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Carbon Dioxide Reduction on Large Area Liquid Metal Gallium-indium Electrocatalysts

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J. William Fulbright
College of Arts & Sciences
Fulbright College Honors Program

Carbon Dioxide Reduction on Large Area Liquid Metal Gallium-indium

Electrocatalysts

An Honors Thesis submitted to fulfill the requirements for Honors Studies in Biochemistry

By Thomas Hollis

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Biochemistry, B.A.

The University of Arkansas

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Introduction

Greenhouse gases contribute to global warming through the burning of fossil fuels. These greenhouse gases, such as CO₂, reflect infrared rays back on to the earth, warming the planet's overall temperature. The carbon dioxide reduction reaction (CO₂RR) is widely studied to reutilize CO₂ to useful products, including methane, ethane, and carbon monoxide. This project studies the use of liquid metal gallium-indium as an electrocatalyst to perform CO₂ reduction to carbon monoxide (CO) or possibly solid carbon in various solutions. Gallium-indium is characterized and studied through its "wetting" properties and adhesion to substrate foil through the measurement of contact angles inside solution. These liquid metal adhesion qualities mirror the study of "hydrophobicity and hydrophilicity" of water. Through the use of mechanical polishing, gallium-indium interfaces with copper to demonstrate more favorable adhesion forces. In conditions without water present, gallium-indium reduces CO₂ to CO at voltages less than - 2.25 volts and performs comparably to other known CO₂RR catalysts that are more expensive, such as gold. Although solid carbon CO₂RR was not discovered, the high catalytic rates suggest its importance as a catalyst for CO production. With the introduction of water to the electrolyte, hydrogen evolution occurs as a competing reaction, limiting the rates of CO production.

Background

Carbon dioxide (CO₂) has been studied for its properties as a greenhouse gas and contribution to global warming. It is produced in mass as a waste product from the burning of fossil fuels. Greenhouse gases lead to the earth's continued heating as it does not allow heat to escape the earth's atmosphere as easily. To eliminate this gas from the atmosphere is a highly proliferative process that can result in very useful products such as carbon monoxide and carbon. Carbon can be used as a fuel source or be repurposed in the ground for storage. Developing approaches for the electrochemical reduction of carbon dioxide (CO₂) into other compounds such as methane, ethylene, and solid carbon is critical for storing renewable electricity as sustainable fuels or developing new approaches to green materials like plastics. More importantly, coupling conversion processes that remove CO₂ from the air are extremely important for combatting anthropogenic climate change. Carbon monoxide (CO) serves as a valuable gas and as a feedstock for the industrial production of alcohols and hydrocarbons. By eliminating CO₂ from the atmosphere, sustainable fuel can be created while also recycling carbon as an energy source.

CO₂ reduction is one process used to break CO₂ molecules apart into their substituent components. These forms can include solid carbon (C) or carbon monoxide (CO) with oxygen (O₂) as a byproduct. CO₂ reduction can be performed under many conditions. Electrochemical methods can be performed in both aqueous and non-aqueous conditions. The production of CO is commonly studied using a substrate such as gold. By applying this electrochemical bias, the splitting of CO₂ becomes more favorable, and CO is released as a product. While gold is widely known as an effective electrocatalysis, its continued use over large scale industrial methods is quite expensive. A more affordable metal needs to be found that can achieve comparable rates of CO₂ reduction. Additionally, solid metal electrodes can erode and lose surface interactions

over long periods of time. Self-regenerating electrodes such as liquid metal catalysts are a possible solution to prevent electrode erosion.

Literature Review

Reduction-oxidation (redox) reactions involve electron transfer and exchange that occurs between molecules. As one ion donates electrons (oxidizes), another ion gains electrons (reduces). This process can occur naturally or under the influence of an electrochemical bias which changes the direction of a reaction. By application of an electrochemical bias, one can donate or remove electrons to perform specific chemical reactions. This causes usually a metal ion to change its oxidation state by the addition and subsequent removal of an electron. Electrochemistry can also be used to separate redox reactions to only have electron transfer without the recombination of products.¹

To study the nature of reduction-oxidation reactions, one must know the predetermined redox potential. Redox potentials are known values that quantify how much voltage needs to be applied for a particular molecule to be reduced. This known value can vary drastically between different molecule types but knowing how much voltage is needed to transfer electrons is crucial when performing electrochemical reactions. The reduction potential can influence the equilibrium of a reaction, favoring the direction of electron transfer when a voltage is applied. Power sources such as batteries are able to deliver this charge on the most basic level, but one can control this more precisely with an instrument like a potentiostat. A potentiostat device is able to deliver exact voltage amounts over a specific period of time. These operations include cyclic voltammetry and chronoamperometry.

To know the exact potential or “voltage” needed, one can relate the known standard potential to the actual reduction potential of the reaction. The Nernst equation defines the

relation between the Gibbs free energy and the potential of an electrochemical reaction as seen in equation 1.

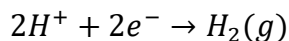
Equation 1

$$\Delta G = -nFE$$

While the Gibbs free energy may partially favor the spontaneity of one reaction, the electrochemical bias lowers the reaction intermediate energy (activation energy), causing the reaction quotient to proceed.²

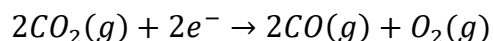
A known process of electrochemistry is hydrogen evolution reaction (HER), which is a well-studied reaction and is used as a standard potential to define other reaction potentials. The standard hydrogen electrode (SHE) is the commonly used reference for most chemical reactions in electrochemistry.

Equation 2



CO₂ to CO has a reduction potential of -0.53 vs RHE and has to be performed cathodically. In this case, the reduction potential is a negative voltage applied. A reduction potential is the amount of energy needed to perform an electrochemical reaction in standard conditions. The electrochemical transfer can best be described in this equation:

Equation 3



There are two electrons transferred in the reaction of carbon dioxide to carbon monoxide. Reduction-oxidation occurs at surface of electrodes, causing carbon monoxide to be formed. This electrochemical bias results to conversion to carbon monoxide due to the electron transfer that is thermodynamically favorable.

When examining equation 3, one must realize this reaction does not occur spontaneously due to the positive ΔG of reaction. From literature, if CO_2 has a ΔG of formation of -394.4 kJ/mol, CO has a ΔG of formation at -137.4 kJ/mol.³ By subtracting reactants from the products, this equates to a total ΔG of reaction of 514.2 kJ/mol, making this reaction non-spontaneous at room temperature.

Electrocatalysis occurs on an electrode surface in an electrochemical reaction, and this allows the organization of the reaction to make the reaction occur more quickly or at lower energy levels. An example of this reaction is a platinum electrode surface, which facilitates the formation of hydrides easily. Platinum performs poorly when attempting to reduce CO_2 , as these surface hydrogen atoms prevent the binding of CO_2 to the surface. Gold, however, does not form hydrides and easily participates in the reaction that reduces CO_2 to carbon monoxide. Another consideration is the concentration used, as the rate of reaction is highly dependent on concentration of the solution of interest. With aqueous solutions, the water concentration will be much higher than any dissolved carbon dioxide. This competing reaction of interest will affect the catalytic rates of reaction.

Electrocatalysis allows one to use a potential difference between electrodes to drive endergonic (work or energy storing) reactions that do not occur spontaneously, or would occur very slowly. Spontaneous reactions are those that occur without the addition of energy, and products are formed that are in a more energetically favorable state than the reactants. The reduction of CO_2 does not occur spontaneously and is an endergonic process, meaning energy input is needed to break apart this molecule. Electrocatalysis is additionally useful as it creates a clear separate boundary through the use of a membrane. Membranes that separate on the basis of charge help eliminate products from reducing or oxidizing on the opposite electrode.

The three-electrode setup establishes a working electrode, a counter-electrode, and a reference electrode. The reaction of interest occurs on the working electrode, where electrons flow through the electrode surface. As mentioned previously, the electrode material, such as various precious metals, can be varied to influence certain reactions. This area of study usually encompasses experiments that test how much potential is needed to perform the reaction of interest, usually reaching a point that achieves the overpotential, the required amount to drive the reaction.

Some catalysts like Au are known to be effective at binding CO₂ to facilitate reduction to CO, as the surface does not bind hydrides nor rebind to CO. Other elements like copper reduce CO₂ to other useful products in the industrial field. Copper additionally does not bind to the products produced, such as methane and ethane. Many of the CO₂RR products from copper form polygenates, polymers, and other long chain hydrocarbon fuels.

Electrochemistry is needed to convert CO₂ into other products like CO. CO₂ molecules are unlikely to change naturally without the input of energy, and the use of electrochemical methods allows CO₂ gas molecules to break apart into its substituent components. This endergonic process occurs due to the transfer of electrons on the surface of the electrode. Electrochemistry is essential for this conversion, as CO₂ requires an electron donor to change the oxidation state of the carbon atoms, facilitating release of one of the oxygen atoms.⁴

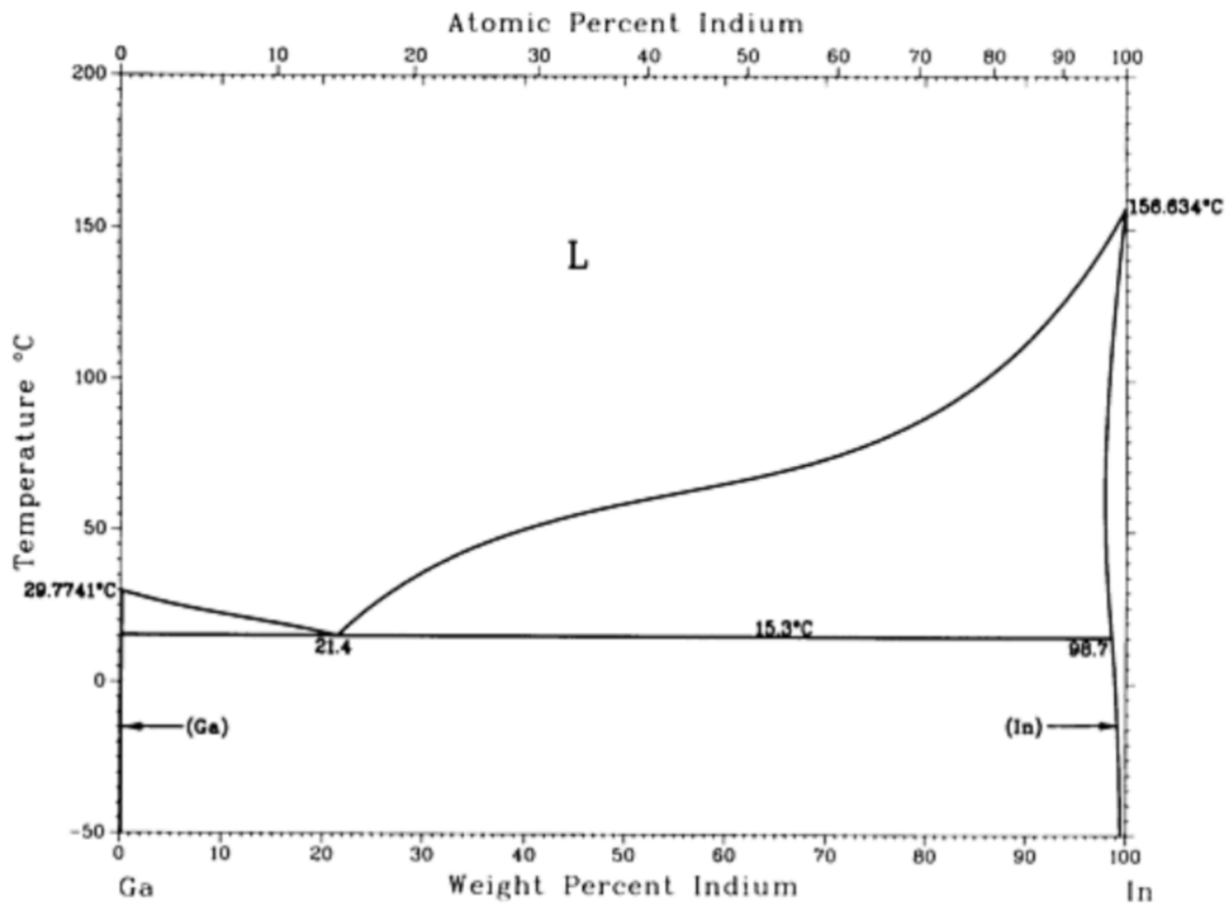
The ability to reduce CO₂ to solid carbon is a relatively newly studied process, and is useful for closing the coal cycle and sequestering carbon to be used or potentially reburied. This process has been studied and reproduced at very high temperatures using a molten salt reactor. In certain conditions, these molten salts have been utilized to create solid carbon. These carbon capture techniques utilize the same principles of preventing global warming to establish useful

products such as graphene and nanotubes. By using a molten salt electrolyte, such as lithium carbonate, carbon dioxide is broken down at these extreme temperatures and quickly converted into solid carbon. However, an issue with this method presents itself, as carbon produced quickly deposits itself on the surface of the electrode, limiting access to further reduction.⁵

New methods may suggest the use of liquid gallium-indium to achieve the creation of solid carbon. One method of room temperature CO₂ to C reduction utilizes a gallium-indium-tin catalyst, also known as Gallinstan, which occurs on a liquid metal drop electrode, occurring with an embedded Ceria catalyst.⁶ Gallium-indium (Ga-In) has the unique property of existing as a eutectic composition, where a certain ratio of these elements results in them existing as a liquid at room temperature even though they are solid in their elemental states. At a mass ratio of 75.5/24.5%, gallium-indium becomes a liquid alloy. A eutectic is a composition in which a certain ratio of the materials lowers the overall melting temperature. In this case, this eutectic composition is able to exist as a liquid metal at room temperature.

Gallium-Indium Eutectic Composition:

Figure 1: Phase diagram demonstrating melting point of gallium-indium at various atomic compositions



ASM Metals Handbook Vol 3: Alloy Phase diagram⁷

This liquid metal is important to serve as a support for electrocatalysts and conductor that can exist in solution with other ions. Although the liquid metal does not dissolve in solution, important reactive properties occur at the surface boundary of the liquid metal. The advantage of the liquid metal is understated in everyday applications, but the goal is to create a regenerative surface area able to rotate fresh ions to the surface while the experiment is running. Liquid metal catalysts can also adapt to the nature of their substrate. By controlling substrate and liquid catalyst interactions, one can use the most favorable interaction to expand the substrate over a large surface area. Other liquid metals such as mercury have been used to facilitate CO₂ reactions in unique ways, such as combination with nickel compound, like Ni(H) species. These can lead to efficient reactions at higher applied voltages in aqueous solution.⁸

To expand on this technique of gallium-indium based CO₂ reduction, the subsequent experiments address the ability to extend the liquid gallium-indium (Ga-In) based electrode by altering the surface structure of underlying metal substrates. Through this technique, one can implement larger surface area electrodes, allowing for more catalysis over time. Additionally, this project investigates gallium-indium as an inert electrode in the various electrolytic solutions, such as polar solvents (acetonitrile or dimethylformamide) or other solvent mixtures that include water. Through these techniques, one can uncover if Ga-In is a good electrocatalyst by itself. Lastly, we attempted to reproduce ceria-catalyzed formation of solid carbon on the extended gallium-indium electrodes.

Section 1

To adapt the substrate to a large surface area, it is important to characterize the interactions of gallium-indium with the substrate. Previous research regarding the wetting of Ga-In for other applications has not quantified the wetting interactions of this liquid metal.⁹ Numerous studies have researched the hydrophilic and hydrophobic surface interactions with water.¹⁰ At an interface, water has a tendency to self-adhere and resist generation of additional surface area. This resistance is the surface tension, measured as the energy required of generating new surface area per unit area. For water, this surface tension is 0.07275 J/m^2 at 20°C . This process is adapted to analyze the wetting properties of Ga-In on structured electrodes. However, rather than analyzing solid-liquid-air interactions, the Ga-In will be studied within solid-liquid-electrolyte.

For substrates, the various structured and roughened surfaces of copper were tested. Structured copper surfaces are created through electrodeposition in various acidic and basic solutions to create a dendritic or planar surface that would improve the liquid metal-electrode surface interactions.¹²

To study the wetting properties of Ga-In, one can conduct contact-angle measurements, precise calculations that indicate the degree of adhesion to a copper substrate. These were conducted on several substrates in order to characterize which substrate allows the greatest degree of wetting, therefore allowing more surface area per volume of Gallium-Indium.

Materials Synthesis

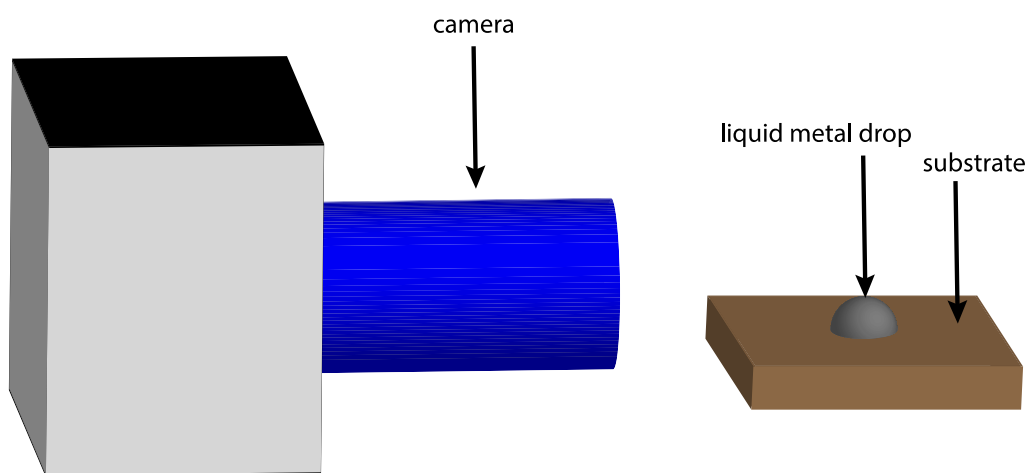
Firstly, materials were gathered and created for use in the subsequent experiments. Gallium-indium eutectic was created by calculating a mass ratio of the two elements based on the known ratio. (ASM Handbook). First, the components were massed before their

combination. For indium, the element was malleable enough to be “cut” into the various pieces. Although gallium has a low melting temperature, gallium was needed to be heated using a hot plate and massed appropriately. The indium was then melted within the gallium to create the eutectic that remained liquid at room temperature. Copper substrate samples were approximately 3cm by 3cm foils. Samples of copper substrate were created via electrodeposition. (Paper)

Methods used also include optical and electron microscopy to image the structure of the electrode surfaces. Contact angle measurements are established as an important approach for measuring the wetting properties of Ga-In eutectic electrocatalyst layers. By measuring the interior angle of the liquid drop to how it contacts a surface, a reproducible contact angle can be found over many replicates. These measurements and experiments were repeated under the same conditions with a camera/tank setup and contact-angle measuring imaging software (ImageJ), which can accurately measure the line shape of drops and therefore the contact angles between surfaces. The measurement of contact angles is a way to quantify the “hydrophobicity” of the liquid metal similar to the description of water wetting surfaces. The role of the surface tension of the liquid metal can be analyzed by varying the mass of liquid metal drops and applying force to the wetting process.

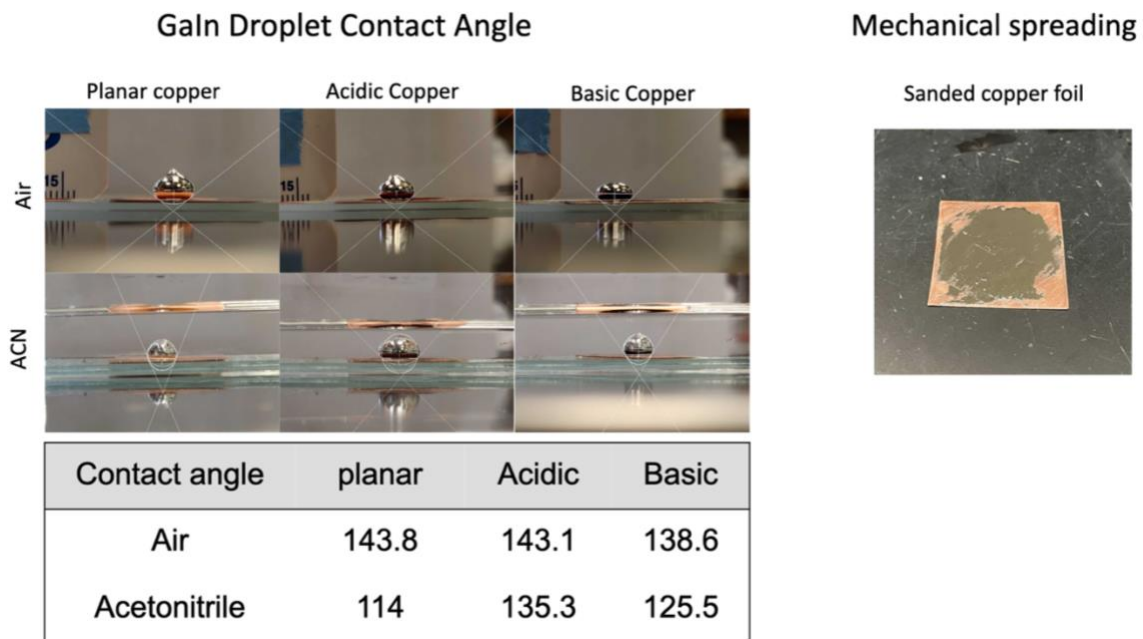
Experimental Setup

Figure 2: Representation of camera positioning used to photograph contact angle measurements



Comparison of various contact angles with the addition of solution

Image 1: Contact angle measurements were made using ImageJ software. The right image shows the effects of a mechanically sanded sample of copper with gallium-indium



Results X.1

From the experimental design established, an effective method of emphasizing the hydrophilic qualities of gallium-indium to substrate were established and used in subsequent experiments. From the figure, the contact angle measurement becomes more acute once in electrolyte solution versus just the air. This demonstrates that acetonitrile emphasizes hydrophobic-like qualities for the substrate and electrode sample. These qualities observed were not enough to completely demonstrate hydrophilic properties until testing on a mechanically polishes copper foil sample. The gallium-indium liquid metal still tended to adhere to itself, but when physically pushed around the sample, some gallium-indium tended to interact with the copper. This interaction allowed the gallium-indium to be spread more easily over the entirety of the sample rather than showing true drop like hydrophobic qualities. It is reasonable to surmise that this is most likely due to micro-scale interactions with the oxide layer here, as a sample that has not been freshly sanded will tend to behave adversely to gallium-indium.

Section 2

Electrochemistry of gallium-indium

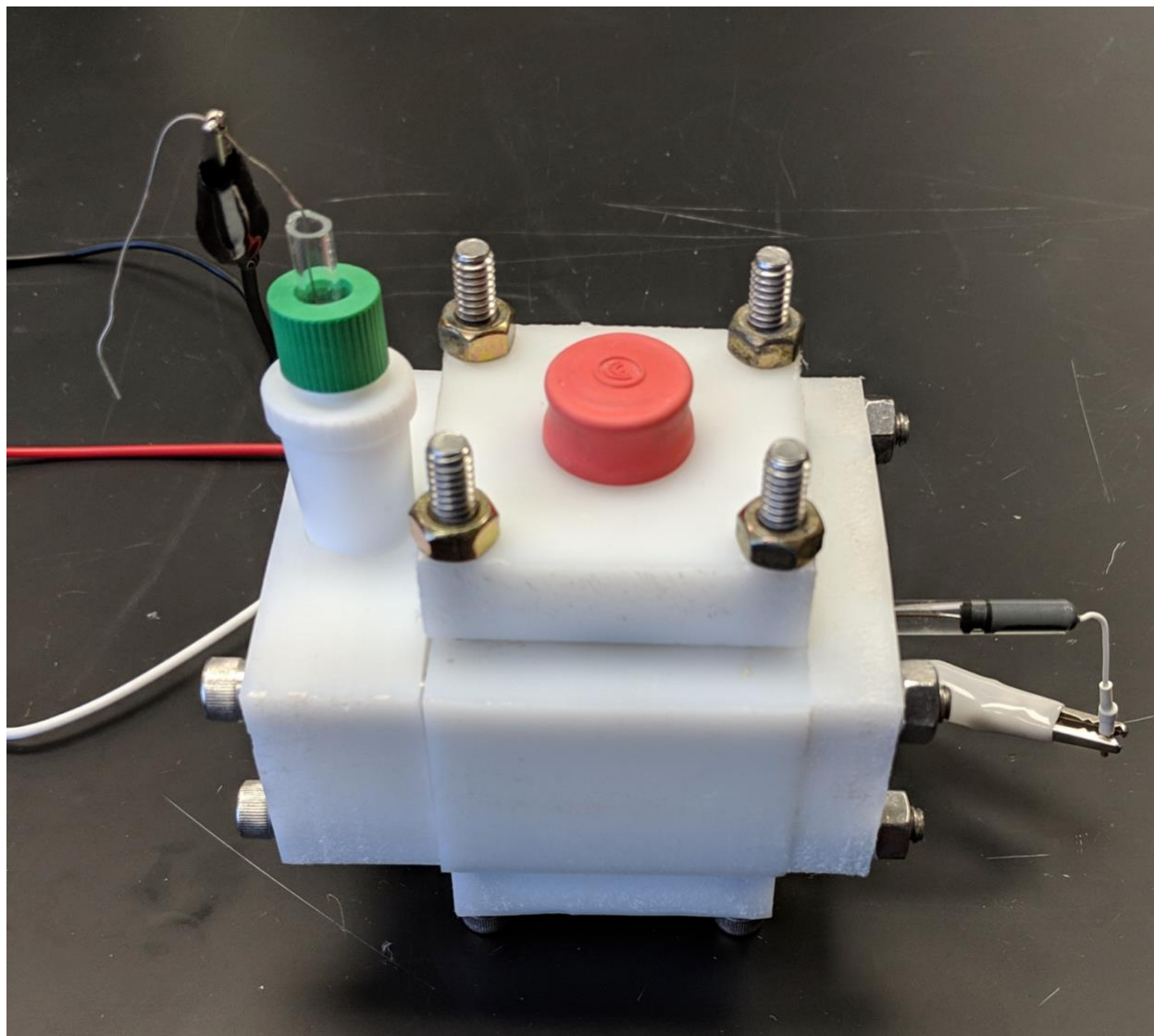
As noted previously, new methods suggest the creation of solid carbon creation via electrochemical methods at low temperatures. The novel process was reproduced and tested within the Coridan lab. To verify claims that is truly inert in the reduction of CO₂, Ga-In by itself is tested as an electrocatalyst.

Drop electrodes have been tested in the past, typically with other liquid metal electrodes, like mercury. These drop electrodes are the least effective utilization of surface area to mass,

and a method to spread this liquid metal over a large surface area would be entirely more effective.

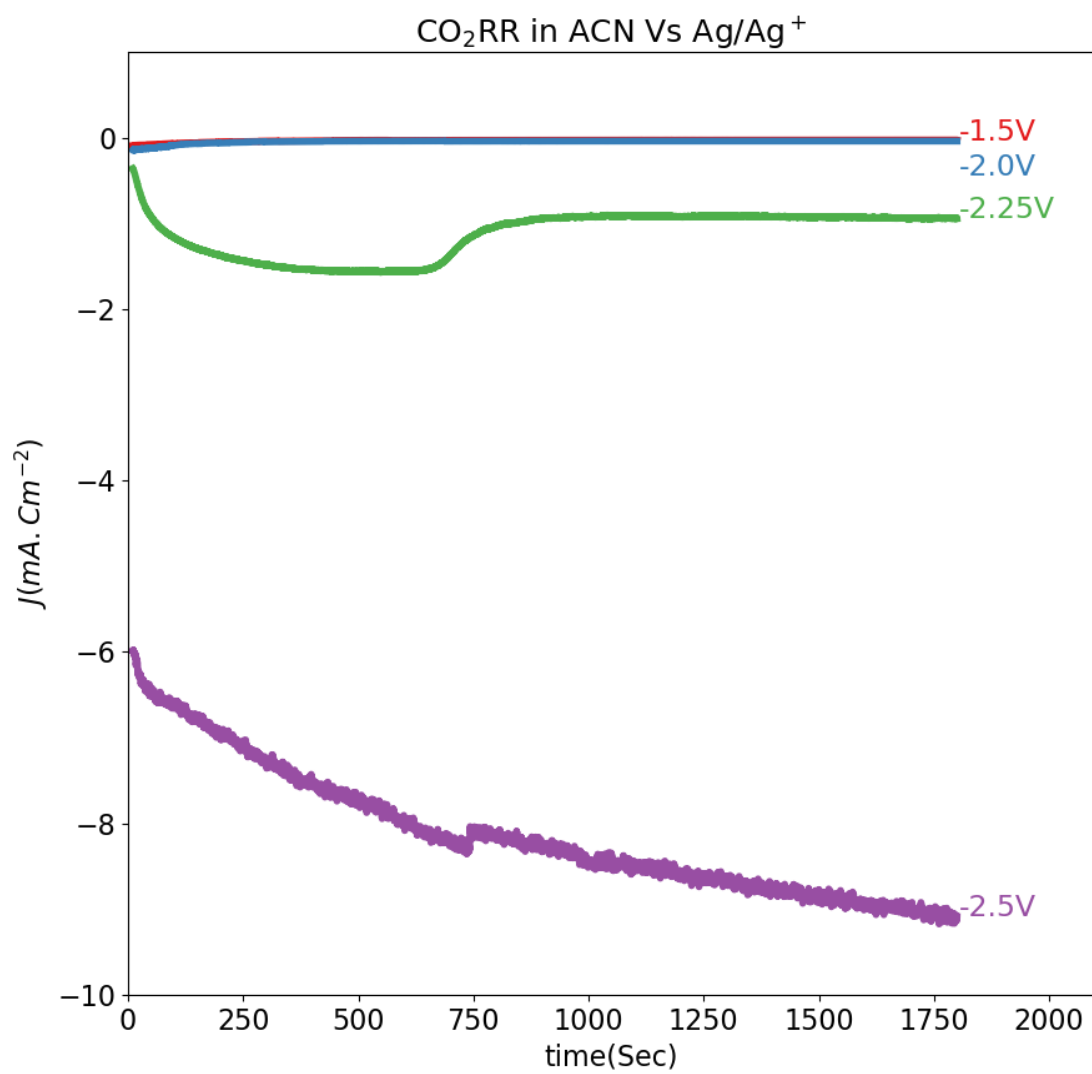
The experimental setup consisted of a cell consisting of three electrodes. The three electrodes help determine how much charge or voltage is delivered to the cell by measuring against a known reference electrode (in this case, a silver-silver⁺ or just silver pseudo-electrode). The main working electrode conducts through a copper substrate that is in contact with the gallium-indium, and the counter electrode (platinum wire) completes the circuit on the opposite side. Use of an anion exchange membrane (selemion) prevents recombination of products into their substituent components. The experimental cell was assembled and sealed from the atmosphere and purged with CO₂ for 15 minutes before performing each experiment. The potentiostat device delivers the required voltage to reduce CO₂. Methods of measurement include cyclic voltammetry (variable potential performed in replicates) and chronic amperometry (consistent potential over time). Gas samples were collected into the gas chromatograph which is able to identify the gases present within the cell's headspace. Different variables such as solution, membrane, electrodes, and charge passed were changed through the experiments.

Image 2: Three-electrode setup sealed chamber allows products to be precisely measured with gas chromatography



Acetonitrile with 100 mM TBABF as an electrolyte was first tested. Several different voltages were tested over the course of 1750 seconds to see which perform the reaction at catalytic conditions. The voltages tested were -1.5 V, -2.0 V, -2.25V, and -2.5V. This chronoamperometry performed by the potentiostat allows us to test at which rates CO is produced. Based on the results, CO begins to produce on gallium-indium at rates below -2.25 V. At -2.5 V, current is passed through the electrode with greater magnitudes, indicating higher rates of reaction. Based on the bubbles witnessed in solution of the electrochemical cell, one can assume that CO produced does not rebind to the surface of Ga-In very well. This can be verified by the gas chromatograph, which detects the gases present in the headspace of the cell. Clearly, gallium-indium is not inert in the CO₂RR.

Figure 3: Current over time using a solution of 100 mM TBABF in acetonitrile



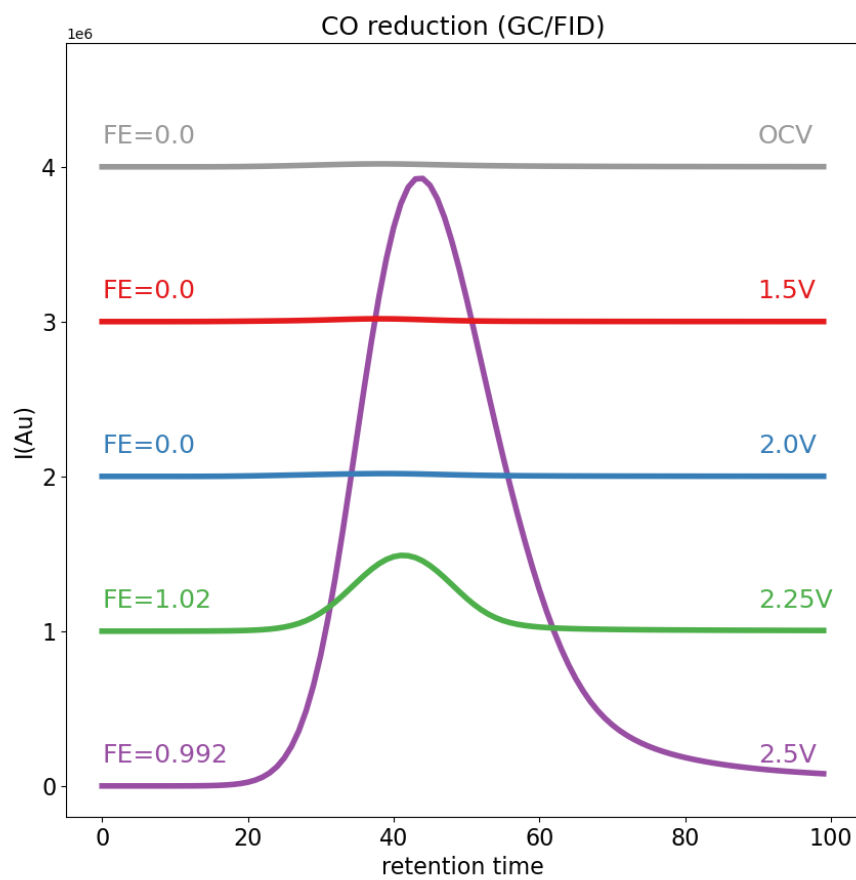
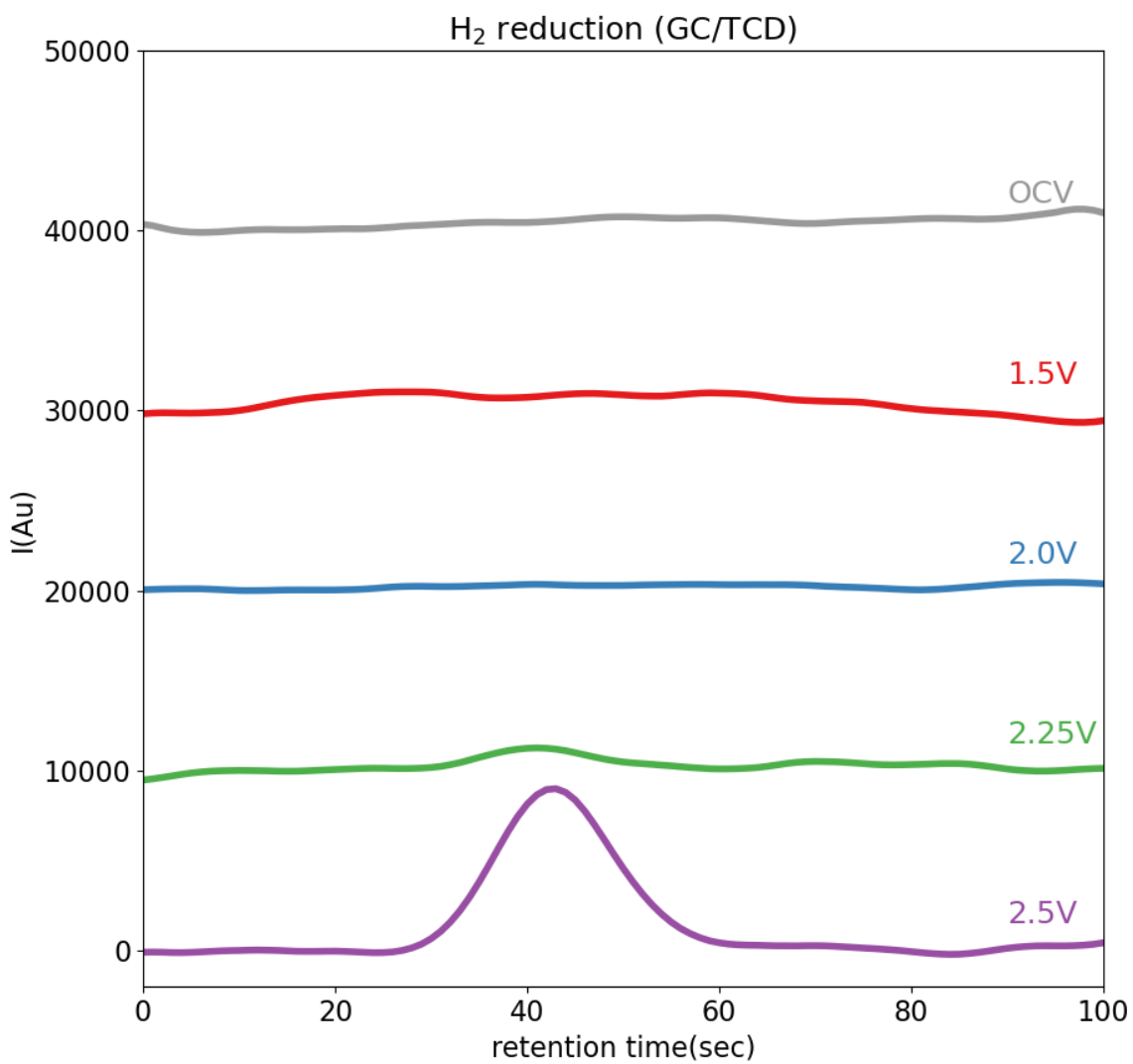
Gas Chromatography results:**Figure 4: Faradaic efficiencies of production of carbon monoxide with Ga-In**

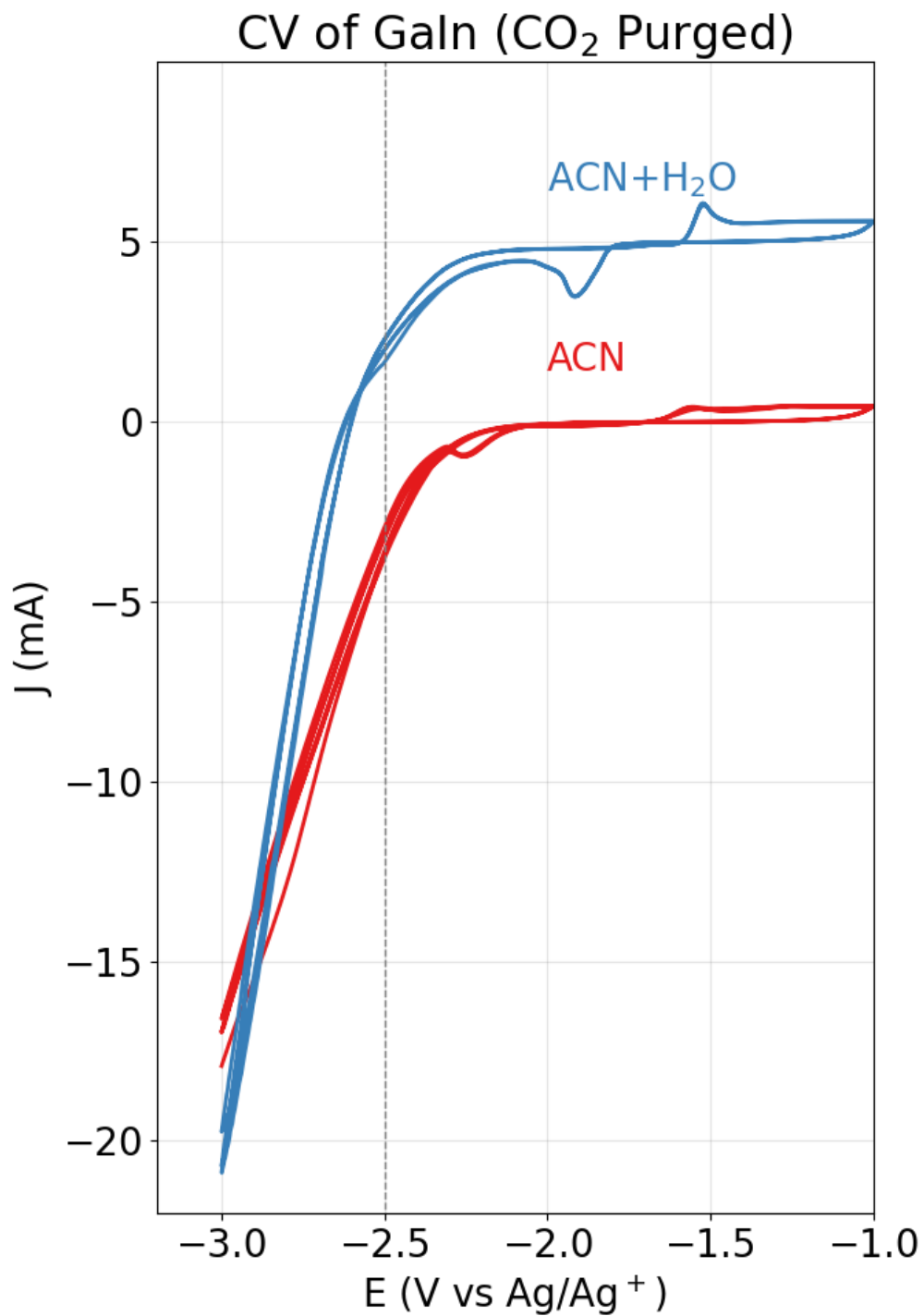
Figure 5: Production of hydrogen gas using gallium-indium. Very low results most likely due to atmospheric water contamination



Cyclic Voltammetry of Ga-In including water and without water

With these results verified in a system without water, it is important to see how catalytic rates vary over different potentials with the addition of water. Water was added to a solution of ACN and 100 mM TBABF at a 2.0 M concentration. Cyclic voltammetry was then performed with 3 replicates to establish which currents still facilitated beneficial CO₂ reduction. The addition of water may behave differently with the gallium-indium substrate and create unique products.

Figure 4: Acetonitrile solution with 2.0 M H₂O and 100 mM TBABF was compared to acetonitrile with only 100 mM TBABF



*ACN + H₂O is offset by 5 mA

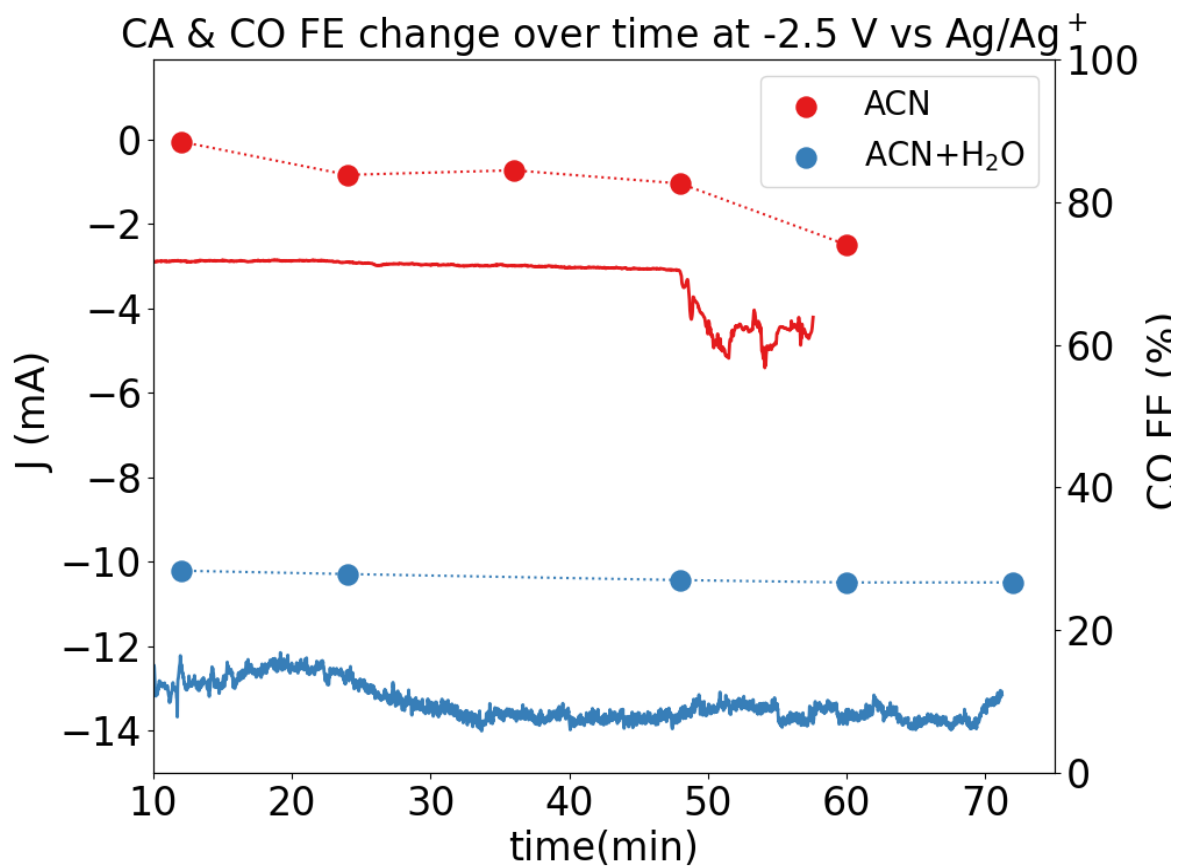
From the cyclic voltammetry performed, one can see the addition of H₂O leads to greater reduction and oxidation of the surface oxides, indicating the presence of water molecules binding on the surface of the electrode. To visualize these graphs clearer, they are offset by 5 mA. ACN and H₂O shows a steeper decline when performing the experiment at negative potentials below -2.5 volts (indicated by the dashed line). This sharper rate indicates higher rates of reaction, or that the reaction processes are occurring more quickly here. The difference in current density between the two experiments is nearly four times more with the addition of water. Additionally, the oxidation and reduction of the electrode surface occurs more prominently with the acetonitrile and water graph. The surface is reducing most likely as water facilitates the changing electrode surface easier.

When analyzing the faradaic efficiencies between the two experiments, one can see the faradaic efficiency is much higher for the experiment lacking H₂O. This is because H₂O acts on the binding sites of the gallium-indium eutectic, blocking CO₂ reduction on the surface. With only Acetonitrile in the system, these faradaic efficiencies are above 80% for the production of CO. This also shows less current being passed at around -2.9 mA. With the addition of water, the current is accelerated to -13 mA, however, much lower faradaic efficiencies occur. The production of CO compared to the current indicate much of the current passed contributed to the production of hydrogen rather than CO.

Acetonitrile does not form bicarbonate in this reaction non-protic. Acetonitrile works positively as there is higher CO₂ solubility in reaction with CO insolubility due to the presence of bubbles. With the addition of water in the system, a new pathway for hydrogen evolution occurs, negatively affecting rates of CO production.

Faradaic efficiencies and results of water introduction

Figure 6: Dashed lines represent Faradaic efficiencies while solid lines shows current passed

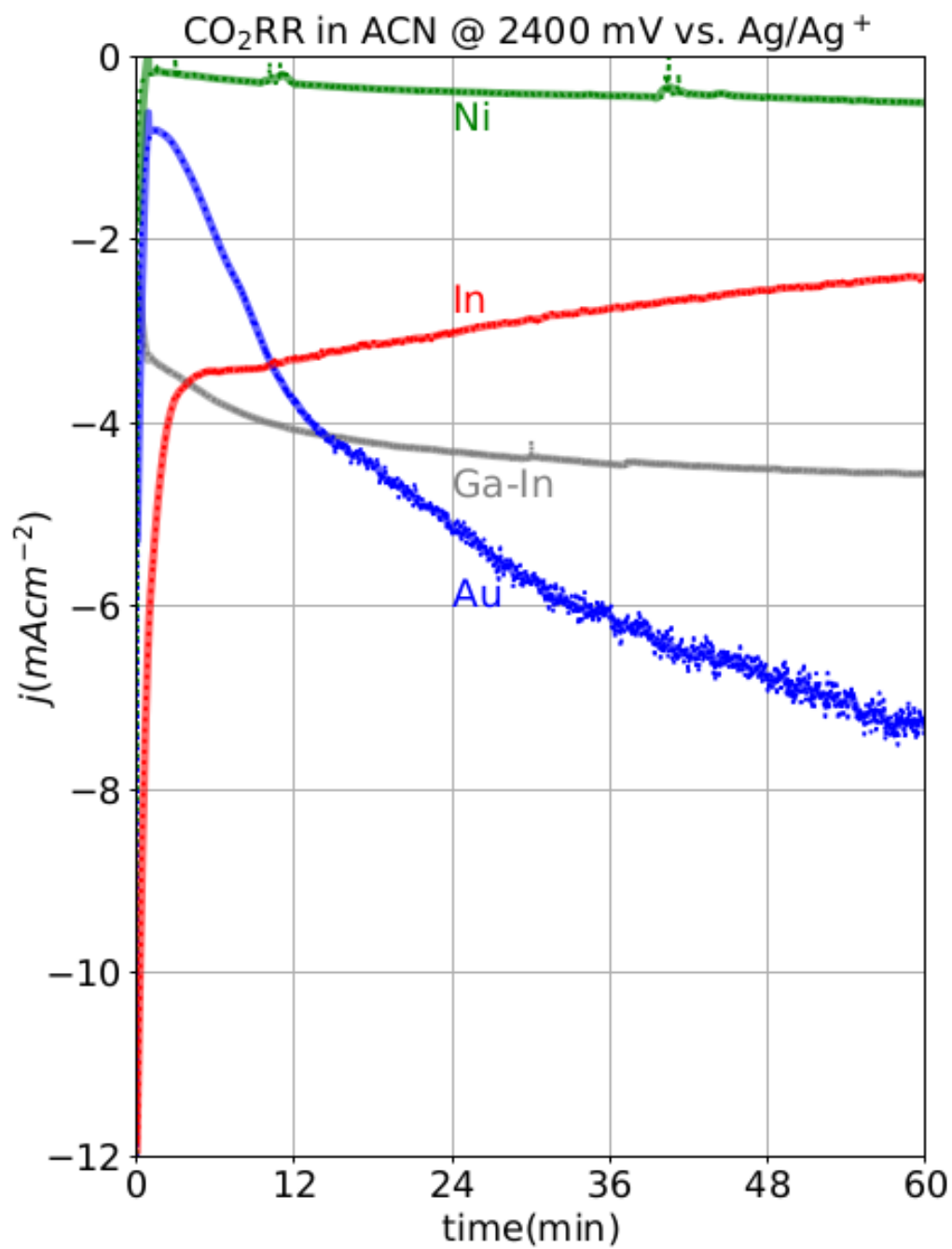


Comparing Ga-In to other electrodes

Next, different electrode samples were sourced and used as substitutes to test for CO₂RR. Nickel foil, indium foil, gallium-indium, and electro-deposited gold samples were all used in our experimental setup in conditions without water. Each sample was used as an electrode in the reaction, with gallium-indium and gold being held on a copper substrate material.

As mentioned previously, performance in CO₂RR can be evaluated by current densities which reflect the rate of reaction. Gold performed the best in the experiment, improving over the course of the experiment as the oxide layer is slowly removed. Gallium-indium performed second, with qualities that matched gold under 12 minutes in the experiment. The indium showed some reaction and current passed. The nickel sample hardly passed any current and was not participating in the reaction to reduce CO₂. From these results, we can conclude that gallium-indium almost performs as well as one of the best known CO evolution catalysts, gold, through a liquid metal interface.

Figure 7: Chronoamperometry of Ni, In, Ga-In, and Au electrodes



Gallium-indium with cerium with water

As a final test, gallium-indium was combined with samples of cerium. This was performed to verify claims of solid carbon using a cerium interface. The cerium was prepared through being finely ground and mixed with the Ga-In. This experiment was performed on a drop electrode with cyclic voltammetry performed to assess activity over a wide variety of potentials. Glass was used so the electrode could be clearly observed during the entirety of the experiment. Dimethylformamide solution was used as an alternative to acetonitrile. These conditions were chosen to replicate the ones done previously (Esrafilzadeh).

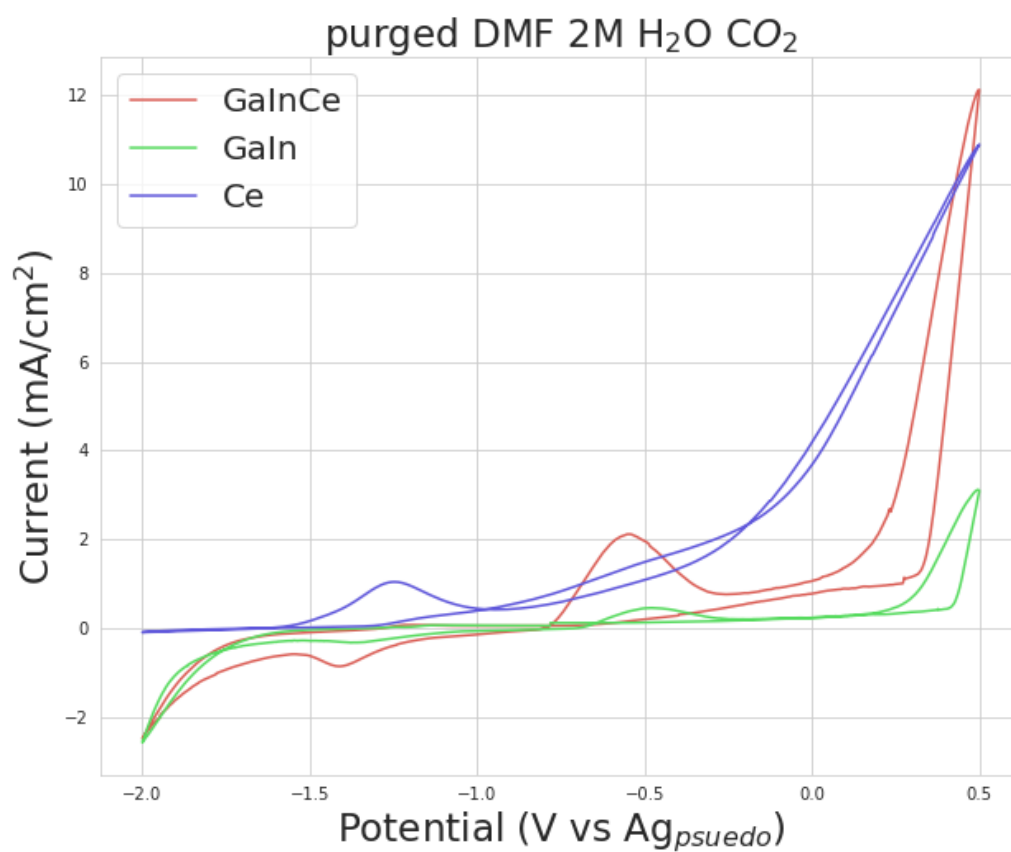
Figure 8: Cyclic Voltammetry comparing introduction of Ce to Ga-In sample

Image 3: Black residue formation on drop electrode surface

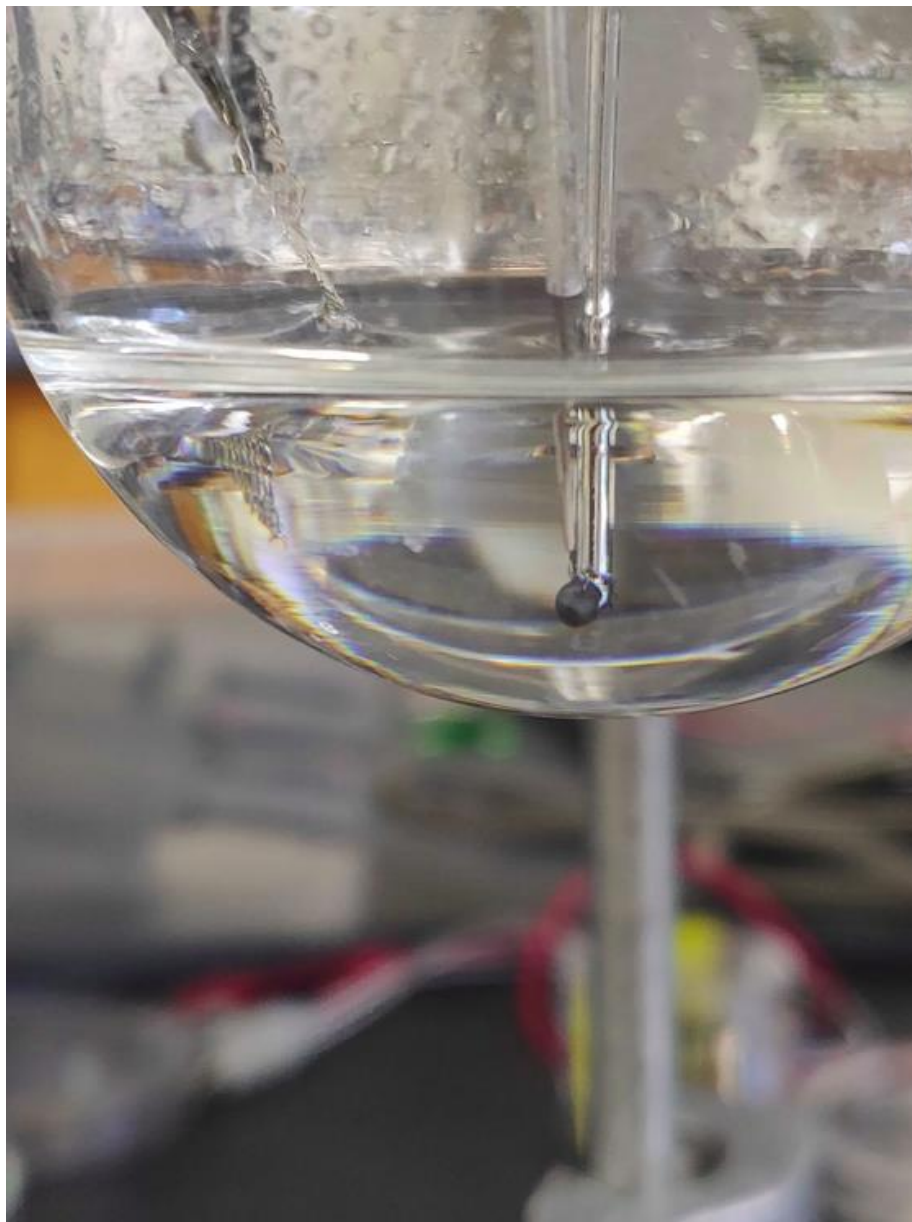


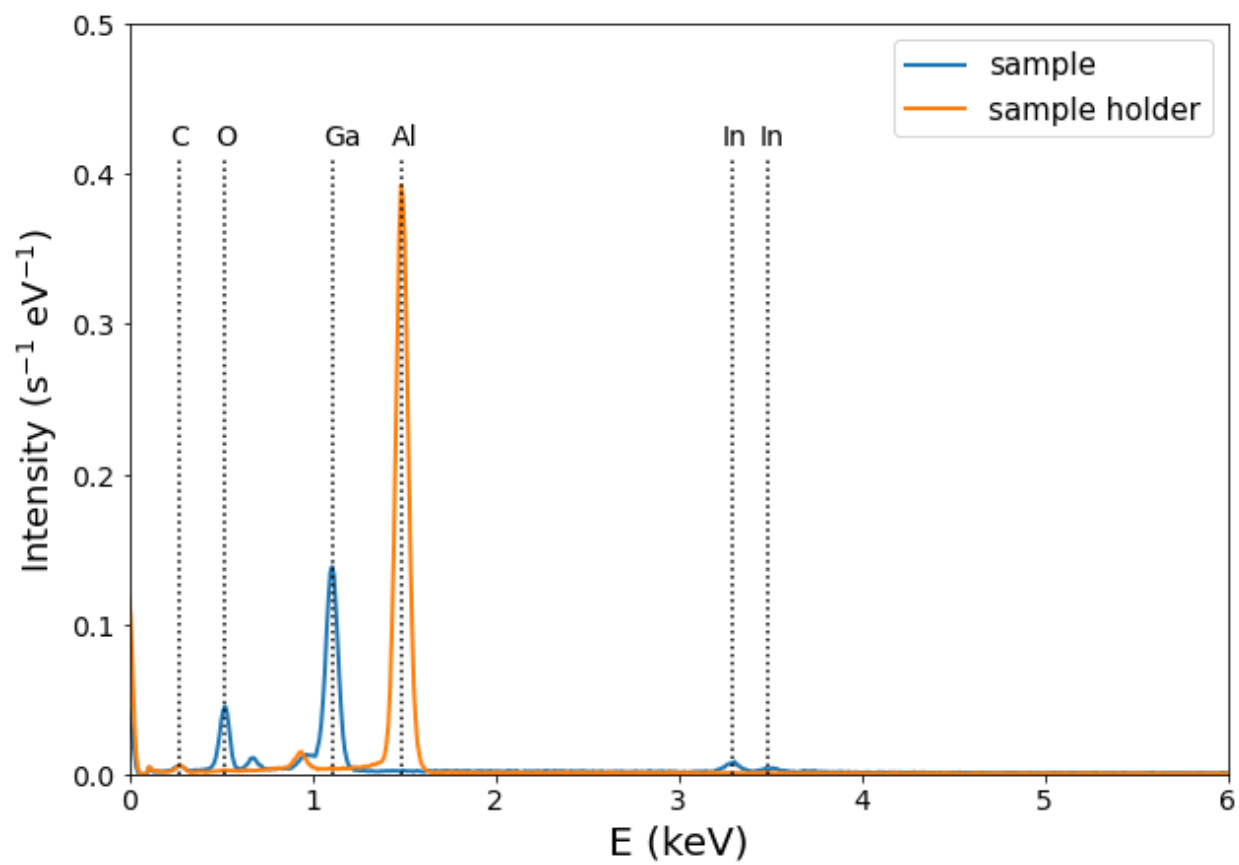
Figure 9: EDX analysis of black residue

Figure 10: Carbon presence analysis is not significantly more than baseline

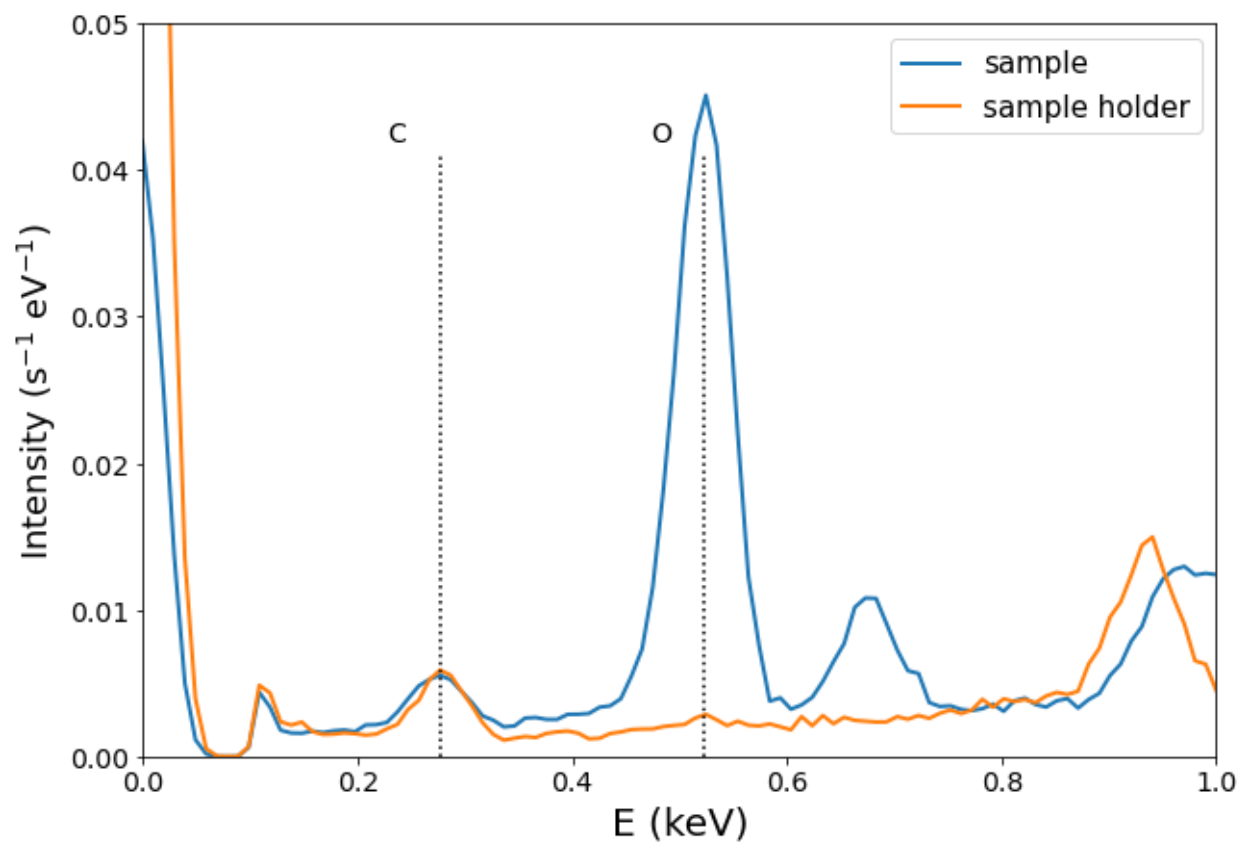


Image 4: SEM image of black residue on the surface of electrode

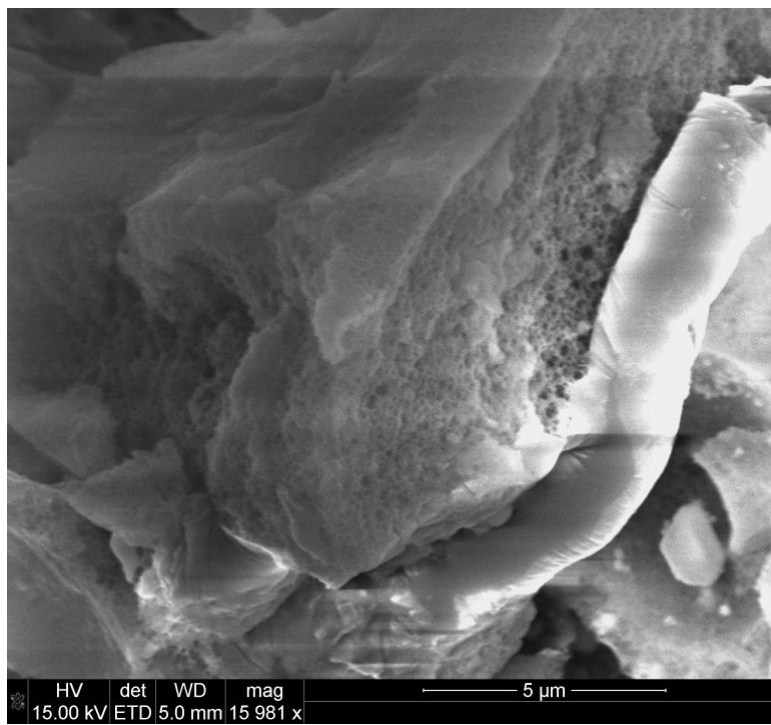
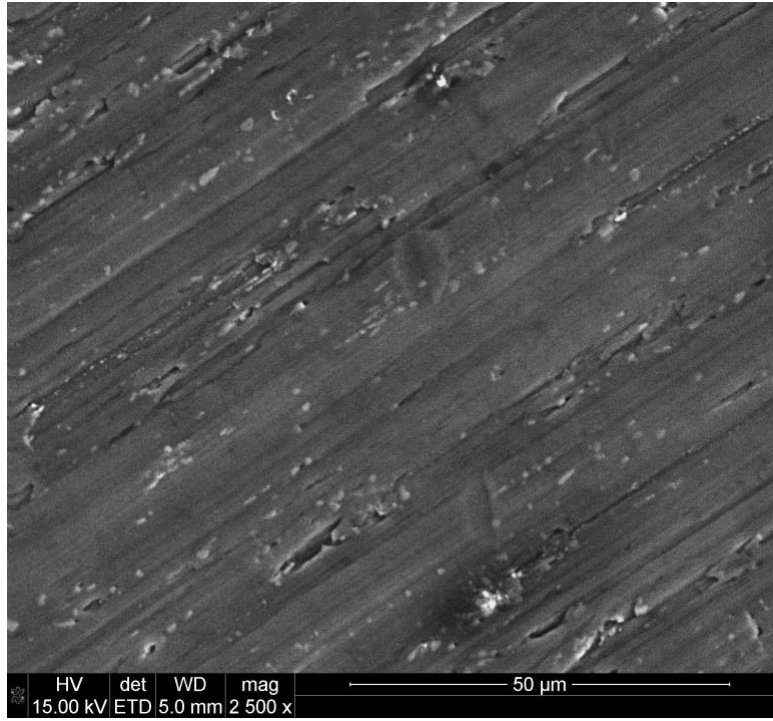


Image 5: SEM image of aluminum baseplate



Conclusion

Overall, activity for cerium was observed at higher, anodic potentials rather than cathodic potentials, where CO_2 reduction would occur. The observance of black residue could be observed forming at these anodic potentials, yet it cannot be concluded this was solid carbon residue. The black solid was observed forming both with and without the addition of cerium to the gallium-indium electrode. Additionally, the cerium sample alone was not active at any cathodic potentials, and gallium-indium with cerium performed similarly to only gallium-indium. This indicates cerium alone does not participate in the CO_2RR at all, as no activity occurs at these cathodic potentials. It can be concluded that gallium-indium is not inert in the CO_2RR as it induces bubbling on the surface and facilitates reduction to CO . When the black material was analyzed using EDX in a scanning electron microscope (SEM), only gallium, indium, and oxygen were found, with carbon only present on the instrument baseline levels. Observations on carbon formation using room temperature electrochemistry could not be reproduced, yet gallium-indium shows potential regarding its high rates of CO production.

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