Ultrasonic Spraying as a Method for Catalyst Deposition in the Electrochemical CO_2 Reduction Reaction

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Abstract

The electrochemical CO_2 reduction reaction (CO_2RR) has attracted attention in recent years due to its ability to both reduce greenhouse gas emissions and convert CO_2 to more valuable chemicals. However, further study is required to better understand the intermediates in the reaction mechanism as well as how catalyst design affects product selectivity. This review will examine the operation techniques in using ultrasonic deposition for catalyst synthesis. The process of preparing the SimCoat ultrasonic sprayer for catalyst deposition will be explored so that future experimentation this fall can successfully produce the catalytic Au_{25} mono- and multi-metal clusters. These clusters' successful synthesis will be evaluated using transmission electron microscopy (TEM), mass spectroscopy (MS), ultraviolet-visible spectrometry and electrochemical voltammetry. Once synthesized, the CO_2RR will be run and any changes in activity or product distribution during the reaction will be evaluated. Due to time constraints, this study will assess the significance of ultrasonic deposition as well as evaluate prior experiments' usage of this technique in catalyst synthesis.

Introduction

Background on CO_2RR Research

The increasingly glaring impacts of climate change have sparked a surge of research into renewable energy in order to mitigate the effects of CO_2 emissions. The electrochemical CO_2 reduction reaction (CO_2RR) has drawn attention as a method of reducing CO_2 emissions because of its ability to be driven by renewable energy and economic potential.[1] The CO_2RR can convert CO_2 into compounds that can be used for other chemical syntheses or as components in hydrocarbon fuels.[1] The reaction can be thought of as a "multiple-electron reaction" which yields a variety of products and water.[2]

$$a\mathrm{CO_2} + b(\mathrm{H^+} + \mathrm{e^-}) \rightleftarrows \mathrm{P} + c\mathrm{H_2O} \quad (1)^2$$

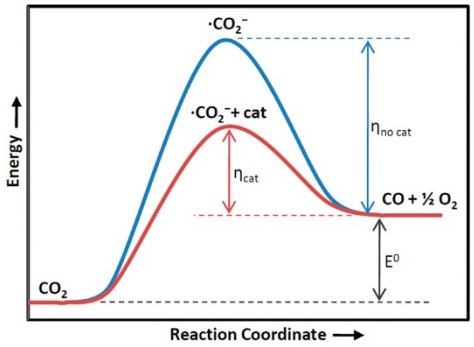
This can be seen in Equation 1 where *a, b,* and *c* are coefficients and P describes typical products resulting from the reaction. Potential products include compounds such as carbon monoxide (CO), formate (HCOO-), methane (CH_4), ethylene (C_2H_4), and ethanol (C_2H_5OH).[3] The coefficients, among other factors, affect the types of products which form. For instance, past studies have determined that the primary product of the reaction where *a* is 1, *b* is 2, and *c* is 1 is carbon monoxide (CO).[2] Reaction selectivity towards ethylene and ethanol products in particular have been explored in detail because of their economic value.[4]

Research into CO_2RR dates back to the 1980s, and while studies into the reaction have proved encouraging, there is still investigation that needs to be done.[4] Further exploration into reaction catalysts, intermediates, and reactor designs are necessary to best maximize CO_2RR's potential in combatting the climate crisis.[1] For instance, while it is known that CO_2RR can harness renewable energy to produce carbon-neutral fuels, such experimentation has only been demonstrated in the laboratory.[5] More advancement is needed before this reaction's benefits can be harnessed commercially, which would include the ability to yield products at a high formation rate, be highly selective, perform at a low cell potential, and do so for long periods of time.[5] There is no CO_2RR electrolyzer that currently meets these requirements.[5] The ultimate goal of future studies is thus for CO_2RR to become a technology utilized to curtail climate change that can transition society to renewable energy.[1]

High Overpotentials and Intermediates

Attempts to increase energy efficiency in CO_2RR experimentation are met with challenges because of the reaction's high overpotentials.[1] Such overpotentials are thought to be caused by the "formation of a $\bullet CO_2^-$ radical anion intermediate" during the reaction's rate-limiting step.[1] This can be seen in Figure 1 where the $\bullet CO_2^-$ radical anion is illustrated at the transition state, and the blue line displays the reaction without a catalyst whereas the red line displays the reaction with a catalyst.

Figure 1. Energy Diagram for CO_2RR



Energy diagram for CO_2RR taken from the Whipple article.[1] Catalysts can lower the energy of the intermediate (as demonstrated by the red line), thereby increasing the reaction's energy efficiency.

As demonstrated in Figure 1, the challenges created by these high overpotentials can be reduced by employing a catalyst to stabilize the intermediate. These catalysts can be optimized according to the Principle of Sabatier, which states that the optimal catalysts "have intermediate adsorbate-surface bond strengths."[1] In other words, the binding energy of reaction intermediates determines catalyst efficiency.[6] An intermediate must bind strongly enough to the catalyst so that the reaction can occur, but not so strongly that the products formed cannot desorb from the catalyst's surface.[6]

CO_2RR electrolytes have been shown to be another method of stabilizing the intermediate.[1] Electrolytes can act as cocatalysts such that the electrolyte's effects on the pH and CO_2 concentration near the electrode can control the course of the reaction.[7] For instance, due to the reaction's dependence on pH the electrolyte can either stabilize the $\bullet CO_2^-$ intermediate or inhibit its formation.[2] Optimal reduction systems thus must consider the nuances of the interactions between the reactants, catalyst, and electrolyte in CO_2RR.

Past Research on CO_2RR Catalysts

In order to take place, CO_2RR requires a catalyst which both activates the CO_2 molecule and controls product selectivity.[3] Past research into CO_2RR demonstrates that the reaction is feasible with metal electrocatalysts, including copper (Cu) and gold (Au) electrodes.[8-9] While copper "has the unique capacity to catalyze C−C coupling," past studies have demonstrated that copper is unselective because it can yield "up to 16 different products."[3] Such products include a variety of aldehydes, ketones, and alcohols, demonstrating the reaction's complexity.[2]

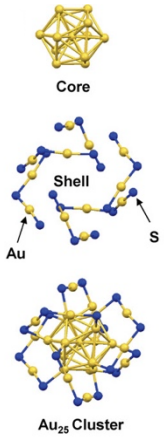
Catalyst design also must take into account the main competing reaction of CO_2RR: hydrogen evolution. As a result, catalytic "metals with high hydrogen overpotentials typically give the highest Faradaic efficiencies."[1] In contrast, past studies suggest that catalysts "with low hydrogen overpotentials" can increase energy efficiency by reducing the amount of hydrogen evolution.[1]

Similarly, researchers have demonstrated that catalysts which are alloys of two or more metals can benefit "the onset potentials" that control product formation.[2] Thus, alloy catalysts can yield products "that both metals separately cannot produce in detectable amounts."[2]

Au_{25} Mono- and Multi-Metal Clusters

While the use of alloys as catalysts presents an interesting venue for future investigation, this research into ultrasonic deposition is aimed at using atomically precise Au_{25} mono- and multi-metal clusters as catalysts. A 3-dimensional model of these clusters can be found in Figure 2.

Figure 2: Structure of Au_{25} Clusters



Structure of the Au_{25} clusters including their core and organochalcogen ligands taken from the Kauffman article.[10]

These clusters contain stabilizing organochalcogen ligands and have been previously studied in catalytic reactions because of their intermediate size "between molecules and larger nanoparticles."[10] Past studies have found that decreasing the size of the Au nanoparticles caused current density to increase and "faradaic efficiency toward CO" to decrease.[2] This is thought to be the result of an increase in the number of "undercoordinated sites."[2] Other research into their structure suggests that gold nanoparticles' edge sites "can facilitate the formation of CO while the corner sites are active sites for hydrogen evolution."[11]

These clusters also differ from traditional gold surface catalysts because of their ligands' stability. This stability is the result of the "unique –S-Au-S-Au-S- bonding motif in the cluster shell," which protects the ligands from deterioration during the reduction reaction.[10] Furthermore, unlike traditional nanoparticles, atomically precise nanoclusters "exhibit strong quantum confinement effects due to [their] ultrasmall sizes."[10] This makes the Au_{25}-based clusters' size optimal for both instrumental analysis and quantum chemical calculations that can help determine the mechanism of CO_2 reduction.[11] Thus, these clusters were chosen based on their stability, high activity, and gold's previously observed high selectivity in reducing CO_2 to CO.[10]

Therefore, this study will investigate the set-up and operation of an ultrasonic sprayer in creating CO_2RR catalysts. With respect to the methodology, the SimCoat ultrasonic sprayer was assembled and its settings set to the parameters of the experiment. The sprayer path was designed using the PathWrite software and then coded into the Simrun software. The sprayer was test run using a solution of isopropanol with carbon black as ink so that the system is ready for use in catalyst synthesis. While it was planned to synthesize the catalysts and run the reaction this

summer, given the time constraint of six weeks, this synthesis and the reaction will be carried out this fall. The methodology that will be used is summarized in the following section.

Experimental Methods

Ultrasonic Spraying in Catalyst Deposition

In order to synthesize the organochalcogen-ligand-stabilized Au_{25} based mono- and multi-clusters, a SimCoat Ultrasonic Sprayer was employed. Before the catalysts can be utilized during CO_2RR in a fuel cell apparatus, a membrane electrode assembly (MEA) must first be fabricated. Methods of creating the MEA include air spraying, ink jet printing, and decal transfer among others.[12] While all of these methods have their benefits, ultrasonic spray deposition is an attractive laboratory technique because it uses small amounts of material and its ability to be automated improves reproducibility.[12] Ultrasonic nozzles convert high frequency sound waves into mechanical energy, which is then transferred into the experimental liquid and creates standing waves.[13] As a result, when the liquid leaves the nozzle tip, the ultrasonic vibrations break it into a mist of uniformly-sized, atomized droplets. This is distinct from pressure nozzles which simply force liquids through a small hole at high pressures to create a spray. Ultrasonic nozzles thus have a tighter drop-size distribution than pressure nozzles, resulting in more uniform coating and thinner layers.[13]

Ultrasonic deposition allows the catalyst layers to be comprised of a "continuous network of ionomer," in this case, the Nafion and the catalyst.[12] This layer encourages the transfer of protons between the polymer electrolyte membranes (PEM) and the catalyst.[12] Additionally, these catalyst layers contain a network of pores in order to promote the transfer of reactant gases to the catalysts and the expulsion of water product.[12] Once the catalyst-coated membranes (CCM) are formed correctly, they are made into an MEA by sandwiching them between gas diffusion media (GDM), which contain layers of both macroporous and microporous carbon fibers.[12] Such layers are necessary to expel water product from the catalyst layer and promote heat transfer.[12] Lastly, in order to utilize the MEAs in a fuel cell, they are surrounded by gaskets which protect the catalyst layers from damage due to compression.[12]

The SimCoat Ultrasonic Sprayer

Previous experimenters have used ultrasonic spray deposition to form platinum and carbon catalyst layers on the PEM. The cathode and anode catalyst layers that are on opposite sides of the Nafion PEM form the CCM.[12] During this formation method, the anode and cathode catalyst layers are deposited onto the Nafion membrane. This was done by employing the SimCoat Ultrasonic Sprayer (See Appendix 1). This apparatus consists of an adjustable head that holds the ultrasonic nozzle. The head is controlled by the Simrun software which dictates conditions including spray height, speed, and the pattern the sprayer follows. A heated vacuum plate was retro-fitted to sit beneath the nozzle head so that the Nafion membrane can both be warmed to prevent expansion and contraction as well as held in place (See Appendix 2). The sprayer apparatus also includes a 25 mL syringe, plunger, and syringe pump which controls the flow rate of the ink being sprayed onto the PEM (See Appendix 4). The 120 kHz frequency atomizer nozzle shapes the catalyst ink droplets into a spray pattern with a median drop size of 27μm (See Appendix 5).[13]

Acrylic Mask Creation

An acrylic mask was 3D-printed in order to fit the vacuum plate's specifications and include openings to allow for the precise spray of the catalyst on the Nafion membrane (See Appendix 3). A 3-D printer was chosen to create this because of the durability of its materials. The optimal temperature at which the vacuum plate must be maintained to secure the Nafion is between 80 – 90˚C.[12] The acrylic mask is made out of polylactic acid (PLA) whose melting point (150 – 160˚C) enables it to withstand the temperatures required for catalyst deposition.[14] Furthermore, the acrylic mask's material was carefully chosen so that it would be compatible with chemicals used in the ultrasonic deposition such as isopropanol, ethanol, and acetone. PLA is insoluble in these materials, so it meets this requirement.[14]

Designing the Spray Path

The catalyst spray pattern was designed in PathWrite and consists of two 50 mm x 50 mm squares of path. The paths are comprised of 1 mm wide lines spaced 1 mm apart in a zig-zag pattern. Each square is sprayed twice to ensure uniform coating. According to past research, it is recommended that both squares be sprayed first before a second coating is begun.[12] This allows the first square time to dry before the second coating is deposited. The program has thus been written in PathWrite to accommodate this (See Appendix 6). Once the Pathwrite program is complete, both its path and position files must be downloaded onto the SimRun software. The machine commands including the opening of the isolation valve, the trigger of the pump, and the trigger of the ECHO generator are then manually coded.

Testing the Deposition

The ultrasonic sprayer apparatus was tested with both isopropanol and a solution of isopropanol with carbon black ink. This was done by placing a piece of cardstock (which functions as the Nafion in this case) under the acrylic mask and on top of the vacuum plate. The heating element was not turned on. The acrylic mask was aligned so that the two deposition squares are centered on the cardstock. The syringe was loaded with 17.5 mL of isopropanol and inserted into the syringe pump. The flow rate was set to 0.75 mL per minute.

Before testing the deposition, the nozzle stall point must be determined. This was found to be 0.5 W, meaning the nozzle should always operate around 1.5 W (the leveling-set point). Then, the deposition is started by first priming the liquid path. The nozzle is left de-energized until the isopropanol just reaches its aperture. It took about 3.39 mL of isopropanol to be released before it reached the nozzle's aperture. At this point, the ultrasonic generator is turned on to 1.5 W so that the spraying commences and follows the pre-coded path.

This same procedure was followed for the solution of isopropanol with carbon black ink. The solution consisted of 20 mL of isopropanol with about 3 small particles of carbon black dust for color. This solution was then sonicated for 30 minutes before being loaded into the syringe. This solution was used in addition to the straight isopropanol so that the range of the spraying path would be visible against the white cardstock. In this way, the success of the ultrasonic spraying set-up and the generated path could be evaluated.

Results

It was intended to run the reaction in a fuel cell and spectroscopically analyze the catalyst clusters, however due to time constraints only tests of the catalyst deposition were completed. The following are the results for that portion of the experiment.

Coating with the Isopropanol/Carbon Black Solution at 5 cm Nozzle Height

Figure 3: The acrylic mask with the deposited carbon black solution on the cardstock.

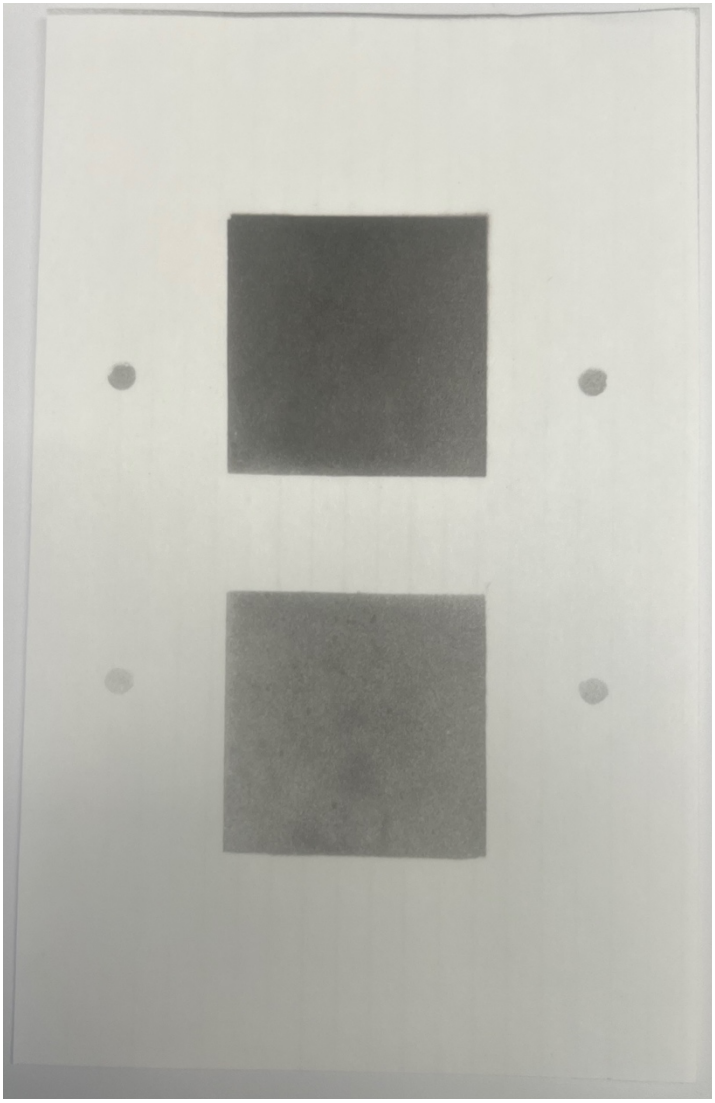


Figure 4: The cardstock with the deposited carbon black solution.

Coating with the Isopropanol/Carbon Black Solution at 2 cm Nozzle Height

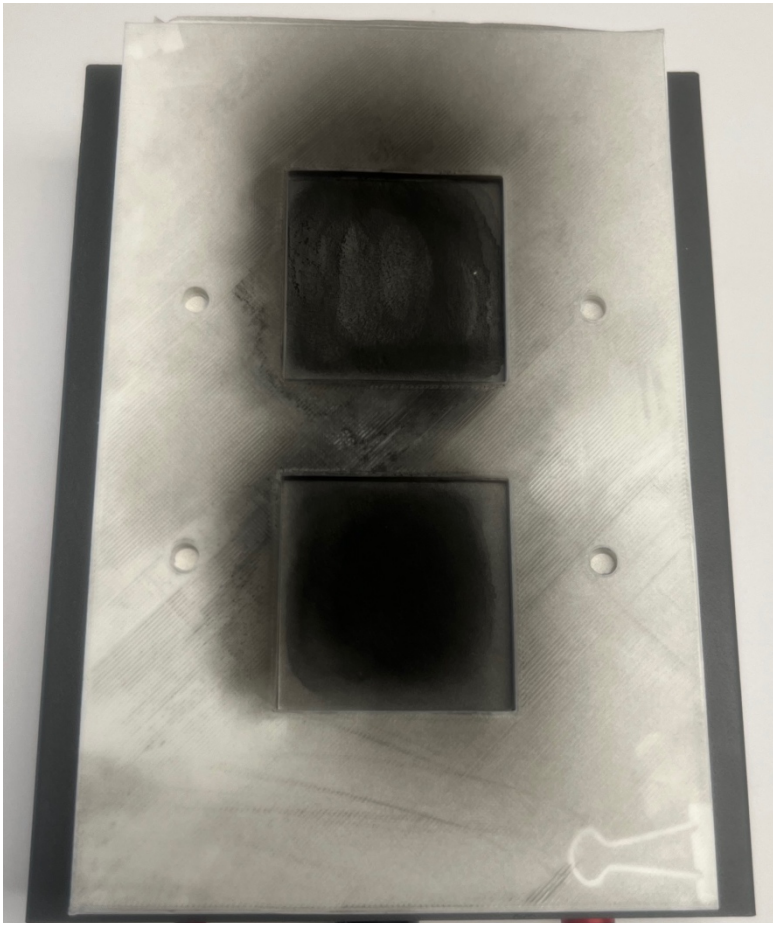


Figure 5: The acrylic mask over the cardstock on the vacuum plate with the deposited carbon black solution.

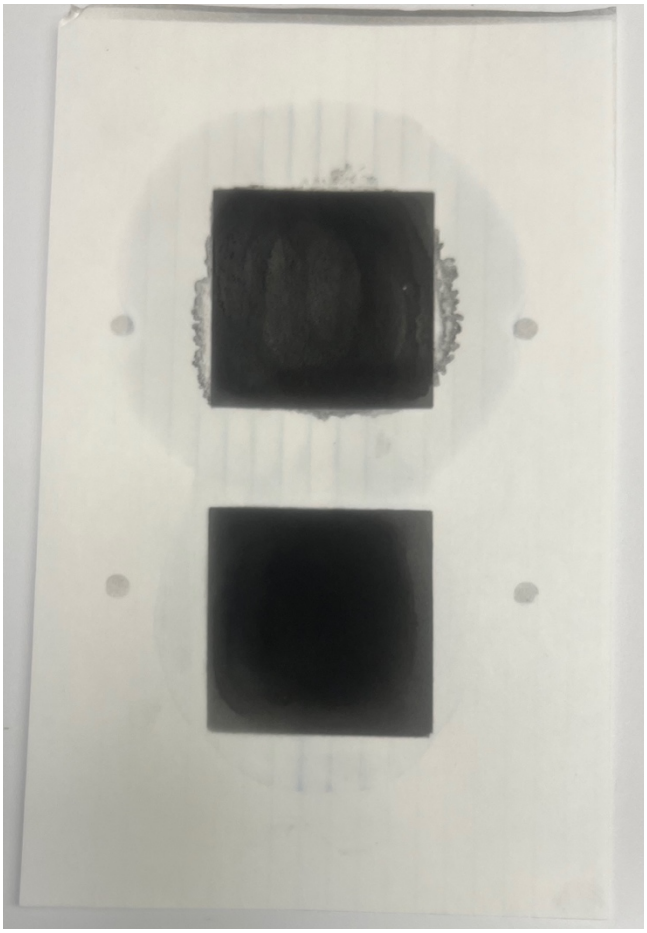


Figure 6: The cardstock with the deposited carbon black solution.

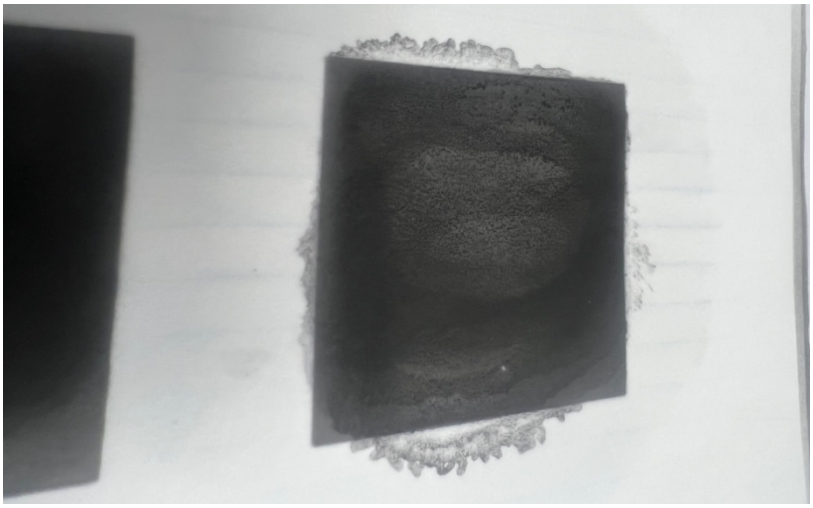


Figure 7: This is an enlarged image of the top square in the deposition on the cardstock.

Discussion

As the catalysts were not synthesized this summer, this discussion will analyze the results of the test-runs performed. Although these were not performed on Nafion membrane, they can nonetheless shed light on what ultrasonic deposition of the catalyst may look like. Additionally, assessing the SimCoat's performance during these test runs as well as the successes and failures in each deposition, can reveal how operating procedures must be altered before the experimental catalyst is synthesized and used in a fuel cell.

The Nozzle Height

A visual comparison of the images from both test runs illustrate the much darker, concentrated deposition when the nozzle height is 2 cm as opposed to 5 cm (see this in Figures 4 versus 6). Both of these test-runs were operated for the same amount of coatings (4 total coatings on each square) and employed the same concentration of isopropanol and carbon black solutions. As such, the primary distinguishing factor between the concentration of the depositions appears to be the nozzle height. Since Figure 6 illustrates the nozzle spraying 3 cm closer to the cardstock than in Figure 4 the range of the spray decreased and thus more isopropanol and carbon black solution was deposited in the square deposition areas as opposed to the acrylic mask and other places in the hood. This is also reflected when comparing Figures 3 and 5. While in Figure 3 the carbon black solution coated most of the acrylic mask with excess spray, the test-run at 2 cm (in Figure 5) contains less spray outside the deposition area. The excess spray on the acrylic mask in Figure 5 is prevalent in a square-like region surrounding each deposition square, whereas in Figure 3 the excess spray coats the mask indiscriminately, the largest portion of which is in the top half of the mask. This comparison also demonstrates that once the nozzle was lowered, it more precisely sprayed in the deposition squares rather than spraying the entire acrylic mask with solution, a portion of which stuck to the deposition squares.

However, while this lowered nozzle height had benefits for the precision of the spray and the reduction of waste, it has implications for the future success of the catalyst deposition. Past studies have found that the optimal nozzle height is between 5.0 and 6.4 cm because this gives the solvent more time to evaporate before reaching the PEM, thereby reducing the number of surface cracks.[12] In contrast, nozzle heights of 3.5 cm and below have been found to contain more cracks which are the result of excess solvent being present in the ink as it is deposited onto the PEM.[12] When this solvent eventually evaporates, it does so from the PEM, causing the surface to deform and crack.[12] These cracks can affect electrochemical performance during CO_2RR. For instance, research indicates that current density is lower for catalysts deposited at 3.5 cm or less as compare to those deposited in the 5.0 to 6.4 cm range.[12] This is thought to be the result of the cracks hindering the removal of water at higher current densities.[12]

While this cracking cannot sufficiently be observed in this experiment because cardstock as opposed to the Nafion membrane was used, it is still important to note this tradeoff between a more precise nozzle spray and potential cracking when depositing the catalyst in the future. Likewise, it also must be noted that while cracking cannot be accurately observed on the cardstock, the lower nozzle height saw carbon black solution seep into the region outside of the deposition squares. This can be seen in Figure 7 where the excess solution outside of the square region as well as the larger isopropanol stain are apparent. This did not occur at the nozzle height of 5 cm as shown in Figure 4. At the lower nozzle height this may be due to the nature of cardstock when it gets wet, however it is still worth noting that the lower nozzle height leads to a

more saturated deposition and could thus lead to spreading outside of the target region if the vacuum plate is not properly engaged.

Also important to note is that other than potential cracking, nozzle height has not been shown to cause any different in the thickness or porosity of catalysts deposited on Nafion membranes.[12] If the ink formula is left unchanged there should not be an expected difference in the catalyst layer network for different nozzle heights.[12]

Aside from the excess spray and ink spreading, the SimCoat machine successfully sprayed the deposition squares where the catalysts are intended to be. As such, ultrasonic deposition will be a reliable technique and more precise than other methods such as air spraying when depositing catalysts this fall. This deposition method also increases the experiment's reproducibility as the catalysts used will follow an identical spraying path and thus the experiment will be more controlled. Overall, this will yield a more effective PEM for usage in the fuel cell.

Fume Hood Exhaust Vacuum

The decision to perform a test-run at a lower nozzle height was both the result of the need to test different heights for catalyst preparation and because of the fume hood exhaust system. During the test-runs it became evident that the vacuum was too strong for the sprayer to overcome. In other words, much of the spray was lost to the back of the hood as it was sucked out by the exhaust. This is illustrated by there being more spray in the top deposition squares in both Figures 4 and 6 as well as more excess spray in the top sections of the acrylic mask in Figures 3 and 5 as opposed to the bottom squares and regions. This can have implications for catalyst synthesis when the experiment is run in the fall. Specifically, if more catalyst is deposited on the top-most square than on the bottom-most square because of the vacuum pulling more of the spray to the back of the hood then the catalyst-coated membrane that will be used in the electrochemical fuel cell will be uneven. This could affect the results' accuracy as not all catalysts would be of the same design.

Future work may improve this by building a box around the SimCoat machine to aid in shielding the sprayer from the fume hood's vacuum. This would lessen the amount of spray sucked into the hood and thus result in a more even deposition of the catalyst onto the Nafion membrane. Once these concerns are addressed, the SimCoat machine is ready to be used for catalyst deposition and thus analysis of CO_2RR in the fuel cell.

Future Directions

Given the time constraints, there is much that needs to be carried out so that CO_2RR can be further evaluated this fall. With the ultrasonic deposition system capable of depositing the catalyst given the results of the test runs, the next steps would involve catalyst creation and running the reaction.

The catalysts solutions must be synthesized and inspected spectroscopically. Techniques that can be used to confirm their successful synthesis include transmission electron microscopy (TEM), mass spectroscopy (MS), ultraviolet-visible spectrometry, and electrochemical voltammetry. The rationale for this examination is two-fold. First, it is important that the correct identity of the catalyst is confirmed before running it through the fuel cell under reaction conditions. Second, this initial assessment will establish a baseline that the post-reaction catalyst can be compared to so that any changes during the reaction become evident. For instance,

characteristics that will be evaluated include the catalyst clusters' size, composition, and molecular-like properties.

In terms of studying the course and products of CO_2RR, an EC flow-cell with an in-line mass spectrometer can be utilized. The decision to use an EC flow-cell is based off research that has shown that EC flows cells provide an optimal environment for studying the reduction of CO_2. Specifically, flow cells enable the experimenter to operate under ambient conditions and have "direct control over surface free energy."[7] Similarly, the in-line mass spectrometer enables one to determine the product distribution. As described in the introduction, a variety of products can result from CO_2RR, so establishing catalyst selectivity is critical to this experiment. The mass spectrometer provides a method for this.

Another method of running the reaction can include performing CO_2RR in an in-situ IR flow cell. This would allow for the intermediates during the reaction to be identified and quantified. As previously mentioned, there are many intermediates that have been theorized for CO_2RR (including the $\bullet CO_2^-$ radical anion), and more experimentation is needed to determine the mechanistic details. Thus, comparing results from an in-situ IR flow cell and an EC flow cell with an in-line mass spectrometer can reveal how different intermediates give rise to different products.

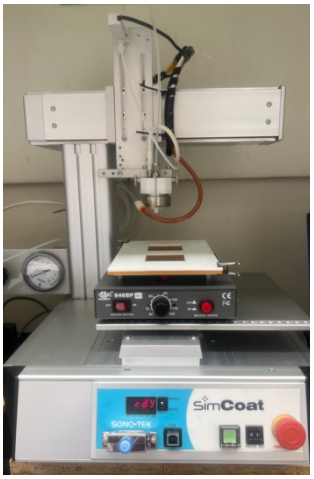
Once the reaction is completed, a second round of spectroscopy will be performed. This will include techniques like the previously performed TEM, ultraviolet-visible spectrometry, and electrochemical voltammetry. Any apparent changes to the Au_{25} catalyst clusters will be examined. Based on this, it will be determined whether the clusters contain their initial ligands and are CO_2 reduction active. In addition, depending on the type and quantity of the organochalcogen ligands remaining, it will be evident how the ligands have an effect on CO_2 reduction activity.

Conclusions

Therefore, the study of CO_2RR has implications not only for the field of electrochemistry but also the larger world affected by climate change. The reaction requires the usage of a catalyst, which has been the subject of much investigation given its effect on product selectivity and the efficiency of the CO_2 reduction. A method of preparing the catalyst for usage is ultrasonic spraying. The results highlight the success of ultrasonic deposition in catalyst deposition. Specifically, the test-runs demonstrate the precision of the spray in the deposition squares as well as the uniformity of the deposited layers. It can be expected that similar results would occur when the intended catalyst ink solution is used in the SimCoat sprayer. While the apparatus can proceed to deposit catalyst layers as it currently exists, several concerns must be addressed before proceeding with deposition in the fall. This includes retro-fitting a box for the SimCoat to reduce the pull of the fume hood exhaust vacuum on the machine's spray. Once this is completed, the nozzle height can be adjusted to balance concerns regarding both potential cracking and excess spray. In doing so, future experimentation can produce the catalytic Au_{25} mono- and multi-metal clusters necessary to perform CO_2RR. As such, due to the time constraints of this experiment only the significance of ultrasonic deposition and prior investigations into this technique were assessed. The plan is to proceed with research by synthesizing the catalysts, spectroscopically verifying their production, running the course of CO_2RR in fuel cell, and spectroscopically analyzing the catalysts for a second time.

Appendix

1. The SimCoat Ultrasonic Sprayer. Note that the machine is in the ready position and has the vacuum plate with the acrylic mask on its mobile platform. The vacuum plate was secured onto the mobile platform so that the new spraying area dimensions (the top of the vacuum plate) correspond with the dimensions in the Pathwrite software (which is preprogrammed according to the mobile platform's dimensions).

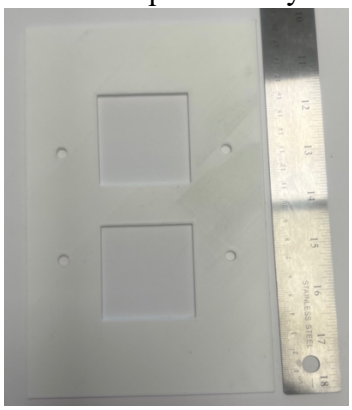


2. The vacuum and heating plate. Note that these images contain the acrylic mask on top of the plate.

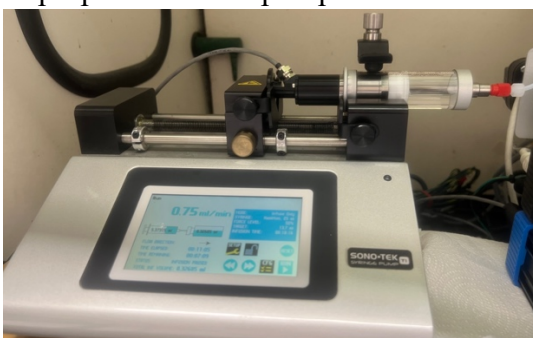
a) side-view

b) top-view

3. The 3-D printed acrylic mask.

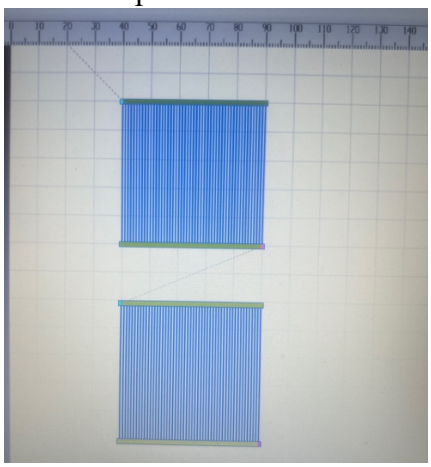


4. The syringe and syringe pump. Note that in this image, the syringe is loaded with 13.7 mL of isopropanol and the pump is set to a 0.75 mL/min infusion rate.



5. This is the complete set-up for the ultrasonic deposition including the syringe, syringe pump, ultrasonic generator, ECHO generator, the SimCoat machine, vacuum plate and acrylic mask, and the connected laptop with the SimRun software displayed.

6. The spraying pattern on the PathWrite software. The path consists of two squares of length 50 mm comprised of 1 mm wide lines arranged in a zig-zag pattern. These squares are aligned with the two square-shaped openings in the acrylic mask, allowing the mask to serve as a stencil on the Nafion membrane. The nozzle is instructed to traverse from the bottom right corner of the top square to the top left corner of the right square at which point it begins the second square's deposition. Once one round of spraying is complete, the software has been instructed to complete another deposition for a total of two coatings on the two squares.



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