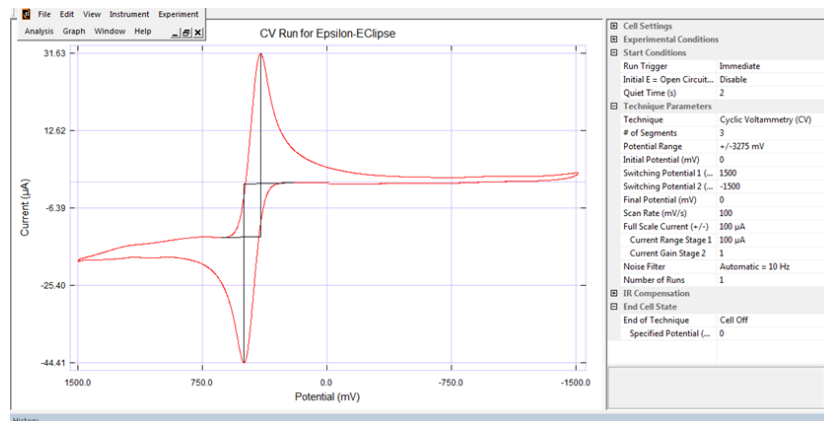
Once we started getting comfortable with the cyclic voltammetry technique, I used this plot and transferred some data into excel to do further investigation and retrieve a parameter. The parameter I was trying to obtain the diffusion coefficient in the Randles-Sevcik equation.

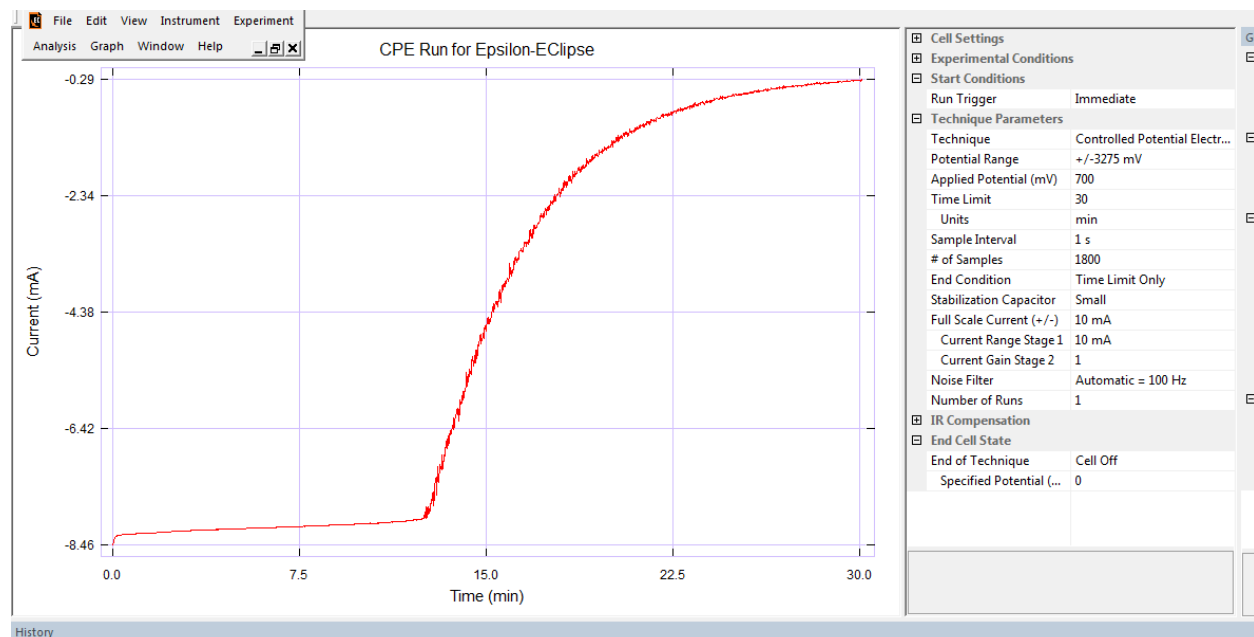### The Randles-Sevcik equation Reversible systems

$$i_p = 0.4463nFAC\left(nFvD/RT\right)^{1/2}$$

$$i_p = \left(2.687\times10^5\right)n^{3/2}v^{1/2}D^{1/2}AC$$

- n = the number of electrons in the redox reaction
- v = the scan rate in V s^{-1}
- F = the Faraday's constant 96,485 coulombs mole^{-1}
- A = the electrode area cm^2
- R = the gas constant 8.314 J mole^{-1} K^{-1}
- T = the temperature K
- D = the analyte diffusion coefficient cm^2 s^{-1}

To obtain the diffusion coefficient, I needed to convert the plot above into an excel plot that is represented by current peak height verse square root of scan rate. The plot should be a linear plot and the slope of the line will result in your diffusion coefficient.
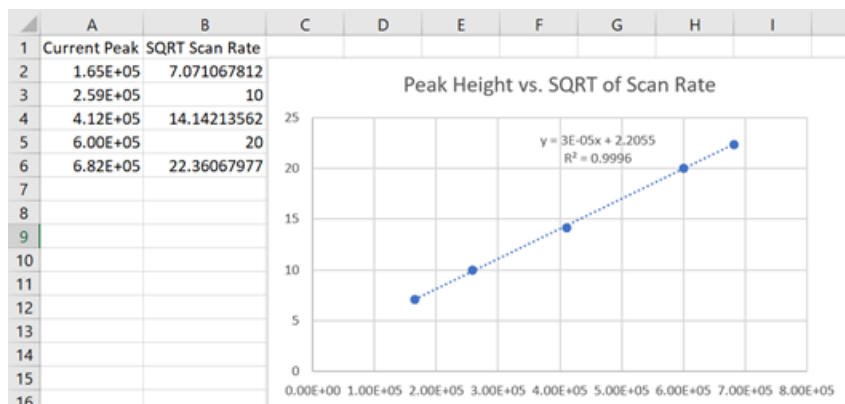
To start up the controlled potential coulometry, it took about 3 weeks to even get a current reading on the plot. The first thing I needed to do was generate a cyclic voltammetric plot and find the oxidation peak. With the oxidation peak, you obtain the potential and add 200mV to that so the oxidation reaction will happen faster inside the cell. After we get the applied potential, we setup the technique and start the reaction. The first thing you notice is a large amount of current is put into the cell for the first 10 minutes and that's when you notice the majority of the color change.


CPE Run for Epsilon-EClipse

⊞ Cell Settings	
⊞ Experimental Conditions	
⊟ Start Conditions	
Run Trigger	Immediate
⊟ Technique Parameters	
Technique	Controlled Potential Electr...
Potential Range	+/-3275 mV
Applied Potential (mV)	700
Time Limit	30
Units	min
Sample Interval	1 s
# of Samples	1800
End Condition	Time Limit Only
Stabilization Capacitor	Small
Full Scale Current (+/-)	10 mA
Current Range Stage 1	10 mA
Current Gain Stage 2	1
Noise Filter	Automatic = 100 Hz
Number of Runs	1
⊞ IR Compensation	
⊟ End Cell State	
End of Technique	Cell Off
Specified Potential (...	0

To calculate the charge, we thought wed be able to use the beers law equation and the Nernst equation the indirectly find the charge. What we first did was generated a bulk electrolysis technique and instead of a 30 minute run we cut up the time to do intervals of 2 minutes for the first 12 minutes, 4 minutes until 20 minutes, and 5 minutes until we reached 30 minutes total. After every interval we would insert the solution into a quartz cell and insert the cell into the UV-VIS spectrophotometer. I received a graph of absorbance verse wavelength graph. We expected an overlay of graphs to have the first peak drop while the second peak increase. What we got was not what we expected.
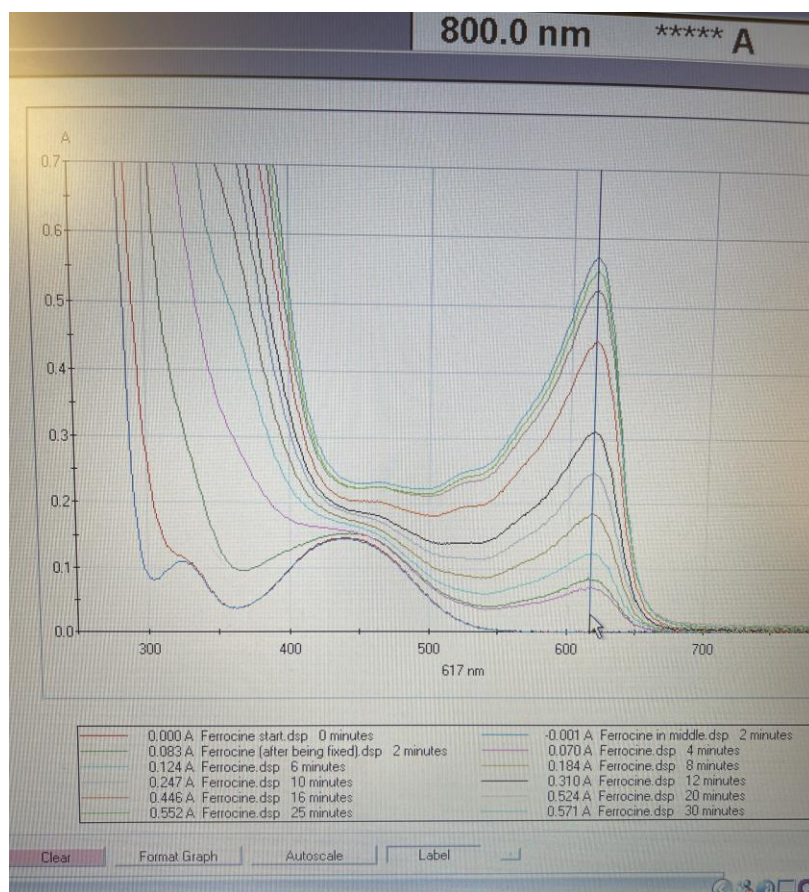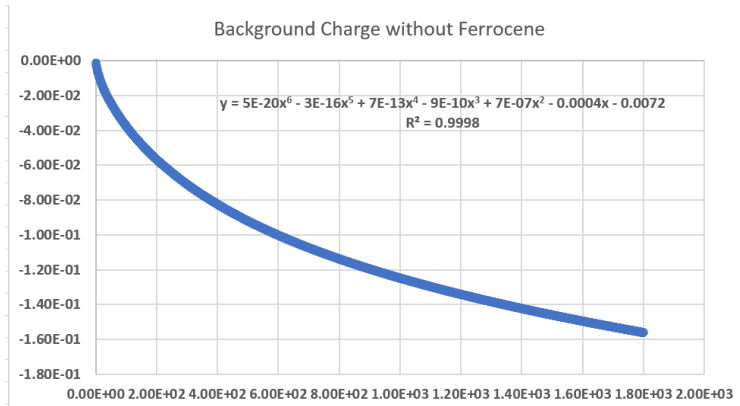

The results from this graph was inconclusive beacause the epsilon value (which is the first peak point) kept increase when we expected that peak to decrease. There may have been a secondary reaction that could absorb more at that wave length but at this moment we have no conclusion for this hypothesis.

We needed to find another way to calculate the charge so I read the manual and I realized I'm able to generate the charge of the system while doing the reaction on the BASi epsilon eclipse. So I ran a new test to generate the charge and I was able to get the charge but I wasn't able to get the net charge. I ran into another issue where we didn't calculate the background charge and subtract it to the charge of the solution. So I ran another test of the background charge for 30 minutes, which had the solution and the supporting electrolyte, got the charge, then did another 30 minute reaction of the solution with the ferrocene molecule. I subtracted the 2 charges from
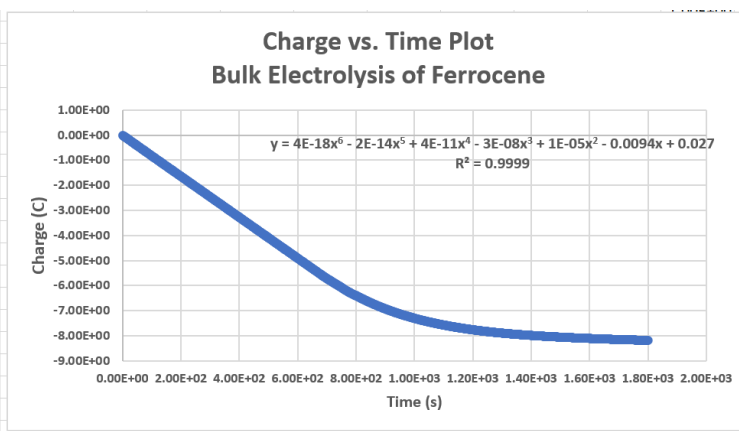
each other and was able to calculate the charge. While doing this second turn of plots, I realized Im able to transition the current verse time graph into a charge verse time graph where I can calculate the charge at any given time.
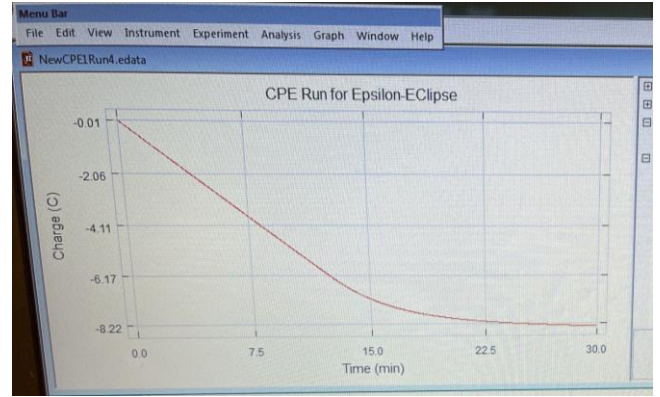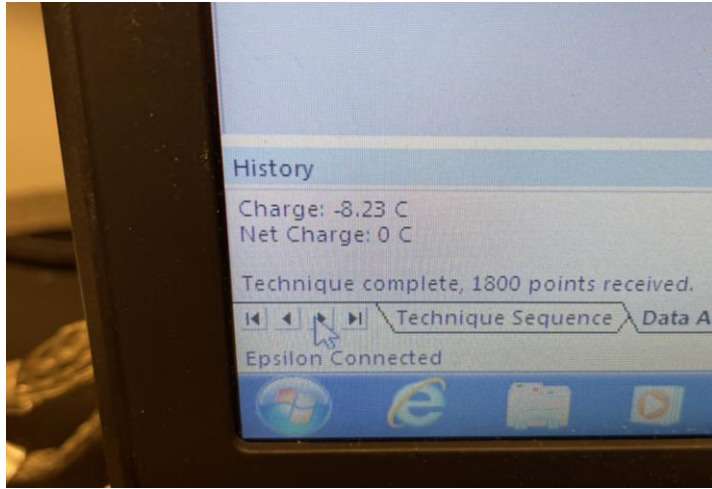
I then transitioned the charge verse time graph into excel and was able to get a polynomial function that respresents the plot to approximately 1% error at most. I'm able to conclude this equation works through the Taylor series in calculus 2 which allows me to create an equation that will give me an answer that's extremely close to the actual value at most by 10^-4 difference.


Background Charge without Ferrocene

$y = 5E-20x^6 - 3E-16x^5 + 7E-13x^4 - 9E-10x^3 + 7E-07x^2 - 0.0004x - 0.0072$
$R^2 = 0.9998$

1.00E+00	-8.33E-03
2.00E+00	-1.67E-02
3.00E+00	-2.50E-02
4.00E+00	-3.33E-02
5.00E+00	-4.16E-02
6.00E+00	-4.98E-02
7.00E+00	-5.81E-02
8.00E+00	-6.64E-02
9.00E+00	-7.47E-02
1.00E+01	-8.30E-02
1.10E+01	-9.12E-02
1.20E+01	-9.95E-02
1.30E+01	-1.08E-01
1.40E+01	-1.16E-01
1.50E+01	-1.24E-01
1.60E+01	-1.33E-01
1.70E+01	-1.41E-01
1.80E+01	-1.49E-01
1.90E+01	-1.57E-01
2.00E+01	-1.66E-01

Charge vs. Time Plot
Bulk Electrolysis of Ferrocene

$y = 4E-18x^6 - 2E-14x^5 + 4E-11x^4 - 3E-08x^3 + 1E-05x^2 - 0.0094x + 0.027$
$R^2 = 0.9999$

Time (s)

Conclusion: In summation, after learning the cyclic voltammetry and controlled potential coulometry, I found out that I can obtain many different parameters like the diffusion coefficient and the charge. My plan is to continue doing research with unknowns that were given to Dr. Ghosh from Stockton University and get different parameters for each unknown as well as figuring out different techniques and get parameters for those different techniques.

I am also able to conclude that a secondary reaction happens when the reaction sits for more than 5 minutes. When I let the solution sit over night, I realized the color was a different color than it was left. Also you can notice that some form of precipitate is at the bottom of the dark brown solution.
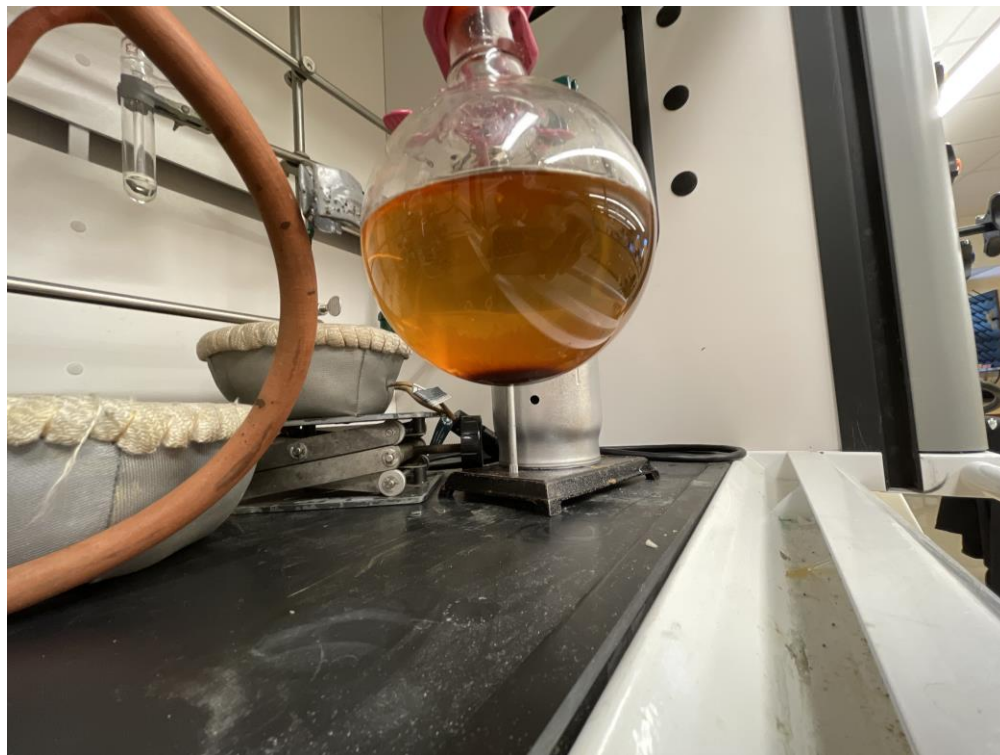
Reference:
- S.J. Hendel; E. R. Young; *Introduction to Electrochemisrty and the Use of Electrochemistry to Sythnesize and Evaluate Catalysts for Water Oxidaation and Reduction*; J. Chem. Educ; 2016; DOI: 10.1021/acs.jchemed.6b00230
- Laboratory techniques in electroanalytical chemistry / edited by Peter T. Kissinger, William R. Heineman. - 2nd ed.; 1996