DISCOVERY, TUNING, AND MECHANISTIC EVALUATION
OF TRANSITION METAL/GROUP 13 METAL ELECTROCATALYSTS
FOR CARBON DIOXIDE REDUCTION

Aubrey R. Paris

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Abstract

The anticipated negative impacts of climate change have prompted efforts to remove excess CO$_2$ from the atmosphere, as well as prevent it from reaching the atmosphere in the first place. Following capture from point emissions sources or directly from the air, CO$_2$ can be transformed into a diverse portfolio of carbon-containing products with both societal and economic value. Electrochemical reduction is an attractive means of converting CO$_2$ into these products, but catalysts capable of facilitating this chemistry are plagued by large energetic requirements, poor selectivities, or limited product distributions. Of all pure-metal electrodes, only copper generates a wide distribution of highly reduced, multi-carbon products, but initial reports of bimetallic catalysts indicate the possibility of unlocking copper-like catalytic behavior using alloys.

In this work, bimetallic alloy, intermetallic, and oxide species combining non-CO$_2$-reducing transition metals and Group 13 metals are studied for their electrocatalytic activity toward CO$_2$, emphasizing three different areas of development: (1) catalyst discovery, (2) catalyst tuning, and (3) mechanistic evaluation. Two new electrocatalysts are shown to produce multi-carbon chemicals from CO$_2$ and serve as formative case studies in higher-order product generation. Namely, a Cr$_2$O$_3$/Ga$_2$O$_3$ alloy produces oxalate in aqueous solution at unprecedented Faradaic efficiencies, overturning historically accepted mechanistic requirements, while the Ni$_3$Al intermetallic serves as the first non-copper-containing electrocatalyst capable of generating three-carbon products from CO$_2$. 

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Furthermore, tuning the intermetallic catalyst $\text{Ni}_3\text{Ga}$ is achieved by altering its carbon solid support and material structure. Carbon supports are demonstrated to exert morphological and surface compositional control over $\text{Ni}_3\text{Ga}$ during synthesis, thereby impacting reactivity toward $\text{CO}_2$ during electroreduction. This sort of tuning can be exploited in catalyst design or optimization efforts, as can an understanding of $\text{CO}_2$ reduction pathways activated by combining transition metals and Group 13 metals in electrocatalysis. Preliminary insight into this latter point is gained by studying a series of spinel oxides, which differentiate between $\text{CO}$- and formate-dependent $\text{CO}_2$ reduction pathways. Ultimately, the progress reported in each of these areas of catalyst development—discovery, tuning, and mechanistic analysis—motivates ongoing $\text{CO}_2$ conversion research and supports the goal of implementing $\text{CO}_2$ utilization strategies for profitable environmental remediation.
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I don’t know what the last four years would have been like if I didn’t have Bryan Kudisch in my life. Bryan, I knew you were a true partner in crime ever since Florida, given your willingness to strategically plan theme park trips and watch (dare I say, enjoy?) National Treasure. From our Ghost Adventures marathons to watching Giants games together, in person or at the ballpark, I’ve been grateful for every moment. Your
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Here’s to the next chapter.

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Chapter 1. Background and Significance

1.1 Motivated by Societal Needs

1.1.1 The CO$_2$ Emissions Problem

Scientific evidence leaves no room for disputing the fact that a high—and rising—concentration of atmospheric CO$_2$ is the primary contributor to global climate change. According to data acquired at the National Oceanic and Atmospheric Administration (NOAA)’s Mauna Loa Observatory, atmospheric CO$_2$ levels had already exceeded 410 ppm by early 2019, representing a near-25 ppm increase over the past decade.$^1$ While many anthropogenic activities have contributed to what amounts to a 44% increase in atmospheric CO$_2$ in recent centuries, emissions derived from the burning of fossil fuels, especially coal, oil, and natural gas, have been the principal drivers, with significant contributions from cement production and land use changes (e.g., forest clearing, development), as well.$^2$ The immediate consequences of this emissions scenario are two-fold. Historically, a large portion of emitted CO$_2$ has dissolved in the oceans, thereby causing ocean acidification and ecosystem endangerment.$^3$ Nonetheless, this natural buffering capacity has not prevented the majority of CO$_2$ emissions from remaining in the atmosphere, trapping infrared radiation close to the earth’s surface and increasing global temperatures.

The effects of such a temperature increase are wide-ranging and expected to impact regions of the world in different ways. For example, rising temperatures will cause global sea level to rise 19 cm by 2050, but localized sea level rise is projected to occur three to four times faster in the northeastern United States compared to the global
average.\textsuperscript{4} Especially in this region, larger volumes of ocean water will, at the very least, exacerbate storm surges during hurricanes, making communities and associated infrastructure extremely vulnerable; it is also likely that warmer ocean temperatures will strengthen severe storms or alter the length of hurricane seasons.\textsuperscript{5} In the middle and western portions of the country, climate change effects are more likely to manifest in the form of water scarcity or changing wildfire patterns which, in some cases, have already been observed.\textsuperscript{6} From an even broader standpoint, climate change threatens the national security of nearly all countries, as food security challenges (e.g., crop failures due to heat and drought intolerance), public health concerns (e.g., saline intrusion in water supplies, surges in vectorborne disease incidence), and conflict potential (e.g., cross-boundary water rights, forced migration, opening of Arctic sea lanes) are expected to increase as a downstream effect of rising global temperatures.\textsuperscript{7}

The severity of these anticipated impacts will be intimately tied to the magnitude of temperature increase measured in the coming decades. A special report published by the Intergovernmental Panel on Climate Change (IPCC) in October 2018 made clear the drastic differences in impending sea level rise, Arctic ice melt, and other outcomes if global temperature increases are limited to +1.5 °C compared to +2 °C versus pre-industrial levels. The report also indicated that halting warming at the +1.5 °C threshold “would require rapid, far-reaching, and unprecedented changes in all aspects of society.”\textsuperscript{8} Since the Paris Agreement went into effect in 2016, many nations have sought to begin addressing this challenge by monitoring and reducing their CO\textsubscript{2} emissions, with actionable items ranging from decommissioning coal-fired power plants to investing in zero-carbon energy supplies.\textsuperscript{9} While facilitating the transition to sustainable energy
sources will be critical for limiting future emissions, this course of action does nothing to address CO$_2$ currently in the atmosphere. Environmental remediation efforts are needed to remove this excess CO$_2$—as well as keep new streams of it from reaching the atmosphere in the first place—since, even in the best-case scenario, CO$_2$-emitting processes will not be halted overnight.

1.1.2 Options for Atmospheric Remediation

Much progress has been made in the development of materials that can be used to capture CO$_2$, particularly from highly concentrated point sources, like smokestacks. The most common CO$_2$ capture method is known as amine scrubbing, which typically employs primary amines to chemisorb CO$_2$ from flue gas.$^{10}$ It is much more challenging, though not impossible, to capture diffuse CO$_2$ from the air—a technique appropriately termed “direct air capture”—and a handful of these projects exist globally. Assuming, based on current research goals, that point source and direct air capture techniques will continue to evolve, an important resulting question involves what to do with the CO$_2$ once it is collected. Removal of the CO$_2$ chemisorbed to amine scrubbers can be easily accomplished using elevated temperature and pressure to generate a concentrated stream of supercritical CO$_2$. The choice of what to do with that CO$_2$ will be instrumental in assuring that it is not re-introduced to the atmosphere, thereby accomplishing effective environmental remediation. Two primary options exist at present.

The most technologically advanced means of dealing with CO$_2$ post-capture is to sequester it underground for long-term storage. Typically, this is accomplished by injecting the supercritical CO$_2$ at high pressure into former fossil fuel reservoirs, saline aquifers, or basalt formations. Once injected, the CO$_2$ interacts with the water, salt,
hydrocarbons, and other materials that exist within the subterranean rock formation and, over long periods of time, carbonate minerals are formed. Underground CO₂ sequestration has been employed around the world for decades, beginning with the Sleipner platform off the coast of Norway in 1996. It is anticipated that around 17.5 million tons of CO₂ will have been stored at the Sleipner site by 2020, and the efficacy of this and similar projects has resulted in the institution of recent incentives such as U.S. Code 45Q, which offers CO₂-emitting entities $50 per ton of CO₂ injected underground for long-term storage.

While the technology used to achieve underground storage is well-established, sequestration is unlikely to solve the atmospheric CO₂ problem on its own due to a handful of challenges and concerns. For example, the sheer quantity of CO₂ that would need to be stored in a relatively short amount of time calls into question the number and capacity of underground storage sites. Careful characterization of geological features must be performed prior to any injection event in order to ensure that leaks into the atmosphere or drinking water aquifers will not occur over time. Based on the magnitude of injections that would be needed, the injection site approval process would need to be hastened, which could introduce questions about long-term safety. Relatedly, environmental justice advocates express concern over injections being sited near certain populations more frequently than others; these populations would be disproportionately affected by possible CO₂ leaks or property value impacts. Furthermore, aside from relatively rare government incentives, few stimuli exist to motivate CO₂ emitters to perform sequestration.
For these reasons, society cannot rely solely on sequestration to address the atmospheric CO$_2$ problem. A second possible solution is CO$_2$ utilization, which involves transforming excess CO$_2$ into useful, marketable materials. The motivation for CO$_2$ emitters or entrepreneurs to invest in research, development, and resulting technologies is much clearer for CO$_2$ utilization than sequestration, as the products generated from CO$_2$ can be sold for a profit. This invites the question of how to best facilitate the conversion of CO$_2$ into desirable products. One possibility, electrochemically reducing CO$_2$, has attracted much interest from the research community, in part because this technique can be used to generate a diverse array of carbon-containing compounds.

Just as storing all the excess atmospheric CO$_2$ underground would be cause for concern due to volume, transforming that CO$_2$ into a single product would result in overwhelming quantities, diminishing the product’s utility. As such, the efficacy of CO$_2$ utilization in complementing sequestration efforts is largely dependent on being able to make a variety of products at high efficiency and selectivity, as well as low cost.\textsuperscript{14} Electrochemical reduction of CO$_2$ is particularly appealing because, in recent decades, it has shown promise for generating small carbon-containing molecules such as methane, ethylene, and alcohols.\textsuperscript{15,16} These sorts of molecules have become essential chemical building blocks used to make a variety of products, including pharmaceuticals, plastics, fabrics, and resins. Interestingly enough, the required chemical building blocks are currently sourced directly or indirectly from fossil fuel extraction,\textsuperscript{17} so if the world truly intends to transition away from fossil fuel-based energy, it will also be necessary to find new sources for these essential small molecules. Electrochemical reduction of CO$_2$
therefore provides an opportunity to assist atmospheric remediation efforts while simultaneously providing essential carbon-containing chemicals.

1.2 The Chemistry of CO₂ Reduction

1.2.1 Thermodynamic and Kinetic Considerations

The reduction of a single molecule of CO₂, the most oxidized form of carbon, to form any number of carbon-containing species requires significant energy inputs. This makes sense when considering the exothermicity of combustion processes that create CO₂ in the first place. Using standard thermodynamic principles, the Gibbs free energy (ΔG_{rxn}) of CO₂ reduction is positive, so reaction spontaneity requires the application of enough energy to make ΔG_{rxn} a negative value. By applying an external potential bias, electrochemistry can be used to directly manipulate ΔG_{rxn} according to Equation 1.1, where ΔG°_{rxn} is the standard change in Gibbs free energy, n is the number of electrons transferred, F is Faraday’s constant, and E°_{rxn} is the standard reaction potential. E°_{rxn}, which is negative for CO₂ reduction reactions given the positive value of ΔG°_{rxn}, can be further described as the sum of the standard cathodic (i.e., reduction) and anodic (i.e., oxidation) reaction potentials. In this way, the thermodynamics of CO₂ reduction are controlled in large part by the standard reduction potential (E_{R}°) associated with converting CO₂ into a product of interest.

\[ \Delta G_{rxn}^° = -nF E_{rxn}° \]  \hspace{1cm} \textit{Equation 1.1}

As previously discussed, many products can be accessed via the reduction of CO₂, ranging from one- to multi-carbon species. Several examples, including products of CO₂ electroreduction that will be discussed in later chapters, are listed in Table 1.1 alongside their E_{R}° values. The stability of the CO₂ molecule is evidenced by these values, since the
one-electron reduction of CO$_2$ to CO$_2^-$ requires application of a large, negative potential. The $E^\circ_R$ values needed to generate higher-order products are considerably less extreme, deceptively suggesting that these reductions would be easier to perform. However, the energetic inputs needed to achieve higher-order products, based on $\Delta G^\circ_{\text{rxn}}$, remain comparable to those needed for lower-order species.$^{18}$

<table>
<thead>
<tr>
<th>Reduction reaction</th>
<th>$E^\circ_R$ (V vs. NHE)</th>
<th>$E^\circ_R$ (V vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$ + e$^-$ → CO$_2^-$</td>
<td>-1.9</td>
<td>-2.1</td>
</tr>
<tr>
<td>CO$_2$ + 2 e$^-$ + H$_2$O → HCOO$^-$ + OH$^-$</td>
<td>-0.67</td>
<td>-0.88</td>
</tr>
<tr>
<td>2 CO$_2$ + 2 e$^-$ → C$_2$O$_4^{2-}$</td>
<td>-0.64</td>
<td>-0.85</td>
</tr>
<tr>
<td>CO$_2$ + 2 e$^-$ + H$_2$O → CO + 2 OH$^-$</td>
<td>-0.52</td>
<td>-0.73</td>
</tr>
<tr>
<td>CO$_2$ + 4 e$^-$ + 3 H$_2$O → HCOOH + 4 OH$^-$</td>
<td>-0.49</td>
<td>-0.70</td>
</tr>
<tr>
<td>CO$_2$ + 6 e$^-$ + 5 H$_2$O → CH$_3$OH + 6 OH$^-$</td>
<td>-0.40</td>
<td>-0.61</td>
</tr>
<tr>
<td>CO$_2$ + 8 e$^-$ + 6 H$_2$O → CH$_4$ + 8 OH$^-$</td>
<td>-0.25</td>
<td>-0.46</td>
</tr>
<tr>
<td>2 CO$_2$ + 12 e$^-$ + 9 H$_2$O → C$_2$H$_5$OH + 12 OH$^-$</td>
<td>-0.33</td>
<td>-0.54</td>
</tr>
<tr>
<td>2 CO$_2$ + 14 e$^-$ + 10 H$_2$O → C$_2$H$_6$ + 14 OH$^-$</td>
<td>-0.34</td>
<td>-0.55</td>
</tr>
<tr>
<td>3 CO$_2$ + 18 e$^-$ + 13 H$_2$O → C$_3$H$_7$OH + 18 OH$^-$</td>
<td>-0.32</td>
<td>-0.53</td>
</tr>
</tbody>
</table>

Experimental factors such as temperature and species activity necessitate adjustments to $E^\circ_R$ as governed by the Nernst equation (Equation 1.2), where $E_R$ is the cell potential, $R$ is the universal gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is temperature, $n$ is the number of moles of electrons transferred, and $a$ is the chemical activity of the reduced ($a_R$) or oxidized ($a_o$) species. The thermodynamic potential given by the Nernst equation is therefore the lowest possible potential that can be applied to allow the reaction to
proceed. Kinetic parameters, however, impose an additional energetic requirement known as the overpotential, which is defined as the difference between the experimentally applied potential and $E_R^\circ$. Lower overpotentials are indicative of smaller kinetic barriers and, from a practical standpoint, are ideal because they correspond to lower voltage inputs. Unfortunately, despite the reasonable $E_R^\circ$ values associated with many possible CO$_2$-derived products, it is not uncommon to witness a need for large overpotentials in the range of 0.5 to 1.0 V in the CO$_2$ reduction literature.

$$E_R = E_R^\circ + \frac{RT}{nF} \ln\left(\frac{a_{\text{R}}}{a_{\text{R}^\circ}}\right)$$  \hspace{1cm} \textit{Equation 1.2}

Aside from overpotential, several other parameters are typically used to assess electrochemical CO$_2$ reduction systems. For example, the rate of reaction is described by the current, defined as the rate of charge passage over time, or current density, which is the current per unit area of the electrode surface. Mathematically, current density and overpotential are exponentially related, which is why higher applied potentials correspond to greater current densities. This, of course, represents a tradeoff when considering practical applications; namely, higher reaction rates are predicated on the application of larger potentials.

Another important factor to consider when assessing the efficacy of electrochemical CO$_2$ reduction is the selectivity for a given product. While a single product may be desired, more than one carbon-containing species may be generated. Plus, the potentials required to achieve CO$_2$ reduction exceed the $E_R^\circ$ values for H$^+$ and water reduction (Equations 1.3 and 1.4), consequently introducing kinetic competition with H$_2$ evolution, particularly in aqueous electrolytes.$^{22}$

$$2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2 \hspace{1cm} E_R^\circ = 0 \text{ V vs. NHE} \hspace{1cm} \textit{Equation 1.3}$$
\[ 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^- \quad \text{E}_R^\circ = -0.82 \text{ V vs. NHE} \quad \text{Equation 1.4} \]

To assess an electrochemical system’s selectivity for a given product, it is necessary to determine what proportion of the total charge passed in an experiment contributed to generating the product of interest. This value, described in Equation 1.5, is known as Faradaic efficiency. Charge balance is achieved when the total Faradaic efficiency across all products of an electrochemical experiment, including H\(_2\), is 100%. When the Faradaic efficiency for a product of interest is multiplied by the total current density in an experiment, the proportion of the current that contributed to formation of that product is indicated. Finally, the catalytic efficiency (\(\xi\)), a newer parameter developed by Pander and Bocarsly,\(^{23}\) will be introduced in Chapter 2.

\[
\text{Faradaic efficiency} = \frac{\text{charge contributing to product}}{\text{total charge passed}} = \frac{\text{mol e}^- \text{contributing to product}}{\text{total mol e}^- \text{used}} \quad \text{Equation 1.5}
\]

Electrochemical CO\(_2\) reduction systems can therefore be developed and compared in a number of ways. The focal point of these systems is the catalyst material selected to facilitate the chemical transformation. Catalysts can be categorized as heterogeneous, homogeneous, or hybrid, depending on whether the active species exists in the solid-state (i.e., typically the working electrode itself), the electrolyte (i.e., a dissolved molecular complex), or some combination of the two.\(^{16}\) While homogeneous and hybrid CO\(_2\) reduction catalysts are interesting from a fundamental perspective, heterogeneous systems tend to exhibit greater stability and achieve wider product distributions, which makes them more attractive from an applied point of view.

1.2.2 Progress and Opportunities in Heterogeneous CO\(_2\) Electrocatalysis

The simplest type of heterogeneous catalyst that can be used to facilitate CO\(_2\) electroreduction is a pure metal electrode. Many metals have been characterized with
respect to their electrocatalytic activity toward CO$_2$ and, as shown in Figure 1.1, most of these metals cannot reduce CO$_2$ in an aqueous environment, instead favoring H$_2$ evolution. Some metals, however, are reasonably effective at reducing CO$_2$ by two electrons; active transition metals, such as gold and silver, generate CO, while post-transition metals, like indium or tin, produce formate. Only one pure metal, copper, can reliably achieve highly reduced products, most commonly methane or ethylene, in the presence of aqueous CO$_2$. Recent efforts in improving heterogeneous CO$_2$ reduction activity have focused on increasing Faradaic efficiencies, lowering overpotential requirements, or improving product selectivity associated with different catalyst species.

![Figure 1.1. Summary of CO$_2$ reduction products generated using transition metal, post-transition metal, and carbon electrodes in aqueous electrolyte. Reprinted with permission from Chem. Rev. 2015, 115, 12888–12935. Copyright 2015 American Chemical Society.](image)

Efforts to elicit enhanced CO$_2$ electroreduction using pure metal electrodes have been largely successful. For example, in 2012, copper foil electrodes were shown to generate as many as 16 different carbon-containing products electrocatalytically from
Since then, morphological tuning has been used to improve selectivity for one or a few carbon products during copper-mediated electrolysis. Copper nanoparticles (~ 7 nm) can selectively generate methane at 80% Faradaic efficiency, while preferential two-carbon product generation was achieved by adjusting the pore sizes of copper foam electrodes. Morphological control over CO$_2$ reduction activity has also proven effective for other transition metal catalysts. In fact, nanostructuring silver electrodes to reveal more active crystal faces has made it possible to achieve near-100% Faradaic efficiencies for CO, even at overpotentials as low as 170 mV. Efforts to improve the formate-generating ability of post-transition metals have largely involved deriving different metal oxide surfaces, especially for tin-based electrodes, likely due to their surface oxide-dependent CO$_2$ reduction mechanism.

Unfortunately, many active single-metal electrocatalysts suffer from limited product scopes, prompting the exploration of alloy and mixed-metal electrodes. As depicted in Figure 1.2, it has been suggested that alloying of two or more metals at the electrode surface can stabilize adsorbed CO$_2$ molecules or reduction intermediates by providing distinct binding sites. Alternatively, alloying may lower energetic barriers associated with different reduction steps, perhaps helping to break hindersome “scaling relations” that pair energetic improvements during one step of the CO$_2$ reduction process with energetic hurdles in another. In any case, the interesting catalytic behavior of pure copper electrodes has resulted in the development of copper-containing alloys, some of which can generate highly reduced products. However, most copper-containing bimetallic alloy catalysts are only able to produce CO or formate.
Far fewer alloy catalysts have been reported that do not contain copper as one of their constituent metals. An early example using Pd$_{70}$Pt$_{30}$ nanoparticles achieved 88% Faradaic efficiency for formate at only 280 mV overpotential,$^{45}$ introducing the possibility that two metals can be combined to generate a CO$_2$ reduction product that neither metal can produce on its own. This possibility was again realized in 2016, when Torelli et al. reported that a thin film of the intermetallic Ni$_5$Ga$_3$ could generate $\sim$2.2% methane, $\sim$1.7% ethane, and trace amounts of ethylene during aqueous CO$_2$ electroreduction.$^{46}$ This species, inspired by a non-electrochemical, high-temperature CO$_2$ hydrogenation catalyst,$^{47}$ takes alloy-induced, non-native CO$_2$ reduction activity to
the extreme, as its component parts, nickel and gallium, are relatively inactive toward CO₂. Furthermore, the Ni₅Ga₃ intermetallic generated two-carbon products at onset potentials ~250 mV more positive than those required for copper electrodes, which had previously been the only materials known to produce multi-carbon chemicals from CO₂.

While Ni₅Ga₃ and associated Ni-Ga intermetallics represent an exciting advancement in the development of catalysts capable of generating diverse, highly reduced, and multi-carbon products, much room for exploration in the alloy and intermetallic space remains. The Faradaic efficiencies for carbon-containing products generated by Ni₅Ga₃ are very low, and questions remain regarding whether this system can be tuned—or other systems can be discovered—that achieve higher Faradaic efficiencies, lower overpotentials, or even more highly reduced products. An interesting feature that seems worth investigating is the combination of transition metals, like nickel, and post-transition metals, like gallium, that electroreduce CO₂ as an ensemble yet primarily facilitate H₂ evolution on their own. From a practical standpoint, this would unlock new chemical reactivity profiles that could be exploited to help address the atmospheric CO₂ problem, and from a fundamental standpoint, interesting electronic effects of alloying could be illuminated. As such, many opportunities exist for catalyst discovery, catalyst tuning, and mechanistic evaluation of alloy, intermetallic, and oxide compositions of various metals.

1.2.3 Dissertation Outline

The work presented herein examines the electrocatalytic activity of a variety of heterogeneous, bimetallic species combining non-CO₂-reducing transition metals and the post-transition metals aluminum and gallium. Aspects of catalyst discovery, catalyst
tuning, and preliminary mechanistic evaluation are explored sequentially, resulting in new catalytic activity profiles that expand the product portfolio of CO2 electroreduction. Included in this portfolio are highly reduced and multi-carbon species.

Chapters 2 and 3 focus on catalyst discovery, introducing two new heterogeneous catalysts combining inactive transition and Group 13 metals to achieve unprecedented activity toward CO2, in some ways rivaling copper-based electrocatalysis. First, an alloy of Cr2O3 and Ga2O3 is shown to generate the two-carbon product oxalate at an impressive 59% Faradaic efficiency. The oxalate-generating pathway reported for this system is the first of its kind, overturning the previously held belief that CO2 reduction to oxalate necessitates a CO2•− intermediate and prohibitively high overpotentials. Second, the intermetallic Ni3Al is proven to electroreduce CO2 to an assortment of one-, two-, and three-carbon products via a commonly invoked CO intermediate. This catalytic system represents the first report of a non-copper-containing electrocatalyst generating three-carbon products from CO2.

Advancements in catalyst tuning are presented in Chapter 4, focusing on the previously reported Ni-Ga intermetallic system46 and emphasizing the Ni3Ga stoichiometry. Specifically, carbon solid supports are shown to indirectly influence the products of CO2 electroreduction on Ni3Ga, and in-depth materials characterization suggests that this impact is rooted in a combination of morphological and surface compositional control during catalyst growth. The outcome of this control is not only distinct product distributions achieved using differently supported Ni3Ga catalysts, but also changes in reactivity toward CO2 and CO. As a result, a system featuring two...
different Ni$_3$Ga electrodes was shown to improve electrochemical reduction of CO$_2$ to methanol compared to either electrode alone.

Finally, preliminary insights into the significance of transition metal and Group 13 metal choice when designing bimetallic CO$_2$-reducing electrocatalysts are reported in Chapter 5. A series of spinel oxides was generated by systematically varying the transition metal (i.e., Mn, Fe, Co) and Group 13 metal (i.e., Al, Ga), thereby allowing for electrochemical evaluation of a common structure type. CO$_2$ was most effectively reduced to methanol, the most highly reduced product of this series, using the spinel materials that operated via a formate-dependent CO$_2$ electroreduction pathway. In all cases, implementation of Al or Ga alongside the transition metals imparted non-native activity toward CO$_2$, further supporting the strategic combination of transition metals and post-transition metals in the search for diversified product distributions.

Ultimately, the results presented here lend valuable insight into electrochemical CO$_2$ reduction using heterogeneous catalysts. These insights are poised to guide further development of electrocatalytically active alloy and intermetallic species, creating a platform for catalyst discovery, tuning, and mechanistic analysis that can be applied to various candidate multi-metal systems. With continued work in this area, CO$_2$ electroreduction is poised to become a profitable option for environmental remediation, complementing a suite of solutions that will collectively allow for a more livable future.

1.3 References

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Chapter 2. Evaluation of a Cr-Ga Oxide Catalyst in the Electrochemical Reduction of CO$_2$ to Oxalate

2.1 Introduction

High atmospheric CO$_2$ concentrations and associated water security, food access, and public health challenges$^{1,2}$ are motivating chemists to develop electrocatalysts capable of transforming CO$_2$ into value-added fuels or chemical feedstocks.$^3$ Future use of these technologies could make CO$_2$ reuse a profitable process, encouraging point-source or atmospheric CO$_2$ capture while simultaneously helping to achieve emission reduction goals. Industrially attractive electrocatalysts of this sort exhibit several key traits, including the ability to generate a multi-carbon product selectively and efficiently.

Because the biggest barrier to market entry in the CO$_2$ reduction space involves finding ways to generate a desired product in a cost-competitive way (i.e., compared to the process currently used to achieve said product), one strategy for devising industrially applicable CO$_2$ electroreduction systems is to pursue an in-demand chemical that stoichiometrically requires few electrons to be added to the CO$_2$ reactant. As such, the two-electron, two-carbon product oxalate is an ideal target because of its small electron requirement coupled with commercial appeal. Oxalate is a precursor to glycols,$^{4,5}$ which themselves are precursors to a variety of materials such as plastics, polyester fabrics, and pharmaceuticals.$^6$

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High-resolution transmission electron microscopy data presented in Section 2.3.1 were collected by Dr. Guangming Cheng.
The standard redox potentials, \( E^\circ_R \), for \( \text{CO}_2 \) reduction to oxalic acid, monoanionic oxalate, and dianionic oxalate are only \(-0.48, -0.52, \) and \(-0.64 \) V vs. NHE, respectively; the latter two potentials can be calculated using Hess’ Law and pK\(_a\) values for oxalic acid (i.e., pK\(_{a1}\) = 1.25, pK\(_{a2}\) = 4.14). However, prior studies have reported that applied potentials of at least \(-2 \) V vs. NHE are necessary to achieve the desired transformation at reasonable reaction rates. Studies on the reduction of \( \text{CO}_2 \) to oxalate have typically employed organic electrolytes to avoid competition with \( \text{H}_2 \) evolution reactions. The need for a nonaqueous solvent, along with a supportive body of kinetic data, has led researchers to assert that oxalate formation occurs through generation of a reactive \( \text{CO}_2^- \) intermediate. This conclusion is based, in part, on the fact that the one-electron reduction of \( \text{CO}_2 \) to form \( \text{CO}_2^- \) occurs at \( E^\circ_R = -1.90 \) V vs. NHE. If oxalate must be formed via this pathway, a minimum effective electrode overpotential of nearly 1.5 V would be required to simply initiate a low rate of conversion. Further, exploration of electrocatalysts for this transformation would be of little value since the best catalyst would still require electrode operation at potentials more negative than \(-1.90 \) V vs. NHE.

In this chapter, the discovery, optimization, and preliminary mechanistic analysis of a novel electrocatalyst active in the reduction of aqueous \( \text{CO}_2 \) to oxalate is discussed. The electrode in question, composed of a \( \text{Cr}_2\text{O}_3/\text{Ga}_2\text{O}_3 \) alloy thin film (3 \( \text{Cr}_2\text{O}_3:1 \) \( \text{Ga}_2\text{O}_3 \); hereafter referred to as \( \text{Cr}-\text{Ga} \)) on glassy carbon, transforms \( \text{CO}_2 \) to oxalate at potentials as positive as \(-0.98 \) V vs. NHE (\(-1.18 \) V vs. \( \text{Ag}/\text{AgCl} \)). Maximum oxalate Faradaic efficiencies of 59% were achieved using pH 4.1 KCl electrolyte at \(-1.48 \) V vs. \( \text{Ag}/\text{AgCl} \), an overpotential of only 690 mV. Based on the observed electrode potential alone,
generation of a CO$_2^-$ intermediate cannot occur, nor can this species serve as an intermediate in the reduction process. Thus, a previously unknown reaction pathway exists which bypasses the one-electron reduction of CO$_2$, providing a low-energy route to oxalate formation during CO$_2$ electroreduction. As such, the reaction pathway employed by the Cr-Ga system introduces new possibilities for catalyst discovery and tangible opportunities for the energy-efficient conversion of CO$_2$ to a commercially attractive, multi-carbon chemical feedstock.

2.2 Experimental Methods

2.2.1 Materials

Chromium(III) nitrate nonahydrate (≥ 99.99%), gallium(III) nitrate hydrate (99.9%), KHCO$_3$ (99.7%), oxalic acid (≥ 99%), NH$_4$Cl (99.998%), (CH$_3$)$_4$NCl ((TMA)Cl; ≥ 98%), NaCN (97%), methanol (≥ 99.9%), $^{13}$C-methanol (99 at% $^{13}$C), formic acid (≥ 98%), 1,4-dioxane (99.8%), acetonitrile (99.8%), ethanol (≥ 99.8%), isopropanol (≥ 99.7%), $^{13}$CO$_2$ (99 at% $^{13}$C), $^{12}$CO ($^{13}$C-depleted), and $^{13}$CO (99 at% $^{13}$C) were obtained from Sigma-Aldrich. KCl, KBr, KI, K$_2$CO$_3$, K$_2$SO$_4$, KH$_2$PO$_4$, LiCl, CsCl, CaCl$_2$, and HCl, all ACS grade, were purchased from EMD Chemicals, and calcium bromide (99.5%) was obtained from Alfa Aesar. Ar, CO$_2$, CO, 95% Ar/5% H$_2$, and 50% CO/50% H$_2$ gases and mixtures were ordered from AirGas. Glassy carbon plates (GLAS11; 25 x 25 x 3 mm; Structure Probe Inc.) were cut in half lengthwise prior to use. Conducting silver and Loctite Hysol insulating epoxies were purchased from Epo-Tek and Grainger, respectively. All chemicals were used as received except for methanol and formic acid for standard curves, 1,4-dioxane for NMR internal standards, and HCl, all of which were diluted prior to use.
2.2.2 Cr-Ga Thin Film Synthesis and Characterization

Synthetic procedures to create Cr-Ga thin films of various stoichiometries (most commonly 3:1) were adapted from the method established by Torelli et al. Briefly, aqueous solutions of 0.052 M chromium(III) nitrate nonahydrate and 0.036 M gallium(III) nitrate hydrate were mixed to achieve the desired Cr:Ga ratio. Glassy carbon pieces were heated to ~120 °C on a hotplate, and 0.1-mL samples of the Cr-Ga nitrate solution were drop-casted onto them. After the solution evaporated completely, the glassy carbon pieces were placed in an alumina boat and loaded into either a Lindberg/Blue M or Carbolite Quartz Tube Furnace. The furnace was ramped at a rate of 3 °C/min to 700 °C under 95% Ar/5% H₂ gas flow; it rested at this state for 5 h prior to cooling to room temperature at a rate of –3 °C/min. Resulting Cr-Ga films (geometric surface area ~0.8 cm²) were olive green in color, with Cr-rich stoichiometries tending toward Kelly green and Ga-rich stoichiometries tending toward gray.

The compositions and morphologies of Cr-Ga films were analyzed by a variety of materials characterization techniques. Powder X-ray diffraction was performed using a Bruker D8 Advance diffractometer with 0.083° step size and CuKα radiation. XRD samples either remained on the glassy carbon support or were scraped from the surface; resulting patterns were identical, except that scraped samples exhibited significantly less carbon intrusion and were therefore selected for presentation. Thin film morphology and additional bulk composition data were obtained using a FEI XL30 FEG-SEM equipped with EVEX EDX detector. SEM images and EDX spectra were obtained using a 5 or 10 keV electron beam with a 10–15 mm working distance. A Titan Cubed Themis 300 Scanning/Transmission Electron Microscope with Super-X EDX detector was used to
obtain high-resolution TEM/EDX data. XPS spectra were collected using a ThermoFisher K-Alpha X-Ray Photoelectron Spectrometer set to 20 eV pass energy and 50 ms dwell time. Resulting data were analyzed using the Thermo Scientific Avantage Data System and CasaXPS software.

Materials characterization was conducted before and after electrochemistry in designated experiments. XPS of electrodes after electrolysis indicated that no surface-contaminating components were generated during electrochemical experiments (e.g., Pt from the counter electrode, which was situated in a separate compartment during electrolysis, or reference electrode species).

2.2.3 Electrode Preparation and Electrochemical Experimentation

Electrodes were prepared in one of two fashions. One electrode configuration involved connecting copper wire to the glassy carbon support using conducting silver epoxy, feeding the wire through a glass tube, and covering both ends of the tube (including any exposed copper or silver) with insulating epoxy. The second configuration featured the same general setup, but the copper wire was attached to an alligator clip, which could then be used to reversibly hold glassy carbon pieces whose tops had been wrapped in copper tape. Experiments using both electrode configurations yielded identical results, both in terms of charge passage and product distribution.

Electrochemical experiments were conducted using CH Instruments 760 and 1140 potentiostats. Bulk electrolysis experiments utilized custom electrochemical cells with gas-tight ports for the working, Pt mesh counter (situated in a gas dispersion tube), and Ag/AgCl reference electrodes. The electrolyte was continuously stirred. Unless otherwise noted, 0.1 M KCl (5–8 mL) was used as the electrolyte, and it was buffered with KHCO$_3$.
to achieve CO$_2$-saturated pH values > 4 or adjusted with 0.01 M HCl for values < 4. Electrolyte solutions were purged with CO$_2$ for 30 min prior to experimentation. In experiments without CO$_2$ (i.e., CO, formic acid, methanol, or combinatorial feedstocks), the pH was adjusted to the appropriate, CO$_2$-analogous value. The majority of electrolysies were conducted at pH 4.1, and post-electrolysis measurements indicated that the final solution pH was consistently between 4.5 and 5.0. Experiments using $^{13}$CO$_2$, $^{13}$CO, and $^{12}$CO ($^{13}$C-depleted) were not completely purged with the respective gas. Electrolysis experiments were performed until 30–40 C charge had passed, unless the experiment was meant to determine catalyst lifetime.

2.2.4 Product Analysis

The solution and headspace of electrochemical cells were sampled for liquid and gaseous products by $^1$H-NMR and gas chromatography, respectively, both during and after bulk electrolysis. Formate and methanol were detected by $^1$H-NMR after combining 530 µL electrolyte with 60 µl D$_2$O and 10 µL 1,4-dioxane (10 mM); the latter served as an internal standard. In $^{13}$C-NMR experiments (used primarily to detect oxalate), only 1 µL 1,4-dioxane (10 mM) was added. A Bruker Avance III 500 MHz NMR Spectrometer with cryoprobe detector was used for all NMR experiments, and the experiments incorporated a custom water suppression method to permit sampling of aqueous electrolyte solutions. Formate and methanol were quantified using 5-point calibration curves for $^1$H-NMR ($R^2 > 0.99$; detection limit ~ 0.1 µM), while oxalate was visualized qualitatively by a large $^{13}$C-NMR signal (in experiments utilizing $^{13}$C-labeling) in the 160–170 ppm range.
Oxalate was quantified using the time-honored method of precipitation by a calcium salt.\textsuperscript{25} A 2-mL sample of the electrolysis solution was treated with 0.5 mL, 1 M HCl (to remove any carbonate present), and then 1 mL, 1 M calcium bromide solution was added, resulting in the precipitation of calcium oxalate. The calcium oxalate sample was dried in an oven at 105 °C overnight and then weighed; this mass was used to calculate the total quantity of oxalate formed. The limit of detection using this method was determined by isolating known quantities of aqueous oxalate (total electrolysis cell detection limit ~ 0.1 mmol; see Figure 2.1). Infrared spectra of calcium oxalate samples were obtained using a Thermo Diamond Smart Orbit IR Spectrometer (1 cm\textsuperscript{-1} resolution). The carbonate byproduct could be quantified by finding the difference in mass between two electrolysis samples, one treated with HCl and the other untreated prior to calcium bromide addition; the difference in mass was attributed to calcium carbonate. Calcium carbonate was also examined by IR spectroscopy. Experimental calcium oxalate and calcium carbonate samples were compared to control compounds made by combining calcium bromide and either oxalic acid or K\textsubscript{2}CO\textsubscript{3} in aqueous solution.
Figure 2.1. Results of control experiments quantifying known amounts of aqueous oxalate ("oxalate added") in 0.1 M KCl by precipitation with Ca\(^{2+}\) ("oxalate quantified"), providing a working curve for the standard oxalate quantification method. The graph inset shows the portion of the working curve utilized for the experiments presented here. Adapted with permission from ACS Catal. 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

Headspace samples were analyzed by gas chromatography to identify and quantify gaseous products. CO was measured using a HP6890 Gas Chromatograph fitted with a Molsieve 5A PLOT capillary column (Agilent) and TCD. The sampling method was a 5-min, 60 °C isotherm with He flow gas. An SRI 8610C Gas Chromatograph with Ar flow, which also used a Molsieve column and TCD, was run for a 7-min isotherm at 80 °C to detect H\(_2\). CO and H\(_2\) were quantified using 30-point calibration curves having \(R^2\) values \(\geq 0.99\). The headspace was sampled following \(^{13}\text{CO}_2\) electrolyses using a KBr-terminated gas cell and Nicolet iS50 FT-IR Spectrometer with 1 cm\(^{-1}\) resolution; this confirmed that the CO product was derived from CO\(_2\). Faradaic efficiencies for all products, gaseous and liquid, were calculated based on the charge passed during each experiment as well as the product quantities determined by gas chromatography, \(^1\text{H}-\)}
NMR, or calcium bromide precipitation. Catalytic efficiencies were calculated based on the following equation established by Pander et al.\textsuperscript{26}:

\[
\text{Catalytic efficiency} = \frac{\text{Faradaic efficiency}}{1 + \left(\frac{\text{overpotential}}{E^\text{product}}\right)} \times 100\% \quad \text{Equation 2.1}
\]

2.3 Results and Discussion

2.3.1 Synthesis, Characterization, and Electrochemistry of Cr-Ga on Glassy Carbon

Thin films of Cr-Ga (3:1 ratio) on glassy carbon solid supports were synthesized using a drop-casting and thermal reduction method adapted from Torelli \textit{et al.}\textsuperscript{27} Powder X-ray diffraction (XRD; Figure 2.2A) coupled with energy-dispersive X-ray spectroscopy (EDX) suggested that the bulk films were comprised of \(\text{Cr}_2\text{O}_3\) and \(\text{Ga}_2\text{O}_3\) in a 3:1 ratio. High-resolution transmission electron microscopy (HR-TEM) with nano-EDX capability indicated that, compositionally, a single oxide phase having 3:1 metal stoichiometry was present as a combination of both amorphous and polycrystalline material (Figure 2.3). Taken together, the XRD and HR-TEM data allow assignment of this material as an alloy of \(\text{Cr}_2\text{O}_3\) and \(\text{Ga}_2\text{O}_3\).
Figure 2.2. Materials characterization of Cr-Ga thin film on glassy carbon. (A) XRD pattern of Cr-Ga referenced to Cr\textsubscript{2}O\textsubscript{3} (PDF 00-038-1479) and Ga\textsubscript{2}O\textsubscript{3} (PDF 01-074-1610). (B) Fitted XPS spectra of Cr (left) and Ga (right), indicating that the surface is made up of metal oxides. Peaks are referenced to adventitious carbon at 284.5 eV (not shown). (C) SEM image of Cr-Ga comprising discontinuous platelets on the solid support surface, obtained using a 10 keV electron beam and 14.2 mm working distance. Adapted with permission from ACS Catal. 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

The bulk film was further analyzed by performing Ar-ion bombardment in the analysis chamber of an X-ray photoelectron spectrometer over multiple 10-s intervals. In this process, the top layers of the film were removed, exposing the bulk material as the new “surface” and allowing for further confirmation of a 3:1 Cr\textsubscript{2}O\textsubscript{3}:Ga\textsubscript{2}O\textsubscript{3} composition.
Without Ar-ion bombardment, X-ray photoelectron spectroscopy (XPS) suggests that surface compositions were also comprised of Cr\textsuperscript{28-30} and Ga\textsuperscript{31} oxides (Figure 2.2B), consistent with the bulk. Scanning electron microscopy (SEM; Figure 2.2C) indicated that Cr-Ga films consisted of discontinuous platelets scattered across the glassy carbon surface, not unlike alternative thin film systems similarly synthesized.\textsuperscript{27,32}

**Figure 2.3.** High-resolution morphological and compositional analysis of Cr-Ga on glassy carbon. (A) Scanning HR-TEM imaging indicates that the Cr-Ga layer (blue arrow) is comprised of both amorphous and crystalline (i.e., starburst-type feature) material situated on top of the carbon support (red arrow). Both the amorphous and crystalline components are porous. (B) EDX analysis depicts uniform distribution of Cr, Ga, and O in the crystalline (top) and amorphous (bottom) components, confirming the presence of a single oxide phase.

Following cyclic voltammetry experiments, which indicated modest current enhancement under CO\textsubscript{2} saturation compared to Ar, initial bulk electrolysis experiments were conducted using a Pt mesh counter electrode and 0.1 M KCl electrolyte (pH 4 after CO\textsubscript{2} saturation). Applying a potential of \(-1.38\) V vs. Ag/AgCl to an electrochemical cell purged with \(^{13}\)CO\textsubscript{2} induced generation of CO and H\textsubscript{2}, sampled by gas chromatography, as well as oxalate, formate, and methanol, detected in the liquid phase by \(^{13}\)C-NMR (Figure 2.4A). Specifically, oxalate was assigned as the high-intensity \(^{13}\)C-NMR peak at 161 ppm that overshadowed formate, methanol, and residual CO\textsubscript{2} signals. To confirm this product assignment, a sample of the electrolyzed solvent (treated with HCl to remove carbonate,
if present) was mixed with aqueous calcium bromide, causing precipitation of a white solid (Figure 2.4B), which was isolated by vacuum filtration and examined by infrared (IR) spectroscopy (Figure 2.5). Only IR transitions associated with calcium oxalate were observed.\textsuperscript{33–35}

**Figure 2.4.** Confirmation of oxalate as a CO\textsubscript{2} reduction product in aqueous electrolysis. (A) \textsuperscript{13}C-NMR following electrolysis of \textsuperscript{13}CO\textsubscript{2} revealed oxalate (161 ppm) alongside methanol (48 ppm), residual CO\textsubscript{2} (126 ppm), and formate (171 ppm). (B) Oxalate could be visualized—and isolated—as calcium oxalate by precipitating with calcium bromide. From left to right: electrolysis sample; calcium bromide solution; oxalic acid plus calcium bromide; electrolysis sample treated with calcium bromide. Adapted with permission from *ACS Catal*. 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.
2.3.2 Optimizing Oxalate Generation by Manipulating Electrochemical Conditions

To optimize the Cr-Ga system for oxalate production, pH and potential dependence studies were undertaken. Gravimetric determination of oxalate is well established\textsuperscript{36,37} and was found to be quantitative in the present study when a 1 M calcium bromide solution was added to post-electrolysis samples. Standard curves were employed for quantifying CO/H\textsubscript{2} and formate/methanol using gas chromatography and \textsuperscript{1}H-NMR, respectively.

All pH-varying experiments were conducted at an applied potential of −1.38 V vs. Ag/AgCl and used CO\textsubscript{2}-saturated KCl electrolyte (buffered with KHCO\textsubscript{3} for pH > 4; adjusted with HCl for pH < 4; 0.1 M concentration). As shown in Figure 2.6A, the Cr-Ga system appears only somewhat sensitive to solution pH, since statistically equivalent
oxalate Faradaic efficiencies were achieved at pH 4.1 and 5.1, while pH 6.1 yielded slightly inferior results. Lower Faradaic efficiencies at pH 7.1 hinted that HCO$_3^-$, detected in trace amounts by gravimetric analysis even in non-buffered experiments, is not involved in oxalate production; its presence is rationalized in later sections. During electrolysis, charge balance was achieved by H$_2$ generation.

Subsequent experiments utilized CO$_2$-saturated, pH 4.1 KCl, because this pH maximized total Faradaic efficiency for carbon-containing products compared to H$_2$. Bulk solution pH consistently rose to 4.5–5.0 by the end of electrolysis (when initial pH = 4.1) but, as shown in Figure 2.6A, maximum oxalate Faradaic efficiencies are still achieved at these final pH values. Potential dependence experiments at pH 4.1 resulted in oxalate formation at all potentials examined between –1.18 V and –1.58 V vs. Ag/AgCl. Notably, the potentials in this window are more positive than the thermodynamic potential required to achieve the one-electron reduction of CO$_2$ to CO$_2$•–, indicating that CO$_2$•– is not generated in this oxalate-forming process. The product Faradaic efficiencies achieved during potential dependence experiments are displayed in Figure 2.6B. An electrode potential of –1.48 V vs. Ag/AgCl was determined to be optimal for oxalate production.
Figure 2.6. Faradaic efficiencies of carbon-containing products obtained by altering electrochemical conditions. (A) pH dependence experiments were performed at −1.38 V vs. Ag/AgCl using CO$_2$-saturated 0.1 M KCl buffered with KHCO$_3$ (pH > 4) or adjusted with HCl (pH < 4). (B) Potential dependence experiments were performed using pH 4.1, 0.1 M KCl electrolyte. Adapted with permission from ACS Catal. 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

A cell employing 0.1 M KCl (pH 4.1) at a potential of −1.48 V vs. Ag/AgCl generated Faradaic efficiencies for oxalate, CO, formate, and methanol of 59 ± 3%, 8.1 ± 0.7%, 0.16 ± 0.02%, and 0.15 ± 0.02%, respectively, over a 4-h period. These values correspond to catalytic efficiencies, as defined by Pander et al.,$^{26}$ of 22% (oxalate), 3.2% (CO), 0.054% (formate), and 0.045% (methanol). As shown in Figure 2.7, current versus time curves exhibited stable current densities at 8–10 mA/cm$^2$, calculated based on geometric surface area of the electrode.
Figure 2.7. Sample current versus time plot recorded during Cr-Ga on glassy carbon-mediated electrolysis at $-1.48 \text{ V vs. Ag/AgCl}$. Inset depicts the first 10 min of electrolysis, where a current spike prior to the 2-min mark likely corresponds to reduction of native Ga surface oxides. Adapted with permission from ACS Catal. 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

To determine the overpotential for CO$_2$ reduction at the Cr-Ga electrode, it is critical to consider the protonation state of the oxalate being generated. The pK$_a$ values of diprotic oxalic acid are reported to be 1.25 and 4.14 for the first and second proton dissociations, respectively.$^8$ All literature reports that reduce CO$_2$ to oxalate in organic or low-proton-activity solvents produce the oxalate dianion. The Cr-Ga system, which yields maximum oxalate Faradaic efficiencies around pH 4.1, generates a combination of monoanionic and dianionic oxalate.$^{39}$ The relative quantities of the monoanionic and dianionic species were calculated at each pH tested, and the results indicated that the quantity of oxalate monoanion slightly exceeds that of the dianion at pH 4.1. This product distribution is unique—further distinguishing Cr-Ga from prior reports of oxalate formation—and adds appeal to the system because protonated oxalates are more favorable industrial targets than their fully anionic analog.$^{40,41}$ Based on this ~50/50
product distribution, $E_R^\circ$ for the Cr-Ga-based electrochemical reaction was approximated to be halfway between the $E_R^\circ$ values for CO$_2$ reduction to the monoanionic and dianionic species, or $-0.58$ V vs. NHE ($-0.79$ V vs. Ag/AgCl). Accordingly, maximum oxalate Faradaic efficiencies were achieved at 690 mV overpotential (operating potential $= -1.48$ V vs. Ag/AgCl), while the onset of oxalate production was noted at overpotentials as low as 390 mV (operating potential $= -1.18$ V vs. Ag/AgCl).

![Figure 2.8](image)

**Figure 2.8.** Plot of oxalate Faradaic efficiency versus time for two Cr-Ga/glassy carbon electrodes held at $-1.48$ V vs. Ag/AgCl. Maximum oxalate production was achieved over the first day of electrolysis (see inset), after which time the Faradaic efficiency stabilized around 40%. Adapted with permission from *ACS Catal.* 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

Post-electrolysis materials characterization suggested that Cr-Ga continued to be chemically and physically stable. XPS analysis revealed that surface-confined Cr and Ga both remained predominantly oxidized, as only Ga’s native surface oxides were reduced during the first few minutes of electrolysis. SEM imaging indicated that the thin film incurred only slight erosion at platelets’ edges during electrolysis, while EDX showed
that the 3:1 stoichiometry of metal oxides was maintained. While maximum Faradaic efficiencies were achieved within the first 24 h of electrolysis, the Cr-Ga/glassy carbon electrode could produce oxalate continuously for at least 10 days (the longest time period studied) at Faradaic efficiencies ≥ 40%, suggesting an attractive catalytic lifetime (Figure 2.8).

2.3.3 Electrocatalytic Ratio of Cr and Ga Oxides

Compared to literature systems, Cr-Ga employs anomalous conditions to achieve high oxalate Faradaic efficiencies from CO₂, inviting questions about the roles of the metal oxides within the catalyst. To address this question, single-metal oxide films were examined as electrocatalysts. At −1.48 V vs. Ag/AgCl (pH 4.1 KCl), neither Cr₂O₃ nor Ga₂O₃ films alone could produce oxalate from CO₂, confirming the importance of having both oxides present. Films of Cr₂O₃ on glassy carbon generated modest amounts of CO, formate, and methanol from CO₂, while the activity of Ga₂O₃ films was dominated by CO production at around 40% Faradaic efficiency. These results for the single-metal oxide thin films vary slightly from those published for their bulk metal analogs.⁴²,⁴³ Both single-metal species remained oxidized after electrochemical testing.

Following electrolysis using plain Ga₂O₃ films, it was noted that about 20% of the aqueous CO₂ had converted to HCO₃⁻, identifiable both in solution and on the electrode surface by XPS (Figure 2.9). Because CO₂ and carbonate species exist in acid-base equilibrium in aqueous solution, it appears that Ga₂O₃ shifted this equilibrium toward HCO₃⁻. To further examine the acid-base equilibrium of CO₂ in the presence of Ga₂O₃, a 0.5-g sample of Ga₂O₃ powder was added to a beaker of CO₂-purged water (~30 mL), and a bulk solution pH change of +0.4 pH unit was recorded within 30 min. With a pKₐ
of 8.1, Ga$_2$O$_3$ surface hydroxide groups should create a basic local environment, shifting the CO$_2$/HCO$_3^-$ equilibrium ($pK_a = 6.4$) toward HCO$_3^-$ and subsequently impacting bulk pH. This phenomenon introduces the possibility that the active redox species is HCO$_3^-$; however, supplying the Cr-Ga system with 30 mM HCO$_3^-$ instead of CO$_2$ failed to result in oxalate production, confirming that the active species is, in fact, CO$_2$. Given that the CO$_2$/HCO$_3^-$ equilibrium involves relatively slow kinetics, the reactant could become kinetically trapped in the HCO$_3^-$ form, stoichiometrically limiting the rate of charge transfer to CO$_2$.

**Figure 2.9.** Confirmation of large quantities of HCO$_3^-$ in solution following electrolysis using Ga$_2$O$_3$-rich stoichiometries. (A) IR spectrum of calcium carbonate precipitated from a post-electrolysis solution using a 1 Cr$_2$O$_3$:6 Ga$_2$O$_3$ electrode (red) compared to a CaCO$_3$ control (black). (B) XPS analysis of a Ga$_2$O$_3$ thin film after electrolysis, focusing on the C binding region and indicating the presence of carbonate. Adapted with permission from *ACS Catal.* 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

Because Ga$_2$O$_3$ facilitates this detrimental equilibrium shift yet needs to be present in the alloy to achieve efficient oxalate production, an optimal Cr$_2$O$_3$:Ga$_2$O$_3$ stoichiometry must exist. To determine this ratio, a range of stoichiometries spanning from 100% Cr$_2$O$_3$ to 100% Ga$_2$O$_3$ were synthesized as thin films on glassy carbon and
analyzed for their performance as CO$_2$ reduction electrocatalysts via bulk electrolysis. All experiments were conducted at −1.48 V vs. Ag/AgCl in 0.1 M KCl (pH 4.1) for comparison to the optimized oxalate outcome for Cr-Ga. Results are presented in Figure 2.10.

![Figure 2.10](image)

**Figure 2.10.** Faradaic efficiencies achieved for carbon-containing products based on Cr$_2$O$_3$:Ga$_2$O$_3$ stoichiometry, suggesting that 3:1 is the optimal (*) ratio for oxalate generation. Adapted with permission from *ACS Catal*. 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.
CO and formate quantities generally amplified as Ga$_2$O$_3$ percentage increased and, as expected, ratios favoring Ga$_2$O$_3$ corresponded to more HCO$_3^-$ detected post-electrolysis. Cr$_2$O$_3$-rich stoichiometries resulted in lower overall quantities of non-oxalate, carbon-containing products compared to Ga$_2$O$_3$-rich variants, but Faradaic efficiencies for CO reached their lowest values at the highest percentages of Cr$_2$O$_3$. Importantly, the highest Faradaic efficiency for oxalate was obtained at the original 3:1 stoichiometry, which appears to provide just enough Ga$_2$O$_3$ for oxalate generation purposes while minimizing the interfacial pH shift that edges the CO$_2$ equilibrium toward HCO$_3^-$. 

2.3.4 Roles of CO and Methanol in Oxalate Generation

Ultimately, the Cr-Ga catalyst demonstrates that CO$_2$ electroreduction to oxalate can occur both in protic environments and at much lower applied potentials than previously recognized. At the potentials studied here, ranging from 530 to 930 mV more positive than the $E_R^*$ required for CO$_2^{•−}$ generation, CO$_2$ reduction to oxalate must occur via a CO$_2^{•−}$-independent pathway. This suggests that one or more of the C1 products observed in the electrochemical cell serve as oxalate precursors. To investigate this possibility, electrolysis experiments were performed by replacing the CO$_2$ feedstock with CO, formate, methanol, or combinations of these carbon-containing compounds. Single-feedstock experiments failed to yield oxalate, although use of either CO or formate as the reactant resulted in trace quantities of methanol. Importantly, electrolysis experiments conducted using a combined feedstock of $^{13}$CO and 15 mM methanol (rather than CO$_2$) did produce oxalate, as confirmed by precipitation with calcium bromide as well as $^{13}$C-
NMR (Figure 2.11A). This $^{13}$CO experiment, which used $^{12}$C-methanol, also verified that the carbon atoms of the oxalate product were derived from CO.

![Figure 2.11](image)

**Figure 2.11.** $^{13}$C-NMR spectra obtained following electrolyses using mixed feedstocks of CO and methanol. (A) Use of a $^{13}$CO/$^{12}$C-methanol feedstock resulted in an oxalate peak. (B) Starting with $^{12}$CO/$^{13}$C-methanol resulted in no oxalate peak even though calcium oxalate was precipitated out of solution. Adapted with permission from *ACS Catal.* 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

The opposite labeling experiment, using $^{12}$CO and $^{13}$C-methanol, was also undertaken, resulting in no $^{13}$C-NMR signal even though calcium oxalate was precipitated out of solution (Figure 2.11B). Therefore, methanol’s carbon atom is not
incorporated into the product, despite the fact that the system requires both methanol and CO to produce oxalate. Further, when the typical CO$_2$-saturated electrolyte (0.1 M KCl) was adjusted to contain 15 mM methanol prior to electrolysis (−1.48 V vs. Ag/AgCl), normal quantities of oxalate were achieved, but 5 M methanol yielded only trace amounts of product. Substituting methanol with either high or low concentrations of acetonitrile, ethanol, or isopropanol resulted in the same effects on oxalate production. This could be attributed to alterations in water’s hydrogen bonding network at or near the catalyst surface facilitated by non-trivial concentrations of organic solvent in the otherwise aqueous solution.$^{44,45}$

To test this hypothesis, Cr-Ga-mediated CO$_2$ electrolysis was performed using 0.1 M KCl in D$_2$O, which exhibits different hydrogen bonding character compared to H$_2$O.$^{46}$ In these experiments, oxalate was not detectable, while CO was generated at 17 ± 2% Faradaic efficiency, approximately double its value in H$_2$O. It appears that oxalate yields suffer when the hydrogen bonding network is significantly altered, but minor amounts of solvent—like the quantity of methanol generated by Cr-Ga—are required for oxalate synthesis. Taken together, these observations point to a strong influence of hydrogen bonding at the Cr-Ga surface. If this is true, one might expect that addition of a hydrogen bond-breaking agent, like the organics used in previous experiments, would fail to recover oxalate generation capacity in D$_2$O, whose hydrogen bonding is already “disrupted” (i.e., compared to H$_2$O). Indeed, oxalate was not produced in a control experiment adding 15 mM methanol to D$_2$O-based electrolyte, further supporting the system’s sensitivity to hydrogen bonding environment.
2.3.5 The Nature of Cr-Ga Surface Sites Active in CO₂ Reduction

Notably, the reactant experiments that initially pointed to oxalate-generating roles for CO and methanol did not implicate an important role for formate, which has been indicated as a competitor of oxalate production in the literature. With a Cr-Ga electrode, use of a formate feedstock resulted in only trace amounts of methanol and failed to generate oxalate. This result suggested that distinct active sites might exist for generation of formate and CO-derived products, including oxalate. Further support for this prediction was provided by electrolyte dependence studies. While experiments varying the electrolyte anion (i.e., KCl, KBr, KI, K₂SO₄, and KH₂PO₄) failed to exhibit significant differences in the distribution of products, a stark dependence was noted when varying the electrolyte cation.

Use of LiCl or NH₄Cl electrolytes (0.1 M) and −1.48 V vs. Ag/AgCl applied potential resulted in similar product distributions and efficiencies as those recorded for KCl. However, analogous experiments using CsCl, (CH₃)₄NCl (hereafter referred to as (TMA)Cl), and CaCl₂ electrolytes failed to generate any detectable quantities of oxalate, and CO Faradaic efficiencies were also reduced. (TMA)Cl supporting electrolyte increased the Faradaic efficiency of formate to 7.7 ± 0.4%, compared to the 0.16 ± 0.02% value achieved using optimal oxalate-generating conditions (0.1 M KCl). These cation-dependence results are summarized in Table 2.1. Furthermore, Cr-Ga electrodes previously used in (TMA)Cl experiments did not regain their oxalate-generating ability when re-introduced into a KCl-containing electrolyte. This KCl electrolyte was subjected to ¹H-NMR after electrolysis, and the resultant spectrum exhibited an overwhelming signal from TMA⁺, which must have come from the Cr-Ga surface. TMA⁺ had therefore
chemisorbed to the catalyst during prior electrolysers, likely contributing to inhibition of oxalate generation in those and subsequent experiments. Formate generation remained higher than usual in these trials.

**Table 2.1.** Products generated by a Cr-Ga on glassy carbon electrode based on electrolyte cation identity.†

<table>
<thead>
<tr>
<th>Electrolyte cation</th>
<th>Oxalate</th>
<th>CO</th>
<th>Formate</th>
<th>Methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li⁺</td>
<td>48 ± 5</td>
<td>13.8 ± 0.7</td>
<td>0.13 ± 0.03</td>
<td>0.09 ± 0.02</td>
</tr>
<tr>
<td>K⁺</td>
<td>59 ± 3</td>
<td>8.1 ± 0.7</td>
<td>0.16 ± 0.02</td>
<td>0.15 ± 0.02</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>45 ± 4</td>
<td>6.4 ± 0.5</td>
<td>0.20 ± 0.04</td>
<td>0.16 ± 0.04</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>0</td>
<td>3.6 ± 0.5</td>
<td>4.2 ± 0.3</td>
<td>0.21 ± 0.03</td>
</tr>
<tr>
<td>TMA⁺</td>
<td>0</td>
<td>1.8 ± 0.5</td>
<td>7.7 ± 0.4</td>
<td>0.95 ± 0.07</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0</td>
<td>3.7 ± 0.6</td>
<td>5.1 ± 0.4</td>
<td>0.52 ± 0.03</td>
</tr>
</tbody>
</table>

†Electrolysers were performed at –1.48 V vs. Ag/AgCl in 0.1 M electrolyte solution (CO₂-saturated, pH 4.1), where Cl⁻ was the counter anion.

‡Standard deviation based on the average of three trials using different Cr-Ga electrodes.

Exacerbation of formate production when oxalate generation is suppressed further supports the proposal that at least two surface active sites are present in the Cr-Ga catalyst: one for CO and CO-derived products and a second for formate. Moreover, chemisorption of TMA⁺ onto the Cr-Ga surface suggests that a surface anion exists. As expected, XPS analysis of Cr-Ga electrodes used in electrolysis experiments with CaCl₂ or CsCl electrolyte revealed distinct Ca²⁺ and Cs⁺ signals (Figure 2.12). The lack of oxalate production in the presence of cations having few waters of hydration (TMA⁺ and Cs⁺) or strong anion-binding capacity (Ca²⁺) hints that this surface anion is critical to CO/oxalate generation.
Figure 2.12. XPS analysis of two post-electrolysis Cr-Ga samples, one used in CaCl$_2$ electrolyte, exhibiting Ca$^{2+}$ chemisorption (left), and another used in CsCl electrolyte, exhibiting Cs$^+$ chemisorption (right). Peaks are referenced to adventitious carbon at 284.5 eV (not shown).

To probe this theory, the Cr-Ga system was treated with 15 mM NaCN prior to electrolysis (0.1 M KCl; $-1.48$ V vs. Ag/AgCl), and it was anticipated that the Lewis-basic, anionic CN$^-$ ligand would bind specifically to a Lewis-acidic, non-anionic surface site. Indeed, after performing electrolysis with this modified system, CO, oxalate, and methanol were detected in typical yields, while no formate was produced. Thus, it appears that the CN$^-$ ligates the formate-generating active site, simultaneously demonstrating that this site is (A) chemically distinct from the CO-generating site and (B) not anionic in character. This experiment, combined with the cation-dependence data, strongly suggests that Cr-Ga contains two types of electrocatalytic surface sites for CO$_2$ reduction: an anionic site leading to CO-derived products and a non-anionic site that produces formate (Figure 2.13).
Figure 2.13. Schematic representation of proposed Cr-Ga surface sites active in electrochemical CO$_2$ reduction. A surface anion facilitates generation of CO and CO$_2$-derived products (including oxalate), while a separate site produces formate, which is not associated with the oxalate-generation pathway. Adapted with permission from ACS Catal. 2019, 9, 2324–2333. Copyright 2019 American Chemical Society.

2.4 Summary and Conclusions

The ability of the Cr-Ga thin film on glassy carbon to generate oxalate from CO$_2$ in acidic aqueous electrolyte at 690 mV overpotential makes it a landmark example of heterogeneous CO$_2$ electroreduction, in part because the electrochemical conditions employed generate an equilibrium mixture of oxalate and its monoanionic form. More importantly, the current work demonstrates a major reduction in system overpotential compared to prior work in aprotic electrolytes. Furthermore, the maximum Faradaic efficiency of 59 ± 3% reported here for a two-carbon CO$_2$ reduction product is competitive with the best reported copper systems,$^{47-51}$ which are frequently considered state-of-the-art yet cannot generate oxalate as a product.$^{52}$

With optimal electrolysis conditions of pH 4.1 aqueous KCl and −1.48 V vs. Ag/AgCl, the pathway used to generate oxalate by the Cr-Ga system cannot include a CO$_2^-$ intermediate. Instead, a surface anion is instrumental in reducing CO$_2$ to CO, which subsequently reacts to form oxalate. Interfering with the catalyst system by
poisoning its critical surface anion sites or adequately disrupting the aqueous hydrogen bonding environment inhibits oxalate generation. Based on these results, ongoing studies seek to use HR-TEM/EDX following treatment of the Cr-Ga film with Ca$^{2+}$ or Cs$^+$ to determine whether surface anion sites are confined to or more prevalent on the crystalline portion, amorphous portion, or crystalline-amorphous interface of the catalyst species. Formate production, which occurs at a separate site, can be eliminated in the presence of a strong, anionic ligand, which interacts with the surface at non-anionic Lewis acid locations. Altering the percent composition of either Cr$_2$O$_3$ or Ga$_2$O$_3$ away from the optimal 3:1 stoichiometry decreases production of the CO intermediate or increases the quantity of unreactive HCO$_3^-$ derived from CO$_2$.

High oxalate Faradaic efficiencies and initial lifetime studies exceeding 10 days of continuous use make the Cr-Ga thin film on glassy carbon electrode a promising CO$_2$ electroreduction system. The fact that Cr-Ga achieves an oxalate product using aqueous solution, atmospheric pressure, and CO$_2$ starting material invites questions about whether, with additional studies, Cr-Ga could be a candidate catalyst for industrial oxalate production. As such, the chemistry facilitated by the Cr-Ga electrode lends real credibility to the goal of using electroreduction to turn society’s problem of excess CO$_2$ into profitable future opportunities. Nonetheless, for CO$_2$ electroreduction to adequately contribute to climate change mitigation, the ability to generate a diverse portfolio of CO$_2$ reduction products will be needed. In Chapter 3, a bimetallic electrocatalyst capable of generating three-carbon products from CO$_2$ will be discussed, further widening the scope of possible CO$_2$ reduction products and the catalysts that may be used to achieve them.
2.5 References


(22) There is one literature report that suggests that oxalate can be generated in ultra-low-proton-activity aqueous electrolyte ([a$_H$]=$10^{-10}$)$^{13,14}$ However, this 30-year old report has not been reproduced and lacks the minimum acceptable control experiments.


(27) Torelli, D. A.; Francis, S. A.; Crompton, J. C.; Javier, A.; Thompson, J. R.; Brunschwig, B. S.; Soriaga, M. P.; Lewis, N. S. Nickel–Gallium-Catalyzed Electrochemical Reduction of CO$_2$ to Highly Reduced Products at Low


Proteins in Solution and at Interfaces: Methods and Applications in Biotechnology and Materials Science; Ruso, J. M., Pineiro, Eds.; John Wiley & Sons, 2013.


Chapter 3. Evaluation of a Ni$_3$Al Intermetallic Catalyst in the Electrochemical Reduction of CO$_2$ to C1, C2, and C3 Products

3.1 Introduction

Expanding the portfolio of products that can be acquired by electroreducing CO$_2$ requires moving well beyond a minimal two-electron reduction process. Indeed, the vast majority of heterogeneous electrocatalysts to-date reduce CO$_2$ to CO$_1$–$^5$ or formate,$^6$–$^9$ and it is now possible to achieve nearly 100% Faradaic efficiency for these products at reasonable overpotentials using transition metals, post-transition metals, and their oxides. However, with the exception of the Cr-Ga oxide electrocatalyst discussed in Chapter 2, moving beyond CO and formate into the multi-carbon product space has largely required the use of copper electrodes exhibiting diverse morphologies and product selectivities.$^{10}$ To further develop the class of catalysts capable of generating C2+ products from CO$_2$, a logical next step involves taking inspiration from the Cr-Ga oxide species by continuing to examine bimetallic alloys—and, more specifically, intermetallics—as electrocatalysts. Of particular interest are bimetallic systems that have variations in either electronic structure or topology when compared to their pure components, thereby leading to products that are not observed with either of the alloy’s component metals separately.

This chapter is based on two publications, (1) ACS Catal. 2017, 7, 6815–6820 and (2) Faraday Discuss. 2019, DOI: 10.1039/C8FD00177D. Figures reprinted and adapted from these articles are used with permission from the American Chemical Society, copyright 2017, and the Royal Society of Chemistry, copyright 2019, respectively.

Data presented in Section 3.3.4 were collected primarily by Brian M. Foster and collaboratively planned and analyzed by the author and Jessica J. Frick.
Bimetallic compositions that have already been studied often contain copper, and typically they either emulate copper’s activity or fail to generate highly reduced products altogether. Of the alloy compositions studied to-date, some are prolific CO or formate generators, others facilitate reduction to alternative C1 products, and a handful produce a combination of C1 and C2 products. In an effort to improve the ability to generate highly reduced carbon products from CO₂, Nørskov developed a theoretical framework that pointed to a select group of intermetallics as electrocatalytically active, though the ultimate determination of CO₂ reduction products still relies on direct electrochemical testing. For example, Nørskov’s calculations examining oxygen binding energies on different alloys predicted that Ni-Ga intermetallics would be capable of reducing CO₂ to methanol. Following electrolysis, however, Ni-Ga compositions surprisingly generated methane, ethane, and ethylene, albeit at small Faradaic efficiencies. Subsequent work focused on tuning the reactivity of a particular Ni-Ga intermetallic, Ni₃Ga, will be discussed in Chapter 4.

From a naive periodic trends point of view, Ni-Ga and Ni-Al might be expected to promote similar chemistry, but the latter material has not been suggested as electroactive toward CO₂. Moreover, the thermodynamic materials properties of these two systems are sufficiently different that comparable electrochemical catalysis cannot be assumed. Ni-Al compositions have been shown, however, to emulate or improve upon Raney nickel catalysts in hydrogenation reactions, with nickel providing adsorbed hydrogen. Furthermore, the amphoteric nature of aluminum has been exploited in homogenous CO₂ reduction. In these systems, a Lewis pair is formed between a molecule’s aluminum atom and one of the oxygen atoms of CO₂, permitting the binding of the carbon atom to an
alternative site for reduction purposes.\textsuperscript{33–36} In an attempt to combine these ideal qualities, Ni-Al was selected as a candidate heterogeneous catalyst material for CO\textsubscript{2} electroreduction, and the Ni\textsubscript{3}Al stoichiometry was chosen as the most nickel-rich, stable intermetallic of this composition.

In this chapter, a thin film electrocatalyst of the intermetallic Ni\textsubscript{3}Al supported on glassy carbon will be shown to generate reduced C1, C2, and C3 products from CO\textsubscript{2} with good performance, stability, and reproducibility at modest overpotential. Competing copper-based electrocatalysts were first reported to carry out the reduction of CO\textsubscript{2} to C2 and C3 products in 1988.\textsuperscript{37–39} However, in the intervening 30 years, no other metal electrodes demonstrated this activity until the more recent report of C2 products using a Ni-Ga electrode. The Ni\textsubscript{3}Al system discussed here can be added to that exceedingly short list and demonstrates for the first time that metal alloys—not just copper-based electrode systems—can generate C3 products from CO\textsubscript{2}.

3.2. Experimental Methods

3.2.1 Materials

Nickel(II) nitrate hexahydrate (99.999%), aluminum(III) nitrate nonahydrate (99.997%), K\textsubscript{2}SO\textsubscript{4} (\geq 99.0%), KHCO\textsubscript{3} (99.7%), 1,4-dioxane (99.8%), 1-propanol (\geq 99.5%), methanol (\geq 99.5%), formic acid (\geq 95%), and \textsuperscript{13}CO\textsubscript{2} were obtained from Sigma-Aldrich and used as received. Ar, CO\textsubscript{2}, CO, 95% Ar/5% H\textsubscript{2}, and 50% CO/50% H\textsubscript{2} gases and mixtures were obtained from AirGas. Glassy carbon plates (GLAS11; 25 x 25 x 3 mm) and highly oriented pyrolytic graphite (HOPG; Grade SPI-3; 10 x 10 x 1 mm) were purchased from Structure Probe Inc. Reticulated vitreous carbon (RVC) foam was
provided by ERG Materials and Aerospace, Corp. Conducting silver and Loctite Hysol insulating epoxies were purchased from Epo-Tek and Grainger, respectively.

3.2.2 Ni₃Al Thin Film Synthesis and Characterization

Thin film Ni₃Al alloys were synthesized using a previously described method.²⁴ Briefly, aqueous solutions of 0.052 M nickel(II) nitrate hexahydrate and 0.036 M aluminum(III) nitrate nonahydrate were combined in appropriate ratios to achieve the Ni₃Al stoichiometry. In 0.1-mL increments, 0.5-mL portions of the nickel-aluminum nitrate solution were drop-casted onto glassy carbon pieces (or alternative solid supports) that had been set on a hot plate and heated to 150 °C. After drop-casting, the solid supports remained on the hot plate for 15 min until the solution completely evaporated, revealing green surface films. The solid supports were then placed in alumina boats and loaded into either a Lindberg/Blue M or Carbolite Quartz Tube Furnace under 95% Ar/5% H₂ gas flow. The furnace was ramped at a rate of 3 °C/min to 700 °C, where it rested for 5 h.

Following synthesis, Ni₃Al thin films (gray in color) on glassy carbon were analyzed for composition by powder X-ray diffraction using a Bruker D8 Advance diffractometer with 0.083° step size and CuKα radiation. A FEI XL30 FEG-SEM equipped with EVEX EDX detector was used to examine thin film morphology and composition before and after electrochemical experimentation. SEM images and EDX spectra were obtained using a 10 keV electron beam with a 10–15 mm working distance. XPS data were collected using a ThermoFisher K-Alpha X-Ray Photoelectron Spectrometer (20 eV pass energy, 50 ms dwell time) and analyzed with CasaXPS
software. Post-electrolysis samples were transferred from the electrochemical cell to the XPS instrument under inert atmosphere.

3.2.3 Electrode Preparation and Electrochemical Experimentation

Electrodes were prepared by affixing a coiled copper wire to the glassy carbon substrate using conducting silver epoxy, extending the length of copper wire through a glass tube, and sealing both ends of the tube using insulating epoxy. It was critical that the insulating epoxy was also used to completely cover the silver epoxy and copper wire attached to the substrate. In some experiments, the top of a film-deposited substrate was wrapped in copper tape and held using an alligator clip attached to copper wire similarly threaded through a glass tube sealed with insulating epoxy. Comparable amounts of charge were passed in electrochemical experiments featuring the two types of electrode preparations. A general description of the electrode fabrication method unique to the preliminary photoelectrochemical experiments discussed at the end of the chapter can be found in Section 3.3.4.

Electrochemical experiments were performed using CH Instruments 760 and 1140 potentiostats. Cyclic voltammetry experiments were completed in a three-neck round-bottom flask using the Ni$_3$Al film on glassy carbon as the working electrode referenced to Ag/AgCl and a Pt mesh counter electrode in 0.1 M K$_2$SO$_4$ at pH 4.5. Bulk electrolysis experiments were undertaken in the same electrolyte solution (with the exception of pH dependence experiments, which utilized K$_2$SO$_4$ buffered with KHCO$_3$) using custom electrolysis cells with gas-tight ports for the above electrodes. In these experiments, the Pt mesh counter electrode was situated in a fritted gas dispersion tube to separate the reduction reaction at the cathode from oxidation processes at the anode, and a stir bar was
employed. The reaction solutions were purged with CO₂, CO, or Ar for 20 min prior to experimental or control trials; experiments using ¹³CO₂ were not completely purged with the starting material, resulting in a small amount of ¹²CO₂ contamination that could be quantified by ¹H-NMR. Bulk electrolysis experiments were performed over intervals of at least 4 h, during which time the headspace was sampled every 20 min and the electrochemical solution was sampled every 60 min.

3.2.4 Product Analysis

During and after bulk electrolysis experiments, both the solution and headspace were sampled for products using ¹H- or ¹³C-NMR and gas chromatography, respectively. Solution samples were prepared by combining 530 μL of the experimental electrolyte with 60 μL D₂O and 10 μL 1,4-dioxane. These samples were examined by ¹H-NMR or ¹³C-NMR using a Bruker Avance III 500 MHz NMR Spectrometer, while HSQC experiments were performed on an Avance III 800 MHz NMR Spectrometer; both spectrometers utilized cryoprobe detectors. A custom water suppression method allowed for sampling of aqueous electrolyte solutions. Major liquid products were quantified using 5-point calibration curves for ¹H-NMR analysis. Further confirmation of these products was achieved by freezing the electrolysis solution in liquid N₂ and performing continuous mass spectrometry with an SRS Residual Gas Analyzer 200 as the frozen pellet warmed to room temperature and then as the liquid melt was heated to boiling.

CO was detected using a 60 °C isothermal method over 5 min on a HP6890 Gas Chromatograph and TCD with a Molsieve 5A PLOT capillary column (Agilent) running He as the flow gas. H₂ was sampled with an SRI 8610C Gas Chromatograph and TCD with a Molsieve column and Ar flow gas. A 7-min isotherm at 80 °C was employed.
Gaseous products were quantified using 30-point calibration curves with $R^2$ values $\geq 0.99$. Following control experiments with $^{13}$CO$_2$, the headspace was sampled using a Nicolet 730 FT-IR Spectrometer with 1 cm$^{-1}$ resolution and a gas cell terminated by KBr plates. Faradaic efficiencies were calculated based on the total charge passed during each experiment, as well as the product quantities determined by gas- and liquid-phase sampling. Catalytic efficiency parameters were calculated based on Equation 2.1 adapted from Pander et al., where achievement of diffusion-limited current under conditions of semi-infinite linear diffusion and a standard hydrogen half-cell anode are assumed.\textsuperscript{40}

3.3 Results and Discussion

3.3.1 Synthesis and Characterization of Ni$_3$Al on Glassy Carbon

Intermetallic Ni$_3$Al thin films on glassy carbon solid supports were synthesized by adapting a drop-casting and furnace reduction procedure employed by Torelli et al.\textsuperscript{24} As shown in Figure 3.1, powder X-ray diffraction (XRD) of the films confirmed the successful generation of the cubic Ni$_3$Al composition as indicated by the (111) and (211) planes; energy-dispersive X-ray spectroscopy (EDX) supported the compositional analysis. Thin films exhibited macroscopic surface areas of approximately 0.75 cm$^2$, while imaging by scanning electron microscopy, also shown in Figure 3.1, indicated that the films were comprised of micrometer-scale platelets uniformly distributed across the glassy carbon surface.
Figure 3.1. The powder X-ray diffraction pattern of the thin film on glassy carbon (black) referenced to PDF 01-071-5883 (red) confirms the assignment of bulk Ni$_3$Al (left). Scanning electron microscopy images of Ni$_3$Al suggest that the films are comprised of uniform, micrometer-scale platelets distributed across the glassy carbon surface (right). Adapted with permission from ACS Catal. 2017, 7, 6815–6820. Copyright 2017 American Chemical Society.

Figure 3.2. XPS analysis of as-synthesized Ni$_3$Al thin film on glassy carbon, indicating that the Ni (left) and Al (right) components of the surface are highly oxidized. Binding energies are referenced to the adventitious C 1s peak at 284.5 eV (not shown). Adapted with permission from ACS Catal. 2017, 7, 6815–6820. Copyright 2017 American Chemical Society.
X-ray photoelectron spectroscopy (XPS) studies suggested that surface Ni was comprised of a mixture of Ni(OH)$_2$, NiO, and Ni metal, with the Ni$^{2+}$ components making up a majority of the composition, while all surface Al adopted the oxidized Al$_2$O$_3$ form (Figure 3.2). In preliminary experiments characterizing the electrochemical response toward CO$_2$, cyclic voltammetry scans performed in aqueous electrolyte under CO$_2$ versus Ar saturation resulted in relatively featureless traces, although current enhancement was observed at more negative potentials leading into a proton reduction wave (Figure 3.3).

![Figure 3.3](image)

**Figure 3.3.** Cyclic voltammograms obtained using Ni$_3$Al on glassy carbon under CO$_2$ (red) and Ar (black) saturation. Voltammograms were obtained using Pt mesh counter and Ag/AgCl reference electrodes in 0.1 M K$_2$SO$_4$ electrolyte. Adapted with permission from ACS Catal. 2017, 7, 6815–6820. Copyright 2017 American Chemical Society.

### 3.3.2 Electrocatalytic Activity of Ni$_3$Al Toward CO$_2$ Reduction

Bulk electrolysis experiments using the Ni$_3$Al thin film on glassy carbon as the working electrode and a Pt mesh counter electrode were performed at an applied potential of −1.38 V vs. Ag/AgCl in a sealed two-compartment cell containing 0.1 M K$_2$SO$_4$.
electrolyte solution saturated with CO$_2$ (pH 4.5). Total current densities of $-2.1 \pm 0.4$ mA/cm$^2$ were recorded and could be maintained for a period of several hours. $^1$H-NMR spectra obtained as a function of electrolysis time (see Figure 3.4A) indicated the growth of largely isolated peaks characteristic of 1-propanol, acetone, ethanol, methanol, and formate. Table 3.1 lists adjusted NMR shifts of these products after referencing to a 1,4-dioxane internal standard.

<table>
<thead>
<tr>
<th>Species</th>
<th>Peak splitting</th>
<th>Shift (ppm)</th>
<th>Adjusted shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol</td>
<td>triplet</td>
<td>0.73</td>
<td>0.87</td>
</tr>
<tr>
<td>2-propanol†</td>
<td>$doublet$</td>
<td>1.01</td>
<td>1.15</td>
</tr>
<tr>
<td>Ethanol</td>
<td>triplet (partial visibility)</td>
<td>1.03</td>
<td>1.17</td>
</tr>
<tr>
<td>1-propanol</td>
<td>sextet</td>
<td>1.38</td>
<td>1.52</td>
</tr>
<tr>
<td>$Acetate†$</td>
<td>$singlet$</td>
<td>1.76</td>
<td>1.90</td>
</tr>
<tr>
<td>Acetone</td>
<td>singlet</td>
<td>2.07</td>
<td>2.21</td>
</tr>
<tr>
<td>Methanol</td>
<td>singlet</td>
<td>3.20</td>
<td>3.34</td>
</tr>
<tr>
<td>1-propanol</td>
<td>triplet</td>
<td>3.40</td>
<td>3.54</td>
</tr>
<tr>
<td>Ethanol</td>
<td>quartet</td>
<td>3.50</td>
<td>3.64</td>
</tr>
<tr>
<td>$1,4$-dioxane‡</td>
<td>$singlet$</td>
<td>3.61</td>
<td>3.75</td>
</tr>
<tr>
<td>2-propanol†</td>
<td>$multiplet$</td>
<td>3.86</td>
<td>4.00</td>
</tr>
<tr>
<td>Formate</td>
<td>singlet</td>
<td>8.29</td>
<td>8.43</td>
</tr>
</tbody>
</table>

† Contaminant; non-CO$_2$ reduction product  
‡ Internal standard

Several analytical methods were employed to confirm the identities of these C1–C3 products and to support the assertion that they were, in fact, derived from the CO$_2$ starting material. Electrolysis experiments performed using $^{13}$CO$_2$ yielded $^1$H-NMR
traces for 1-propanol, ethanol, methanol, and formate exhibiting the peak splitting expected for $^{13}\text{C}$-coupling. However, a large doublet signal of 2-propanol (believed to be generated from acetone reduction$^{41}$) obscured the ethanol triplet, and acetone splitting was inconclusive using simple $^1\text{H}$-NMR. To resolve these ambiguities, $^{13}\text{C}$-NMR spectra were obtained and illuminated a clear set of ethanol peaks (Figure 3.4B).

**Figure 3.4.** Confirmation of C1–C3 products generated during electrolysis at $-1.38\text{ V vs. Ag/AgCl}$ using Ni$_3$Al. (A) $^1\text{H}$-NMR following $^{12}\text{CO}_2$ reduction points to 1-propanol, methanol, and formate as major products. The broad peak at 4.66 ppm is a suppressed water signal. (B) $^{13}\text{C}$-NMR following electrolysis of $^{13}\text{CO}_2$ confirms the presence of these species as well as ethanol. Adapted with permission from *ACS Catal.* 2017, 7, 6815–6820. Copyright 2017 American Chemical Society.
In addition, a $^1$H–$^{13}$C heteronuclear single quantum correlation (HSQC) NMR experiment was performed to confirm the presence of $^{13}$C-labelled acetone. The resulting spectrum is shown in Figure 3.5 and the cross-peak assignments are listed in Table 3.2. Peak splitting within the $^{13}$C-NMR spectrum, particularly in the C2 and C3 products, implied that all product carbon atoms were derived from the original $^{13}$CO$_2$ material. Mass spectrometry further supported the NMR results.

![Figure 3.5. $^1$H–$^{13}$C HSQC NMR indicates that $^{13}$C-labelled acetone and previously confirmed products were generated during electrolysis of $^{13}$CO$_2$ at −1.38 V vs. Ag/AgCl. Adapted with permission from ACS Catal. 2017, 7, 6815–6820. Copyright 2017 American Chemical Society.](image-url)
Table 3.2. $^1$H–$^{13}$C HSQC NMR cross-peak assignments for samples obtained after electrolysis of $^{13}$CO$_2$. Peak positions are pre-adjusted with respect to a 1,4-dioxane internal standard.

<table>
<thead>
<tr>
<th>Species</th>
<th>$^1$H-NMR shift (ppm)</th>
<th>$^{13}$C-NMR shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol</td>
<td>0.88</td>
<td>9.68</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.17</td>
<td>16.93</td>
</tr>
<tr>
<td>1-propanol</td>
<td>1.54</td>
<td>24.74</td>
</tr>
<tr>
<td>Acetone</td>
<td>2.23</td>
<td>30.34</td>
</tr>
<tr>
<td>Methanol</td>
<td>3.35</td>
<td>49.01</td>
</tr>
<tr>
<td>1-propanol</td>
<td>3.55</td>
<td>63.78</td>
</tr>
<tr>
<td>Ethanol</td>
<td>3.65</td>
<td>57.60</td>
</tr>
<tr>
<td>1,4-dioxane†</td>
<td>3.75</td>
<td>66.65</td>
</tr>
<tr>
<td>Formate</td>
<td>8.30</td>
<td>167.6</td>
</tr>
</tbody>
</table>

† Internal standard

Faradaic efficiencies of 1.9 ± 0.3% for 1-propanol, 1.0 ± 0.2% for methanol, and 0.75 ± 0.03% for formate were observed, with lesser contributions from ethanol and trace amounts of acetone. As shown in Figure 3.6A, the potential dependence of CO$_2$ electroreduction to these liquid products confirms −1.38 V vs. Ag/AgCl as the optimal potential at which to operate the electrochemical cell. Furthermore, pH dependence studies summarized in Figure 3.6B indicate that a moderately acidic pH of 4.5 best facilitates the conversion of CO$_2$. It is worth noting that the solution pH does not change more than a few tenths of a unit from the beginning to the end of an electrolysis experiment. This suggests that any pH increase at the electrode’s surface during electrolysis is slight and, according to Figure 3.6B, should not drastically alter the product distribution, especially when coupled with solution stirring.
Figure 3.6. Gas- and liquid-phase CO\textsubscript{2} reduction product distribution of Ni\textsubscript{3}Al. (A) Faradaic efficiencies for CO, 1-propanol, methanol, and formate are reported at a range of applied potentials. (B) Faradaic efficiencies for H\textsubscript{2}, CO, and liquid products are plotted as a function of pH and confirm charge balance (top); the liquid products are also shown individually for clarity (bottom). Adapted with permission from ACS Catal. 2017, 7, 6815–6820. Copyright 2017 American Chemical Society.

3.3.3 Mechanistic Insights into CO\textsubscript{2} Reduction on Ni\textsubscript{3}Al

Some understanding of the mechanism facilitated by the Ni\textsubscript{3}Al film would allow for future work in optimizing the generation of select C1, C2, or C3 products. As such, studies to probe mechanistic details sought to determine the significance of the following factors: (A) the choice of carbon solid support; (B) the intermetallic nature of the catalyst; and (C) the intermediates required to achieve multi-carbon reduction products. The first of these considerations, solid support choice, has occasionally been shown in the literature to directly affect catalytic activity.\textsuperscript{42–45} Here, the magnitude of its influence was
easily tested by synthesizing Ni$_3$Al on alternative carbon-based support materials, including reticulated vitreous carbon (RVC), a structural relative of glassy carbon, and highly oriented pyrolytic graphite (HOPG). Ultimately, when electrolysis experiments were conducted with these differently supported Ni$_3$Al films under the optimized electrochemical conditions, the only observable differences, especially for liquid-phase products, were slight changes in Faradaic efficiencies. As shown in Figure 3.7, product distributions were not affected, suggesting that the carbon solid support does not play a direct role in CO$_2$ electroreduction facilitated by Ni$_3$Al.

![Figure 3.7](image.png)

**Figure 3.7.** Faradaic efficiencies for CO$_2$ reduction products achieved using Ni$_3$Al films on different carbon solid supports. Adapted with permission from *Faraday Discuss.* 2019, DOI: 10.1039/C8FD00177D. Copyright 2019 Royal Society of Chemistry.

A second factor warranting consideration is the intermetallic nature of Ni$_3$Al.

When working with a multi-metal catalyst that facilitates a multi-step reduction process, one might imagine two overly simplistic scenarios that could define the role of each component metal in electrocatalysis. For example, considering a binary metal catalyst A–B, if metal A reduces CO$_2$ to CO and metal B selectively reduces CO to a multi-carbon
final product, then a heterogeneous mixture of A and B would be expected to perform the catalytic task, while an intermetallic or alloy phase, AB, would potentially effect a different chemistry and product distribution. In the case of Ni₃Al, it is instructive to know whether generation of multi-carbon products is predicated on the presence of an intermetallic compound, as well as what this might mean for the mechanism underlying this catalyst’s unique activity.

To examine the importance of electrode structure for Ni₃Al, an analogous electrode consisting of non-mixed nickel- and aluminum-based films was prepared (i.e., such that the two metal components were isolated from one another on the same glassy carbon solid support). These electrode species, referred to as 3Ni-Al, exhibited the same 3:1 ratio of metals as the parent intermetallic. A complete summary of characterization data comparing Ni₃Al to the non-mixed 3Ni-Al electrode is provided in Table 3.3, which indicates nearly identical surface compositions.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Bulk</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni₃Al (cubic)</td>
<td>Ni(II) oxides + Ni</td>
</tr>
<tr>
<td>Ni₃Al</td>
<td>Ni₃Al (cubic)</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>3Ni-Al</td>
<td>Ni (cubic)</td>
<td>Ni(II) oxides + Ni</td>
</tr>
<tr>
<td></td>
<td>Al₂O₃ (amorphous)</td>
<td>Al₂O₃</td>
</tr>
</tbody>
</table>

However, upon electrochemical testing of the 3Ni-Al electrode at –1.38 V vs. Ag/AgCl (pH 4.5, 0.1 M K₂SO₄), a different electrocatalytic performance was immediately observed. As shown in Figure 3.8, while the Ni₃Al intermetallic
electrochemically reduces CO<sub>2</sub> to form measurable quantities of CO, 1-propanol, methanol, and formate, the non-mixed 3Ni-Al electrode only generated small quantities of CO and formate. H<sub>2</sub> evolution accounted for the remaining charge, reaching Faradaic efficiencies of approximately 94% for 3Ni-Al. These results suggest that the intermetallic character of Ni<sub>3</sub>Al is required to achieve higher-order products from CO<sub>2</sub>. Additionally, while surface oxides are consistently present, Table 3.3 shows that the surface compositions of the intermetallic and non-mixed electrodes are matching, so variation in surface oxide composition in and of itself cannot explain the differences in catalytic activity. These observations lead to the conclusion the two metals interact synergistically, rather than simply perform complementary tasks, in the CO<sub>2</sub> electroreduction process.

**Figure 3.8.** Distribution of CO<sub>2</sub> reduction products achieved using intermetallic Ni<sub>3</sub>Al and non-mixed 3Ni-Al electrodes on glassy carbon solid supports. Adapted with permission from *Faraday Discuss.* 2019, DOI: 10.1039/C8FD00177D. Copyright 2019 Royal Society of Chemistry.
Of course, another important indicator of catalytic mechanism is the identity of intermediates required to achieve the final products. In the case of Ni$_3$Al, it was immediately evident that generation of CO was maximized (33 ± 3% Faradaic efficiency) at the same operating potential as the major liquid-phase products, suggesting that CO might be an intermediate in CO$_2$ electroreduction to 1-propanol and methanol. To test this hypothesis, CO$_2$ was replaced with CO as a feedstock in electrolysis, and the resulting reduction products were examined by $^1$H-NMR. Ni$_3$Al thin films on glassy carbon reduced CO to methanol as well as the C2 and C3 liquid products achieved using a CO$_2$ feedstock and in the same relative quantities. Electrolysis experiments utilizing a mixed $^{13}$CO$_2$/$^{12}$CO feedstock indicated that 1-propanol, methanol, ethanol, and acetone were preferentially generated from CO, with only small contributions from $^{13}$CO$_2$. In these experiments, trace or no formate was produced.

Furthermore, plotting 1-propanol and methanol quantities obtained during CO-feedstock trials against the amount of charge passed during an experiment, as shown in Figure 3.9, illuminated differences in the rates of product generation. Specifically, when the electrochemical cell was saturated with CO$_2$, both 1-propanol and methanol increased linearly with charge passed. However, when the feedstock was switched to CO, though 1-propanol retained its linearity (but had a slope that was greater by two orders of magnitude than that of the CO$_2$-derived analog), methanol formation adopted an exponential growth curve.
Accordingly, it appears that CO is, in fact, an intermediate leading to Ni₃Al’s generation of methanol, C₂, and C₃ products from CO₂. The product generation curves in Figure 3.9 may be rationalized by considering the number of carbon atoms in each of the two major liquid products. Only one CO₂ molecule, and therefore one CO molecule, must be present to produce methanol, so when the system is supplied with the intermediate CO it generates methanol relatively easily, leading to an exponential production curve. The
generation of 1-propanol necessitates three carbon atoms, so accumulation of three carbon-containing intermediates—at least one of which is CO—near each another on the film surface is still required to achieve the final species, thereby limiting the product generation rate.

It is worth noting that many researchers describe copper-mediated CO₂ electroreduction to highly reduced products as a mechanistically Fischer-Tropsch-type process,⁴⁶-⁴⁸ though specific C₂ products (e.g., ethylene) have been attributed to different pathways.⁴⁹,⁵⁰ Fischer-Tropsch catalysis has long been known to exhibit isotope effects when substituting H₂, the key reactant alongside CO, with D₂.⁵¹ Specifically, H₂/D₂ studies of Fischer-Tropsch catalysis typically reveal an inverse isotopic effect on the order of r₅/D₅ = 1.2–1.6, where r₅ and r₇ denote reaction rates in the presence of D₂ and H₂, respectively, though a few catalysts exhibit normal kinetic isotope effects (i.e., r₅/D₅ < 1).⁵²,⁵³ Given the similar activity profiles of copper electrocatalysts and Ni₃Al, it is therefore possible that the intermetallic operates via an analogous mechanism.

To indirectly probe this possibility, the Ni₃Al on glassy carbon electrode was subjected to electrolysis experiments featuring D₂O-based electrolyte (0.1 M K₂SO₄). Interestingly, under these conditions, Faradaic efficiencies for CO increased to 49 ± 7% while multi-carbon product generation was inhibited. A similar effect was observed in Chapter 2 when the C₂ product oxalate could no longer be generated in D₂O, though this was attributed to alterations in the localized hydrogen bonding network. In the case of Ni₃Al in D₂O, the sustained generation of CO coupled with an inability to reduce it further introduces the possibility that CO reduction may be rate-limiting. Furthermore, these results suggest that Ni₃Al may not operate via a traditional Fischer-Tropsch-like
mechanism since, to-date, no Fischer-Tropsch catalysts have been reported to fail to generate hydrocarbons altogether when in the presence of D₂ or D₂O. This sort of mechanistic analysis, though preliminary, will help to improve the design and optimization of future alloy catalysts.

<table>
<thead>
<tr>
<th>System</th>
<th>Product</th>
<th>Potential (V vs. Ag/AgCl)</th>
<th>Faradaic efficiency (%)</th>
<th>Catalytic efficiency† (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni₃Al thin film</td>
<td>1-propanol</td>
<td>–1.38</td>
<td>1.9</td>
<td>0.52</td>
</tr>
<tr>
<td>Ni-Ga thin film²⁴</td>
<td>Methane</td>
<td>–1.38</td>
<td>~2.1</td>
<td>0.45</td>
</tr>
<tr>
<td></td>
<td>Ethane</td>
<td>–1.38</td>
<td>~1.7</td>
<td>0.44</td>
</tr>
<tr>
<td></td>
<td>Ethylene</td>
<td>–1.38</td>
<td>~0.4</td>
<td>0.12</td>
</tr>
<tr>
<td>Cu electrode³⁸</td>
<td>1-propanol</td>
<td>–1.61</td>
<td>4.2</td>
<td>0.96</td>
</tr>
<tr>
<td>Cu nanocrystals³⁹</td>
<td>1-propanol</td>
<td>–1.06</td>
<td>10.6</td>
<td>4.0</td>
</tr>
<tr>
<td>Organically modified Cu-Pt⁵⁶</td>
<td>1-propanol</td>
<td>–1.16</td>
<td>1</td>
<td>0.03</td>
</tr>
</tbody>
</table>

†Calculation assumes conditions of diffusion-limited current under semi-infinite linear diffusion and a standard hydrogen half-cell anode.

When comparing the efficacy of catalysts such as Ni₃Al to those reported in the literature, it is instructive to consider certain factors beyond Faradaic yield. Pander et al.’s catalyst efficiency parameter summarizes both the overpotential and turnover frequency (i.e., catalytic current) of an electrocatalytic reaction independent of mechanistic details.³⁶ Applying this calculation (see Equation 2.1) to Ni₃Al’s performance resulted in a catalytic efficiency of 0.5 ± 0.1% for the C₃ product 1-propanol (Eₖ = –0.32 V vs. NHE⁵⁵). This is comparable to the catalytic efficiency for Torelli et al.’s Ni-Ga thin film in the generation of ethane (0.44%; based on maximum Faradaic efficiency), their major C₂ product.²⁴ Catalytic and Faradaic efficiencies for
Torelli et al.’s other products, as well as 1-propanol generated using various copper-based catalysts, are listed in Table 3.4.

Furthermore, it is well established that copper electrodes suffer from instability in solution and excessive overpotential requirements for the formation of higher order organic products, making their usage to-date impractical.\textsuperscript{55} Ni\textsubscript{3}Al, on the other hand, is stable in aqueous solution, and post-electrolysis XPS analysis demonstrates that the surface composition remains unchanged during electrochemical CO\textsubscript{2} reduction. Scanning electron microscopy confirms that the thin film is physically robust and, as demonstrated by the small amount of material loss observed, withstands exposure to electrochemical conditions while maintaining initial efficiencies for CO\textsubscript{2} reduction (Figure 3.10). In addition to its stability, Ni\textsubscript{3}Al has also been shown to generate electroreduced products from CO\textsubscript{2} continuously over a period of four to five days.

\begin{table}[h]
\centering
\begin{tabular}{|l|c|}
\hline
Element & Atomic % \\
\hline
Ni (L) & 69 \\
Al (K) & 31 \\
\hline
\end{tabular}
\caption{Table 3.4. Elemental Composition of Ni\textsubscript{3}Al Thin Film}
\end{table}

\textbf{Figure 3.10.} SEM image and corresponding EDX analysis (tabular inset) of a Ni\textsubscript{3}Al thin film on glassy carbon following electrolysis for 48 h. Adapted with permission from \textit{ACS Catal.} \textbf{2017}, \textit{7}, 6815–6820. Copyright 2017 American Chemical Society.
3.3.4 Photoelectrochemical Adaptation Using a CuInSe$_2$/Ni$_3$Al+TiO$_2$ Composite Electrode

The versatility of the Ni$_3$Al catalyst in facilitating CO$_2$ reduction has been further suggested by preliminary work combining the intermetallic with the well-characterized semiconductor CuInSe$_2$.\textsuperscript{57} Recent progress toward this photoelectrochemical adaptation of Ni$_3$Al will be summarized here, providing an outlook for future interconversions between electrochemical and photoelectrochemical CO$_2$ reduction systems.

A composite electrode, hereafter referred to as CuInSe$_2$/Ni$_3$Al+TiO$_2$, was prepared by painting an aqueous slurry of Ni$_3$Al, scraped from the glassy carbon support post-synthesis, and TiO$_2$, a known protective layer for chalcopyrite semiconductor stabilization,\textsuperscript{58,59} onto the surface of a CuInSe$_2$ pellet. As seen in the SEM image in Figure 3.11, the alloy and TiO$_2$ were uniformly distributed across the surface of the electrode. This coating exhibited a thickness of approximately 2–3 µm, thereby providing substantial semiconductor coverage. The pellet was then fashioned into an electrode as previously described.\textsuperscript{60}

![SEM image of CuInSe$_2$/Ni$_3$Al+TiO$_2$](image.png)

**Figure 3.11.** SEM image of CuInSe$_2$/Ni$_3$Al+TiO$_2$, confirming surface homogeneity. The inset depicts the pellet cross-section and indicates that the thickness of the Ni$_3$Al+TiO$_2$ layer is 2–3 µm. Images were obtained using a 5 keV electron beam.
As shown in Figure 3.12A, preliminary linear sweep voltammograms (LSV) using the CuInSe₂/Ni₃Al+TiO₂ composite electrode exhibited current enhancement around -0.4 V vs. Ag/AgCl under CO₂ saturation compared to Ar, suggesting the onset of CO₂ reduction. In addition, the presence of a photocurrent was revealed using chopped-light LSVs obtained in a CO₂-saturated environment (Figure 3.12B). This confirms that light penetration reaches beyond the 2–3 µm layer of Ni₃Al+TiO₂, in agreement with the absorbance measurements and subsequent absorption depth calculations performed by Frick et al.⁶⁰ This result is further supported by LSVs obtained separately in light and dark conditions, which show a noticeable difference in current density.

![Figure 3.12. Preliminary electrochemical analyses using the composite CuInSe₂/Ni₃Al+TiO₂ electrode. (A) LSVs collected under illumination and either Ar or CO₂ saturation indicate current enhancement in the presence of CO₂. (B) The chopped-light LSV (where dark current is subtracted to portray differential current density) and standard LSVs collected under dark and light conditions (inset) were obtained under CO₂ atmosphere. Data were collected using 0.1 M KHCO₃ electrolyte (pH 7), 25 mV/s scan rate, and 100 mW/cm² light intensity, where applicable.](image)

Based on ¹H-NMR analysis of the electrolyte following preliminary electrolysis experiments, methanol was the primary CO₂ reduction product achieved; this was confirmed via electrolysis of ¹³CO₂. The remainder of charge passed contributed to H₂ evolution. Subsequent bulk photoelectrolysis experiments, whose results are summarized
in Figure 3.13, were performed using 0.1 M KHCO$_3$ electrolyte, a 200 mW/cm$^2$ light source, and operating potentials ranging from –0.6 to –1.4 V vs. Ag/AgCl. At most potentials, methanol Faradaic efficiencies ranged from 2–6%. However, the CO$_2$ reduction activity of the photoelectrochemical system is highly potential-dependent. This is evidenced by a maximum Faradaic efficiency of 25% achieved at –0.8 V vs. Ag/AgCl, representing nearly five times greater methanol production than the second highest efficiency.

![Graph showing Faradaic efficiencies for methanol achieved using CuInSe$_2$/Ni$_3$Al+TiO$_2$ in photoelectrochemical CO$_2$ reduction at various operating potentials. Experiments were conducted in 0.1 M KHCO$_3$ (pH 7) using a light intensity of 200 mW/cm$^2$ until 1.0–1.4 C of charge had passed.](image)

As discussed in the preceding sections, the purely electrochemical Ni$_3$Al system achieved a maximum methanol Faradaic efficiency of 1.0%—alongside 1-propanol (1.9%) and CO (33%)—using an operating potential of –1.38 V vs. Ag/AgCl. Interestingly, the photoelectrochemical CuInSe$_2$/Ni$_3$Al+TiO$_2$ system failed to generate detectable quantities of 1-propanol or CO. The absence of 1-propanol may be attributed
to the lower overall current densities and smaller electrode size compared to Ni$_3$Al on glassy carbon. CO, an intermediate en route to more reduced products, may have been generated and efficiently converted to methanol at the CuInSe$_2$/Ni$_3$Al+TiO$_2$ surface. In fact, use of a CO feedstock in the composite photoelectrochemical system in place of CO$_2$ did yield methanol, albeit at somewhat lower Faradaic efficiencies. Nonetheless, the methanol Faradaic efficiencies achieved photoelectrochemically using CuInSe$_2$/Ni$_3$Al+TiO$_2$ exceed those achieved by the electrochemical Ni$_3$Al analog at all potentials studied. However, a large dark current in LSV experiments facilitated some methanol production during electrolysis (i.e., Faradaic efficiencies < 15%), so efforts to eliminate this dark current are the focus of ongoing studies.

In any case, the CuInSe$_2$/Ni$_3$Al+TiO$_2$ composite electrode represents the formative case study combining a CO$_2$ reduction catalyst with a chalcopyrite photoabsorber to achieve photoelectrochemical reduction of CO$_2$ to methanol. Moreover, the overpotential of methanol production was reduced by three-quarters from 800 mV, required by the purely electrochemical Ni$_3$Al system, to just 200 mV for the photoelectrochemical composite. These results offer a promising outlook for future combinations of electrocatalysts and semiconductors to lower the electrical inputs needed to achieve more highly reduced products from CO$_2$.

### 3.4 Summary and Conclusions

The Ni$_3$Al thin film on glassy carbon electrode is the first copper-free, heterogeneous catalyst capable of generating C3 products, including 1-propanol and acetone, from CO$_2$ starting material, and its Faradaic efficiencies for 1-propanol generation are competitive with those achieved on most copper species.$^{37,38}$ Like copper
analogs, Ni₃Al facilitates multi-carbon product generation via a CO-dependent pathway, though it is unlikely that this pathway resembles traditional Fischer-Tropsch catalysis. The electrocatalyst also exhibits enhanced electrocatalytic stability, performing continuous CO₂ reduction over several days while incurring minimal physical and no compositional degradation. Preliminary evidence has shown that this unique catalyst can be converted into a selective photoelectrochemical system for methanol production when paired with a suitable photoabsorber.

Ultimately, the electrochemical activity of Ni₃Al represents a significant advancement in catalyst discovery, widening the portfolio of products that can be generated in CO₂ reduction as well as the species that can be used to achieve them. Ongoing catalyst development efforts in the intermetallic space and beyond are poised to further expand this scope. However, the discovery of new catalytically active materials is just one way that enhanced activity can be elicited. Manipulating the properties of existing catalysts, as will be discussed in Chapter 4, offers tangible opportunities for tuning electrochemical CO₂ reduction activity.

3.5 References


Kortlever, R.; Peters, I.; Koper, S.; Koper, M. T. M. Electrochemical CO₂ Reduction to Formic Acid at Low Overpotential and with High Faradaic Efficiency


4.1 Introduction

While catalyst discovery is important for expanding or tailoring product distributions achieved in CO$_2$ electroreduction, another strategy for improving activity involves tuning existing catalyst species to achieve more favorable outcomes. Such outcomes may include lower overpotential requirements, higher product efficiencies, or greater selectivity for one product over others. Materials that facilitate the transformation of CO$_2$ are wide-ranging, so many catalytic species exist that can be tuned to improve their response toward CO$_2$ reduction. In fact, this strategy has been employed widely by individuals studying CO$_2$ reactivity at noble metal electrodes. In the case of heterogeneous silver electrocatalysts, for example, numerous researchers have modified the structure, morphology, or composition of what is nominally the same electrode material and, as a result, elicited new or improved activity toward CO$_2$.\textsuperscript{1-8}

The rationale for employing these sorts of tuning strategies is clear. When a known CO$_2$-reducing material is altered to include novel structures or morphologies, it is
anticipated that the newly introduced characteristic may change the base material’s activity by increasing the concentration of surface active sites or improving intermediate stability, thereby impacting catalysis. As an example, the Kanan group has reported that copper catalyst morphology influences the distribution and Faradaic efficiencies of CO\textsubscript{2} reduction products.\textsuperscript{9} The recognized importance of morphology is one reason why nanoparticles and thin films have garnered much attention in catalysis research in general. However, the selection of heterogeneous electrocatalysts in non-bulk form involves immobilizing nanoparticles, thin films, and other specialty structures on electrodes, and thus a second material, the solid support, is added to the electrochemical system.

As briefly mentioned in Chapter 3, it is well-established that solid support identity can directly impact material or catalytic properties. For example, Rakhi \textit{et al.} grew Co\textsubscript{3}O\textsubscript{4} nanowires on carbon fiber paper and planar graphitized carbon paper and achieved startlingly different morphologies,\textsuperscript{10} while other authors witnessed similar morphological impacts for alternative systems.\textsuperscript{11,12} Superconductivity,\textsuperscript{13,14} material hardness,\textsuperscript{15} and especially catalytic efficacy in the oxygen reduction reaction\textsuperscript{16–19} have been attributed to solid supports interacting with or changing properties of surface materials that are typically the focus of the study. These works suggest that properties such as catalyst morphology, which is important for CO\textsubscript{2} electrocatalysis, may be intimately tied to solid support identity.

Many solid supports ranging from silver metal\textsuperscript{7} to titanium-based nanotube arrays\textsuperscript{20} have been employed in electrocatalytic CO\textsubscript{2} reduction, but carbon-based materials are by far the most widely used for this purpose, as summarized by Yang and
coworkers. These carbon supports vary in terms of their structural and electronic properties and surface functionalities and, importantly, some researchers have noted a carbon solid support dependence in electrochemical CO$_2$ reduction with copper-based catalysts. As such, the dependence of CO$_2$ electroreduction on carbon support was tested for the Ni$_3$Al intermetallic in Chapter 3, but no such dependence was observed. Nonetheless, it clearly cannot be assumed that the support material plays an innocent role in the CO$_2$ reduction process. This characteristic therefore warrants examination as part of a catalytic system, especially when it exhibits the multi-carbon product generation ability reminiscent of copper. This calls into question the Ni-Ga intermetallic system, whose catalytic activity has been examined with respect to alloy composition, but solid support and morphological impacts on its behavior toward CO$_2$ have yet to be discussed. These factors may be important in maximizing the system’s ability to generate its highly interesting CO$_2$ reduction products (i.e., ethylene, ethane, methane), which are currently limited to Faradaic efficiencies below 2%.

In this chapter, the electrochemical activity of five different Ni$_3$Ga morphologies will be compared: thin films on (1) highly ordered pyrolytic graphite (HOPG), (2) glassy carbon, and (3) reticulated vitreous carbon (RVC) solid supports; (4) nanoparticles; and (5) unsupported, bulk alloy. For this study, Ni$_3$Ga was selected as the target intermetallic after preliminary tests featuring films with 1:1, 3:1, and 5:3 stoichiometries indicated that the 3:1 variant was the most successful at reducing CO$_2$ to CO, a possible intermediate leading to more highly reduced products. Ni$_3$Ga thin films are shown here to exhibit different surface morphologies and electrocatalytic behaviors when deposited on different carbon solid supports. Furthermore, unsupported, bulk Ni$_3$Ga, though unreactive toward
CO₂, is a modest CO reduction catalyst capable of generating methanol; introducing a carbon solid support alters this behavior to make the material more active toward the CO₂ reactant. Following detailed materials characterization studies, these characteristics will be attributed to a catalyst deposition effect exerted by the carbon solid support, whereby the support dictates thin film morphology and gives the film a different surface composition compared to unsupported materials. This product tuning effect can potentially be used to elicit improved CO₂ electroreduction activity using Ni₃Ga, other known catalysts, or ones that have yet to be discovered.

4.2 Experimental Methods

4.2.1 Materials

Nickel(II) nitrate hexahydrate (99.999%), gallium(III) nitrate hydrate (99.9%), nickel powder (< 150 μm, 99.995%), gallium (99.99%), nickel(0) bis(1,5-cyclooctadiene) (Ni(cod)₂), gallium(III) acetylacetonate (Ga(acac)₃; 99.99%), K₂SO₄ (≥ 99.0%), 1,4-dioxane (99.8%), 1-octadecene (90%), toluene (99.8%), isopropanol (≥ 99.7%), ¹³CO₂, and ethane were purchased from Sigma-Aldrich and used as received. Tanks of Ar, N₂, CO₂, CO, 95% Ar/5% H₂, and 50% CO/50% H₂ gases and mixtures were obtained from AirGas. Bottles of methanol (> 99.9%) and formic acid (≥ 98%), used to create standard curves, were purchased from Sigma-Aldrich and diluted to known concentrations prior to use.

Glassy carbon (GLAS11; 25 x 25 x 3 mm) and highly oriented pyrolytic graphite (HOPG; Grade SPI-3; 10 x 10 x 1 mm) plates were purchased from Structure Probe Inc., and glassy carbon pieces were cut in half lengthwise prior to use in electrochemical experiments. Glassy carbon and HOPG electrode plates were cleaned using wet 1.0-μm
alumina on a polishing pad and Scotch brand tape, respectively. Reticulated vitreous carbon (RVC) foam was acquired from ERG Materials and Aerospace, Corp., and cut into pieces approximately 2 x 0.5 x 0.5 cm in size before use. New RVC pieces were prepared for each experiment. Copper tape was obtained from Structure Probe Inc. Conducting silver epoxy and Loctite Hysol insulating epoxy were purchased from Epo-Tek and Grainger.

4.2.2 Synthesis and Characterization of Ni₃Ga Structural Variants

Ni₃Ga films on HOPG were synthesized according to the method reported by Torelli et al.⁴ This synthetic method was adapted to achieve Ni₃Ga films on glassy carbon and RVC foams. Briefly, aqueous solutions of 0.052 M nickel(II) nitrate hexahydrate and 0.036 M gallium(III) nitrate hydrate were mixed in a 3:1 ratio, and 0.5-mL samples of the combined solution were drop-casted onto either glassy carbon plates or RVC foam pieces that had been heated to 150 °C on a hot plate. The solid supports were left on the hot plate until the water from the solution had evaporated. The solid supports were placed in alumina boats and loaded into a Carbolite Quartz Tube Furnace under 95% Ar/5% H₂ gas flow. The furnace was ramped at a rate of 3 °C/min to 700 °C, where it rested for 5 h. Then, the furnace returned to room temperature at a rate of –3 °C/min. Upon removal from the furnace, Ni₃Ga films appeared tan in color and adhered to the surface of the glassy carbon and both on the surface and within the pores of the RVC foam.

Polycrystalline samples of bulk Ni₃Ga were prepared by an initial solid-state reaction method using high-purity, elemental nickel and gallium. Stoichiometric amounts of starting materials were placed into quartz tubes and sealed under vacuum. The tubes
were heated to 1000 °C at a rate of 3 °C/min and held at that temperature for 12 h. The samples were then cooled by quenching in room temperature water. The resulting polycrystalline chunks were loaded onto a water-cooled copper hearth and arc-melted under Ar atmosphere. Each sample was turned over in the Ar-filled chamber and re-melted twice to ensure homogeneity in the polycrystalline spheres. No mass loss occurred during this melting treatment.

The synthesis of Ni$_3$Ga nanoparticles was adapted from Kirkeminde et al.$^{25,26}$ First, 16 mL of 1-octadecene (ODE) was added to a three-neck flask equipped with a condenser and attached to both a standard Schlenk line and a side-arm adapter connected to a secondary bubbler; the solution was purged with Ar. A separate flask was loaded with 0.5 mmol Ga(acac)$_3$ and 3 mL ODE, purged with Ar for 15 min, and heated to 85 °C. In a third flask, 0.5 mmol Ni(cod)$_2$ was dissolved in 5 mL toluene under N$_2$ atmosphere. The temperature of the original three-neck flask was adjusted to 310 °C. The system was set such that Ar gas flowed out of the secondary bubbler, and the two metal solutions were simultaneously and slowly injected into the three-neck flask to ensure complete evaporation and escape of the toluene vapor. The reaction was left to stir under reflux at 310 °C for 1 h, after which time a black precipitate was collected, washed with 50:50 toluene:acetone, and centrifuged at 5500 RPM for 15 min; the supernatant was discarded. The washing procedure was repeated twice, and the product was collected in acetone and dried under vacuum. Finally, the collected material was annealed at 550 °C for 12 h in a Carbolite Quartz Tube Furnace under 95% Ar/5% H$_2$ gas flow.

All Ni$_3$Ga samples were analyzed by powder X-ray diffraction using a Bruker D8 Advance Diffractometer Eco with CuKα radiation and a LynxEye-XE detector. The scan
parameters were 0.02°/step with 0.085 s/step, resulting in a total scan time of 8 min. XRD patterns of thin films on glassy carbon, RVC, and HOPG were obtained both while the film was affixed to the solid support and after the film had been scraped from the solid support. Both patterns yielded the same Ni₃Ga peaks, while the scraped versions exhibited significantly less background carbon intrusion. Bulk Ni₃Ga was ground to a powder prior to examination by XRD.

A FEI XL30 FEG-SEM equipped with EVEX EDX detector was used to examine the morphology and composition of all materials before and after electrochemical experimentation. SEM images and EDX spectra were obtained using a 5 or 10 keV electron beam with a 10–15 mm working distance. Nanoscale images of Ni₃Ga nanoparticles were achieved using a FEI CM200 FEG-TEM. A ThermoFisher K-Alpha X-Ray Photoelectron Spectrometer was used to collect surface compositional data. These data were obtained using 20 eV pass energy and 50 ms dwell time, and analysis was performed using Thermo Scientific Avantage Data System and CasaXPS software.

4.2.3 Electrode Preparation and Electrochemical Experimentation

Electrodes were prepared using slightly different strategies depending on the form of the alloy. HOPG, glassy carbon, and RVC foam electrodes were prepared by affixing copper tape to the solid support and then separately preparing a support “holder” comprised of an alligator clip attached to a copper wire, which was threaded through a glass tube sealed on both ends using insulating epoxy. The alligator clip was then used to hold the solid support of interest. In all experiments, care was taken to ensure that the copper tape was not exposed to the electrolyte. Control experiments were carried out to confirm that the copper tape was not inadvertently acting as a CO₂ reduction catalyst.
Additionally, copper was not detected on electrode surfaces during post-electrolysis XPS analysis.

Bulk Ni$_3$Ga electrodes were created by sanding a polycrystalline sphere of the alloy using progressively finer sandpapers to achieve a round, flat surface having a diameter of 2–3 mm. The surface was then polished using 1.0-µm diamond paste. Copper wire was attached to the back of the pellet (i.e., the side opposite the flat, polished surface) using conducting silver epoxy, while the length of the wire was fed through a glass tube. As previously described, both ends of the glass tube were sealed with insulating epoxy. The insulating epoxy was used to cover any exposed silver epoxy as well as non-polished surfaces of the Ni$_3$Ga pellet.

Working electrodes containing the Ni$_3$Ga nanoparticles were prepared using a drop-casting procedure established by White.\textsuperscript{27} To begin, 2 mg/mL of nanoparticles were suspended in isopropanol and sonicated for 30 min. Then, 30 µL of 15 wt% LIQUion Solution LQ-1115 1100EW (Ion Power) was added, and the solution was sonicated for an additional 60 min to form a black ink. The mixture was drop-casted onto glassy carbon or RVC pre-heated to 120 °C, and the liquid was permitted to evaporate.

Cyclic voltammetry and bulk electrolysis experiments were performed using CH Instruments 760 and 1140 potentiostats. Cyclic voltammetry experiments utilized a three-neck round-bottom flask as the electrochemical cell, which was equipped with a Ni$_3$Ga working electrode alongside the Ag/AgCl reference and Pt mesh counter electrodes. An aqueous solution of 0.1 M K$_2$SO$_4$ was used as the electrolyte. After thorough CO$_2$ purging, the pH of the electrolyte was ~4.5; therefore, during cyclic voltammetry under Ar or CO, the pH was adjusted to this value with 0.01 M H$_2$SO$_4$. The same electrolyte
solution was used in bulk electrolysis experiments featuring custom electrolysis cells with gas-tight ports for the previously listed electrodes. During bulk electrolysis, the Pt mesh counter electrode was held in a fritted gas dispersion tube and the electrolysis solution was stirred. Cyclic voltammetry and electrolysis solutions were purged with CO₂, CO, or Ar for 20 min prior to experimental or control trials; experiments featuring ¹³CO₂ starting material were not completely purged and therefore witnessed minor amounts of ¹²CO₂ intrusion. pH dependence experiments utilized K₂SO₄ electrolyte buffered with KHCO₃ (to achieve CO₂-purged pH values > 4.5) or adjusted with 0.01 M H₂SO₄ (to achieve CO₂-purged pH values down to 3.5). In general, bulk electrolysis experiments were performed until 30 °C (HOPG, bulk) or 60 °C (glassy carbon, RVC foam) of charge had passed. Bulk solution pH was measured before and after each electrolysis experiment to confirm that pH changes were negligible (i.e., ≤ 0.2 pH units).

4.2.4 Product Analysis

During and/or after bulk electrolysis experiments, the electrolysis cell was sampled for liquid and gaseous products. To sample the solution, ¹H-NMR was performed with a Bruker Avance III 500 MHz NMR Spectrometer and cryoprobe detector after combining 530 µL of the experimental electrolyte with 60 µL D₂O and 10 µL 1,4-dioxane (internal standard). A custom water suppression method was employed. Liquid products were quantified using 5-point calibration curves.

The headspace of the electrolysis cell was sampled using gas chromatography. CO was detected using a HP6890 Gas Chromatograph and TCD with a Molsieve 5A PLOT capillary column (Agilent) running He as the flow gas for a 5-min, 60 °C isothermal method. Ethane was detected using the same instrument running a 5-min, 150
°C isothermal method after the electrolysis cell was subjected to an acetone/ice bath for 10 min to minimize the occurrence of water in the headspace. H\textsubscript{2} was sampled using a 7-min isotherm at 80 °C on an SRI 8610C Gas Chromatograph and TCD with a Molsieve column and Ar flow. Gaseous products were quantified using 30-point calibration curves having R\textsuperscript{2} ≥ 0.99. After bulk electrolyses using \textsuperscript{13}CO\textsubscript{2}, a headspace sample was collected in a gas cell terminated by KBr plates and subsequently examined using a Nicolet 730 FT-IR Spectrometer with 1 cm\textsuperscript{-1} resolution.

Faradaic efficiencies were calculated based on the total charge passed during each experiment, as well as the product quantities determined by gas- and liquid-phase sampling. Catalytic efficiencies (ξ) were calculated based on Equation 2.1 developed by Pander and Bocarsly.\textsuperscript{28}

4.3 Results and Discussion

4.3.1 Ni\textsubscript{3}Ga Thin Films on HOPG, Glassy Carbon, and RVC

To evaluate differences in Ni\textsubscript{3}Ga-catalyzed CO\textsubscript{2} electroreduction based on the solid support employed, several carbon-based electrode materials were selected on which to synthesize Ni\textsubscript{3}Ga thin films. HOPG was chosen to emulate the original report of Ni-Ga thin film-facilitated CO\textsubscript{2} reduction, and the film was obtained by drop-casting metal nitrate solutions onto the support before reducing to the metallic state in a tube furnace.\textsuperscript{24} The composition of the resulting material was examined by powder X-ray diffraction (XRD) as shown in Figure 4.1A, which confirmed that Ni\textsubscript{3}Ga having a face-centered cubic lattice had been synthesized.
Figure 4.1. Powder XRD patterns of Ni$_3$Ga thin films synthesized on (A) HOPG, (B) glassy carbon, and (C) RVC solid supports referenced to PDF 01-071-8619.

Cyclic voltammetry with Ni$_3$Ga on HOPG exhibited current enhancement under CO$_2$ atmosphere with an onset around −0.8 V vs. Ag/AgCl (Figure 4.2A). Here and throughout this chapter, current density presented in cyclic voltammograms is calculated based on geometric surface area. Subsequent bulk electrolysis experiments were performed in 0.1 M K$_2$SO$_4$ having an initial pH ~6.8; however, CO$_2$ saturation caused the pH to drop to 4.5 and remain largely unchanged during electrolysis. K$_2$SO$_4$ was chosen as a pH-neutral electrolyte with the anticipation of performing pH dependence studies by buffering with KHCO$_3$, since proton availability has been shown, especially in copper-mediated CO$_2$ reduction, to drastically impact product selectivity.$^{29,30}$

Ni$_3$Ga/HOPG electrodes were subjected to bulk electrolysis using a Pt mesh counter electrode and an operating potential of −1.38 V vs. Ag/AgCl, as reported by Torelli et al.$^{24}$ This resulted in the production of ethane at 0.10 ± 0.01% Faradaic efficiency ($\xi = 0.026\%$) as the only carbon-containing product observed. The rest of the
charge contributed to H₂ generation (98 ± 1%), which was visible by rapid bubbling at the electrode surface during experimentation; Faradaic efficiencies for both products were pH-independent. Control experiments sealing the non-Ni₃Ga-containing sides of the HOPG electrode, including where edge planes are expected to exist, with insulating epoxy suggested that the carbon product was likely generated on the basal plane-confined Ni₃Ga film. This result accords with the findings of Torelli et al. who, on HOPG, found Ni-Ga films to generate small amounts ethane, as well as methane and ethylene. Their bulk electrolysis and cyclic voltammetry results also suggest that the mechanism of CO₂ reduction on this material passes through a CO intermediate.²⁴ This assertion was confirmed here by using CO as a feedstock (in place of CO₂) after adjusting the bulk pH to 4.5, which resulted in ethane production at a slightly higher Faradaic efficiency of 0.31 ± 0.02% (ξ = 0.042%). Furthermore, by emulating experiments described in Chapter 3, intermetallic character was shown to be required to achieve the C₂ product. Specifically, striped, non-alloyed 3Ni-Ga on HOPG failed to generate ethane from CO₂.

Figure 4.2. Cyclic voltammograms obtained using Ni₃Ga thin films on (A) HOPG and (B) glassy carbon solid supports under CO₂ versus Ar atmosphere. Data were collected using a Pt mesh counter electrode and 0.1 M K₂SO₄ electrolyte (pH 4.5 after CO₂ saturation; Ar scans adjusted with H₂SO₄). Adapted with permission from J. Electrochem. Soc. 2018, 165, H385–H392. Copyright 2018 Electrochemical Society.
Intrigued by the inhibition of highly reduced products on Cr-Ga (Chapter 2) and Ni$_3$Al (Chapter 3) in the presence of D$_2$O-based electrolyte, Ni$_3$Ga/HOPG was also examined under this condition. Consistent with the alternative bimetallic species studied, ethane was no longer detected following electrolysis, yet CO was generated at 3.3 ± 0.4% Faradaic efficiency. Despite being an intermediate en route to ethane under typical H$_2$O-based conditions, CO had not been detected in the gas-phase even when ethane was produced. Since these overarching observations have now been demonstrated for three distinct intermetallic systems, the D$_2$O effect appears to be more of a trend than an anomaly, warranting further investigation in the future.

With the catalytic activity of Ni$_3$Ga on HOPG established, analysis of alternative carbon supports was necessary. While HOPG is comprised of layered graphene sheets, glassy carbon is made up of an sp$^2$ network resembling distorted fullerenes, so choice of glassy carbon as a solid support provided a morphologically different material having an electronic structure related and in some ways similar to that of HOPG. The Ni$_3$Ga thin film on glassy carbon, whose XRD pattern is displayed in Figure 4.1B, produced cyclic voltammograms as shown in Figure 4.2B. Like HOPG-plated films, current enhancement is observed under CO$_2$ atmosphere, but the onset of this enhancement begins at a more positive potential around –0.6 V vs. Ag/AgCl.

Bulk electrolysis was performed using Ni$_3$Ga films on glassy carbon, and a difference in reactivity toward CO$_2$ was immediately evident. No multiple-carbon products were formed, and the major product of the reaction, using the optimized conditions of –1.38 V vs. Ag/AgCl and pH 4.5, was CO with a Faradaic efficiency of 11.2 ± 0.7% ($\xi = 5.0\%$). Formate and methanol were also formed in the liquid phase in
small amounts, having Faradaic efficiencies of 0.23 ± 0.05% and 0.06 ± 0.01% (\(\zeta = 0.084\) and 0.020%), respectively. As this is the first report of Ni\(_3\)Ga on glassy carbon electrocatalysis, product distribution based on bulk solution pH (using K\(_2\)SO\(_4\) buffered with KHCO\(_3\)) was determined. This study (Figure 4.3) motivated the selection of pH 4.5 as optimal for electrolysis experiments. Control experiments using \(^{13}\)CO\(_2\) as the reactant confirmed that all three products were generated from CO\(_2\). Based on the HOPG results, it was expected that using a CO feedstock with the glassy carbon-plated film would result in similarly small amounts of methanol, but instead only H\(_2\) was observed. A different—or at least a second—CO\(_2\) reduction pathway independent of CO must therefore be possible when Ni\(_3\)Ga is plated on glassy carbon.
To determine what differences existed in the HOPG- versus glassy carbon-plated films that could help explain the dissimilar product distributions and mechanistic pathways, the two materials were characterized as follows. The powder XRD pattern of Ni$_3$Ga/glassy carbon indicated no difference in the alloy’s crystalline plane preference when compared to the HOPG variant (Figure 4.1). Energy dispersive X-ray spectroscopy (EDX) analysis suggested similar metal stoichiometries and oxygen content regardless of solid support identity. However, examination by scanning electron microscopy (SEM) demonstrated that the morphology of the thin film depends on the solid support material.
As shown in Figure 4.4 (A and B), the Ni$_3$Ga film on HOPG is a discontinuous array of microparticles having rough or layered surfaces, while the same film on glassy carbon is comprised of uniform platelets with relatively flat surfaces. As discussed previously, dependence of morphology$^{10,11}$ or other material properties$^{12,13}$ on solid support identity, particularly considering cases in which materials are grown directly onto a solid support, is not unprecedented. To further test this concept, a third carbon support material, reticulated vitreous carbon (RVC), was examined. While chemically equivalent to glassy carbon, RVC exhibits a porous macrostructure and high surface area.

Ni$_3$Ga thin films were prepared on 80 ppi RVC foam and analyzed by XRD (Figure 4.1C) and EDX to confirm the intermetallic identity. SEM imaging (Figure 4.4C) revealed that the morphology of the RVC-plated film resembled that achieved on glassy carbon. Namely, the film was comprised of uniform platelets distributed across the struts of the solid support; the platelets, while flat, appeared slightly rougher than their glassy carbon-deposited counterparts. This similar morphology may be attributed to the fact that carbon foams and glassy carbon are microstructurally comparable and electronically identical vitreous materials.$^{35,36}$
Figure 4.4. SEM images of Ni$_3$Ga thin films synthesized on (A) HOPG, (B) glassy carbon, and (C) RVC solid supports at low (left) and high (right) magnification. Images were obtained using a 5 or 10 keV electron beam. Adapted with permission from J. Electrochem. Soc. 2018, 165, H385–H392. Copyright 2018 Electrochemical Society.

Cyclic voltammograms were obtained using Ni$_3$Ga/RVC but proved relatively featureless, so bulk electrolysis was conducted at $-1.38$ V vs. Ag/AgCl. The RVC-plated films generated CO, formate, and methanol at Faradaic efficiencies of $26 \pm 2\%$, $1.0 \pm 0.1\%$, and $0.10 \pm 0.02\%$ ($\zeta = 12$, 0.37, and 0.033\%), respectively. As displayed in Figure
4.5, RVC-derived products are the same as those achieved on glassy carbon, and the products are generated in the same relative proportions independent of the solid support. Even so, the Faradaic efficiencies for carbon-containing products achieved on RVC are approximately double those obtained on glassy carbon. The pH dependence plot for RVC (Figure 4.3B), when compared to glassy carbon, tends to follow the same trend. Thus, the facilitated chemistry is equivalent on the two catalysts, despite one form being more charge-efficient than the other. The remainder of the charge passed in the Ni$_3$Ga/RVC electrolyses contributed to H$_2$ evolution ($71 \pm 3\%$). Like Ni$_3$Ga/glassy carbon, RVC-plated films generated either no or negligible quantities of formate and methanol when supplied with CO in place of CO$_2$ as a feedstock gas, suggesting that the films generated on vitreous carbon solid supports, rather than HOPG, reduce CO$_2$ using a similar reaction mechanism.

![Figure 4.5. CO$_2$ product distribution achieved using Ni$_3$Ga films deposited on vitreous carbon solid supports. Relative product ratios are generally the same, while the Faradaic efficiencies from RVC were approximately double those obtained from glassy carbon (indicated by the relative sizes of the circle plots). Adapted with permission from J. Electrochem. Soc. 2018, 165, H385–H392. Copyright 2018 Electrochemical Society.](image_url)
4.3.2 Polycrystalline, Unsupported Ni$_3$Ga

Considering that two distinct sets of products could be achieved using the same intermetallic species on different solid supports, an unsupported, bulk Ni$_3$Ga alloy was also investigated. Following powder XRD characterization of the freestanding alloy (Figure 4.6A), electrodes were used in cyclic voltammetry experiments in 0.1 M K$_2$SO$_4$ under Ar and CO$_2$ saturation (pH 4.5). Unlike the supported systems, and as shown in Figure 4.6B, current density decreased under CO$_2$ compared to Ar when using unsupported Ni$_3$Ga electrodes, suggesting that H$_2$ evolution was disrupted by CO$_2$ at or near the electrode surface.\textsuperscript{37} Bulk electrolysis experiments after CO$_2$ purging appeared to generate trace or no liquid products, and Faradaic efficiencies of only 0.91 ± 0.05% ($\xi = 0.40\%$) for CO were achieved across a range of applied potentials. Besides H$_2$, quantified at nearly 100% Faradaic efficiency, no other gaseous products were detected. Thus, bulk Ni$_3$Ga is not active toward CO$_2$ electroreduction.

![Figure 4.6.](image)

**Figure 4.6.** Material and electrochemical characterization of bulk Ni$_3$Ga electrodes. (A) Powder XRD pattern of bulk Ni$_3$Ga referenced to PDF 01-071-8619. (B) Cyclic voltammograms obtained using a bulk Ni$_3$Ga working electrode under CO$_2$, CO, or Ar saturation. Adapted with permission from *J. Electrochem. Soc.* 2018, 165, H385–H392. Copyright 2018 Electrochemical Society.
Bulk Ni$_3$Ga electrodes were also evaluated using CO as the reactant. At an applied potential of $-1.38$ V vs. Ag/AgCl (pH 4.5), methanol was detected in the liquid phase with a Faradaic efficiency of $2.1 \pm 0.4\%$ ($\xi = 0.20\%$); electrolysis of $^{13}$CO starting material confirmed that the product was derived from CO. Furthermore, cyclic voltammetry performed under CO saturation exhibits a higher current density than that achieved using CO$_2$ (Figure 4.6B). Thus, it is evident that the catalytic activity of this alloy material can be adjusted using a carbon-based solid support, transforming a material with modest reactivity toward CO and no catalytic activity toward CO$_2$ into a material that can reduce CO$_2$.

4.3.3 Ni$_3$Ga Nanoparticles

Since the results reported here indicate that vitreous carbon-supported Ni$_3$Ga favors CO generation from CO$_2$ and unsupported Ni$_3$Ga is specific for the reduction of CO, it was hypothesized that putting unsupported Ni$_3$Ga onto a vitreous carbon material might improve methanol formation from CO$_2$. To test this idea, unsupported Ni$_3$Ga nanoparticles were synthesized and then applied to a carbon support for electrochemical analysis. Ni$_3$Ga nanoparticles were synthesized using a procedure adapted from Kirkeminde et al.$^{25,26}$ As shown in Figure 7 (A and B), powder XRD of the annealed nanoparticles confirmed the desired stoichiometry and, along with transmission electron microscopy (TEM) imaging, determined that the nanoparticles were 10–20 nm in diameter. The nanoparticles were suspended in Nafion solution (1100EW) and drop-casted onto a glassy carbon or RVC electrode.
Figure 4.7. Material and electrochemical characterization of annealed Ni$_3$Ga nanoparticles. (A) Powder XRD pattern of Ni$_3$Ga nanoparticles referenced to PDF 01-071-8619. The broad peak at 61.5° is attributed to NiO. (B) TEM image of a nanoparticle cluster. (C) Cyclic voltammograms obtained using Ni$_3$Ga nanoparticles on glassy carbon under CO$_2$ or Ar saturation. Data were collected using a Pt mesh counter electrode and 0.1 M K$_2$SO$_4$ electrolyte (pH 4.5). Adapted with permission from J. Electrochem. Soc. 2018, 165, H385–H392. Copyright 2018 Electrochemical Society.

Using identical conditions to those previously described, cyclic voltammograms obtained from glassy carbon-bound nanoparticles more closely resembled those recorded for the bulk Ni$_3$Ga electrodes than the thin films, as higher current was observed leading into the proton reduction wave when the atmosphere was saturated with Ar than CO$_2$ (Figure 4.7C). Accordingly, bulk electrolysis performed at a variety of potentials failed to generate any liquid CO$_2$ reduction products. Though CO was detected at < 1% Faradaic
efficiency, most of the charge passed contributed to H\textsubscript{2} evolution, as would be predicted based on cyclic voltammetry data resembling bulk Ni\textsubscript{3}Ga. Therefore, simply having Ni\textsubscript{3}Ga supported on vitreous carbon is not sufficient to activate the CO\textsubscript{2} reduction channel.

These data show that the application of Ni\textsubscript{3}Ga onto glassy carbon \textit{after} the alloy’s synthesis does not induce CO generation comparable to Ni\textsubscript{3}Ga grown directly onto the solid support. This suggests that the solid support’s role in altering CO\textsubscript{2} reduction products is indirect; the support does not play a chemical role during CO\textsubscript{2} electroreduction. This assertion is further supported by the fact that CO generation still occurs when CO\textsubscript{2} reduction is performed using a glassy carbon-bound Ni\textsubscript{3}Ga film after coating the solid support’s exposed surfaces (i.e., where the Ni\textsubscript{3}Ga thin film is not situated) with insulating epoxy.

4.3.4 \textit{Ni\textsubscript{3}Ga Tandem Electrode System}

To test the finding that different morphologies of Ni\textsubscript{3}Ga differ in their reactivity toward CO\textsubscript{2}, two types of Ni\textsubscript{3}Ga electrodes were employed in the same electrochemical cell. The first electrode was comprised of a Ni\textsubscript{3}Ga morphology specific for generating CO from CO\textsubscript{2}, while the second electrode morphology was selected for its ability to generate organic products from CO. If the hypothesis is correct that the first morphology is a relatively efficient CO\textsubscript{2}-reducer and the second morphology performs CO reduction, then this setup would produce CO from CO\textsubscript{2} \textit{in situ} at the first electrode’s surface and provide a higher effective concentration of CO at the second electrode’s surface (i.e., as it is generated) for use in methanol synthesis.
Figure 4.8. Schematic representation of the dual-electrode electrochemical setup utilizing two morphologies of Ni$_3$Ga. WE#1 and WE#2 were Ni$_3$Ga/RVC and unsupported Ni$_3$Ga, respectively. The reference electrode (REF) was Ag/AgCl, and the Pt mesh counter electrode (CE) was fitted inside a gas dispersion tube. Schematic not to-scale. Adapted with permission from *J. Electrochem. Soc.* 2018, 165, H385–H392. Copyright 2018 Electrochemical Society.

As the best CO generator of the Ni$_3$Ga thin films, the 80 ppi RVC-plated variant was selected as the first working electrode, and a bulk Ni$_3$Ga electrode was chosen as the second, since this material does not react with CO$_2$. A schematic representation of the cell is provided in Figure 4.8. Electrolysis experiments were performed at –1.38 V vs. Ag/AgCl in CO$_2$-saturated, pH 4.5 K$_2$SO$_4$ electrolyte using the RVC and bulk electrodes either in series or in tandem. In series experiments, the Ni$_3$Ga film on RVC was situated as the first operational working electrode. As expected, CO was generated at a Faradaic efficiency around 20%. After a few hundred micromoles of CO had been generated, the
experiment was stopped, and the working electrode was switched to the bulk Ni$_3$Ga disk. The second electrolysis was run until at least 4 C of charge had passed, at which time a noticeable decrease in headspace CO was recorded. Analysis of the electrolyte indicated that methanol was generated from CO at a Faradaic efficiency of $7.1 \pm 0.1\%$ ($\xi = 0.66\%$). In tandem-use experiments, RVC and bulk electrodes were operated simultaneously, CO was once again detected in the headspace, and electrolyte analysis revealed that methanol was generated from CO at $13.2 \pm 0.4\%$ Faradaic efficiency ($\xi = 1.2\%$).

![Figure 4.9. Faradaic efficiencies for methanol achieved using bulk Ni$_3$Ga electrodes exposed to CO in solution. CO was either supplied to the system prior to electrolysis (ex situ) or generated from CO$_2$ internally by the system using a Ni$_3$Ga thin film on RVC (in situ). Adapted with permission from J. Electrochem. Soc. 2018, 165, H385–H392. Copyright 2018 Electrochemical Society.](image)

Figure 4.9 compares the Faradaic efficiencies for methanol achieved using an external CO purge with those calculated when CO was generated in situ during series or tandem Ni$_3$Ga-mediated experiments. Methanol Faradaic efficiencies obtained when operating the RVC and bulk electrodes in tandem were nearly double those noted when
the electrodes were used in series. These data make sense, as operating both electrodes simultaneously lowers the ability of Ni\textsubscript{3}Ga/RVC-generated CO, which exhibits poor solubility in water, to escape to the headspace before being further reduced by bulk Ni\textsubscript{3}Ga. Control trials indicated that negligible quantities of methanol were formed during the RVC stage of in-series electrolysis, confirming that CO was in fact converted to methanol on bulk Ni\textsubscript{3}Ga.

4.3.5 Influence of Solid Support on Electrocatalysis via Morphology

Having determined the electrochemical CO\textsubscript{2} reactivity profiles of supported and unsupported Ni\textsubscript{3}Ga, experiments were undertaken to understand how variation in carbon support materials induces Ni\textsubscript{3}Ga, a material whose native activity is modest toward CO reduction, to be active toward CO\textsubscript{2}. The previously described experiments featuring Ni\textsubscript{3}Ga nanoparticles drop-casted onto glassy carbon after their synthesis suggest that the impact of a carbon solid support in altering electrochemical behavior is indirect (i.e., the support is not playing a chemical role during electrolysis). Instead, the carbon support must affect the material properties of the film, perhaps having its effect during synthesis of the Ni\textsubscript{3}Ga thin films in such a way that CO\textsubscript{2} reduction behavior is impacted later.

During synthesis, the carbon solid support is not instrumental in the reduction of the nickel and gallium ions to their metallic, alloyed state, because use of alternative, non-carbon solid supports still results in generation of a Ni\textsubscript{3}Ga film (i.e., silicon wafer, ZnSe disk, and nickel sheet were all evaluated). Therefore, the solid support’s impact during synthesis must manifest in the structures of the films themselves. Powder XRD and EDX confirm that the bulk compositions of the Ni\textsubscript{3}Ga films studied here are identical whether the films are synthesized on HOPG, glassy carbon, or RVC. However, SEM
imaging demonstrates that surface morphologies distinctly depend on the identity of the carbon solid support. It was therefore hypothesized that the surfaces of Ni$_3$Ga alloys might be further differentiated based on atomic composition.

To answer this question, X-ray photoelectron spectroscopy (XPS) was performed with Ni$_3$Ga films supported on HOPG and glassy carbon, as well as unsupported bulk Ni$_3$Ga for comparison. The atomic percentages of surface nickel and gallium derived from bulk Ni$_3$Ga (i.e., unsupported), Ni$_3$Ga/HOPG, and Ni$_3$Ga/glassy carbon are listed in Table 4.1. XPS of bulk Ni$_3$Ga indicates that the material’s surface is comprised of a nearly exact 3:1 ratio of nickel and gallium, which has been reported as a relatively poor CO$_2$-reducing stoichiometry.$^{24,38,39}$ On the other hand, the surfaces of Ni$_3$Ga thin films synthesized on HOPG and glassy carbon are both gallium-rich, despite the fact that the bulk compositions of these films exhibit their namesake 3:1 Ni:Ga stoichiometry.

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<th>Ni (atomic %)</th>
<th>Ga (atomic %)</th>
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<tr>
<td>Bulk Ni$_3$Ga</td>
<td>73 ± 2</td>
<td>27 ± 2</td>
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<tr>
<td>Ni$_3$Ga/HOPG</td>
<td>17 ± 2</td>
<td>82 ± 2</td>
</tr>
<tr>
<td>Ni$_3$Ga/glassy carbon</td>
<td>28 ± 4</td>
<td>72 ± 4</td>
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Considering that heterogeneous CO$_2$ reduction occurs at the electrode’s surface, the different surface stoichiometries achieved on bulk versus thin film Ni$_3$Ga are likely instrumental in determining the materials’ reactivities toward CO$_2$ in solution. Namely, unsupported Ni$_3$Ga is unreactive toward aqueous CO$_2$, while films on glassy carbon or HOPG, exhibiting the same gallium-rich surface composition, are active CO$_2$ reduction
catalysts. To study the effect of a gallium-rich surface further, plain gallium-based films (i.e., monoclinic Ga$_2$O$_3$ by XRD) on RVC were subjected to CO$_2$ electroreduction experiments and yielded CO at a maximum Faradaic efficiency of 57 ± 4% (Figure 4.10).

![Bar chart showing Faradaic efficiencies for CO$_2$ reduction products generated during potential (left) and pH (right) dependence experiments using monoclinic Ga$_2$O$_3$ on RVC; the lower plots zoom-in on liquid-phase, minor products. Potential dependence experiments were conducted using pH 4.5, CO$_2$-saturated K$_2$SO$_4$ electrolyte, while pH dependence experiments utilized an operating potential of –1.38 V vs. Ag/AgCl. The high CO Faradaic efficiencies reported here differ from the results obtained by other researchers using gallium metal or Ga$_2$O$_3$ single crystal electrodes.40,41 Adapted with permission from Faraday Discuss. 2019, DOI: 10.1039/C8FD00177D. Copyright 2019 Royal Society of Chemistry.

However, when comparing the XPS data for Ni$_3$Ga films on HOPG and glassy carbon, it is evident that the nickel and gallium present on both surfaces are mixtures of
metals and metal oxides. As listed in Table 4.2, the relative quantities of surface metal and metal oxides making up Ni$_3$Ga films on HOPG and glassy carbon are comparable, confirming that surface composition of thin films is not dependent on choice of solid support.

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<th>Ni metal (%)</th>
<th>Ni oxides (%)</th>
<th>Ga metal (%)</th>
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<tbody>
<tr>
<td>Ni$_3$Ga/HOPG</td>
<td>24 ± 6</td>
<td>76 ± 6</td>
<td>8 ± 3</td>
<td>92 ± 3</td>
</tr>
<tr>
<td>Ni$_3$Ga/glassy carbon</td>
<td>30 ± 5</td>
<td>70 ± 5</td>
<td>7 ± 2</td>
<td>93 ± 2</td>
</tr>
</tbody>
</table>

Moreover, while differences in electrochemically active surface area, and thus carbon coverage by the Ni$_3$Ga thin films, could theoretically explain the differing activities, particularly when comparing product identity profiles observed on HOPG versus vitreous materials, measurements of surface coverage do not support this possibility. Based on SEM data, the percentages of carbon support covered by Ni$_3$Ga on HOPG, glassy carbon, and RVC were approximately 48%, 42%, and 17%, respectively. RVC exhibited the lowest surface coverage and, as such, the highest amount of exposed carbon, so it was important to determine whether this exposed carbon could provide beneficial effects during CO$_2$ electroreduction. Experiments analyzing ferrocyanide/ferricyanide, hydroquinone/benzoquinone, and several other common redox couples indicated that vitreous carbon materials (i.e., both glassy carbon and RVC) lost their ability to facilitate these redox reactions after heat treatment, likely due to loss of native surface functionalities in the high-temperature, slightly reducing furnace
Thus, synergistic effects between drop-casted Ni$_3$Ga and these carbon supports are unlikely during electrochemical experimentation. The product distribution differences observed on HOPG and vitreous carbon supports also cannot be explained by differences in carbon surface coverage because the percentage of exposed support is generally equivalent in the HOPG and glassy carbon cases.

A final piece of support for the indirect influence of the carbon support—rather than the support playing a direct, chemical role in catalysis—comes from a series of experiments implementing the striped 3Ni-Ga electrode format mentioned in Section 4.3.1. Recall that in an experiment depositing nickel and gallium adjacent to one another on HOPG, resulting in a striped, non-alloyed electrode, the C2 product ethane was no longer generated during CO$_2$ electrolysis. This experiment suggested that intermetallic Ni$_3$Ga character is necessary to elicit carbon-carbon bond formation, as was the case for Ni$_3$Al in Chapter 3. However, Ni$_3$Al exhibits no electrocatalytic dependence on its solid support, whereas Ni$_3$Ga clearly does. If Ni$_3$Ga’s solid support plays a direct, chemical role in catalysis, one might therefore imagine that changing the carbon solid support could “rescue” the multi-carbon generation ability of 3Ni-Ga in the absence of alloying. This possibility was tested by determining the CO$_2$ electrolysis results of 3Ni-Ga on glassy carbon and RVC, since 3Ni-Ga on HOPG was examined earlier. The results, shown in Figure 4.11, demonstrate that multi-carbon product generation was not recovered, supporting the assertion that the solid support does not play a direct role in catalysis.
Figure 4.11. Faradaic efficiencies for CO$_2$ reduction products achieved using intermetallic Ni$_3$Ga and non-mixed 3Ni-Ga films on GC and RVC solid supports, indicating that the intermetallic and non-mixed species exhibit the same products. Electrolysis experiments were conducted at $-1.38$ V vs. Ag/AgCl in pH 4.5, CO$_2$-saturated K$_2$SO$_4$ electrolyte. Adapted with permission from Faraday Discuss. 2019, DOI: 10.1039/C8FD00177D. Copyright 2019 Royal Society of Chemistry.

4.4 Summary and Conclusions

After thoroughly considering material composition, solid support coverage, and alloy versus non-alloy reactivity, the only remaining—and glaring—difference in Ni$_3$Ga thin film surfaces having dissimilar carbon supports is their morphologies. Recalling Figure 4.4, SEM imaging shows that Ni$_3$Ga on HOPG has a significantly rougher surface than Ni$_3$Ga on glassy carbon, whose surface is flatter and more uniform. Due to the microstructuring and high surface area of Ni$_3$Ga/HOPG, one might imagine that surface-bound reduction intermediates would exist in close proximity to one another, facilitating carbon-carbon bond formation on HOPG-deposited films. This sort of intermediate binding and coupling would, based on geometry, not be promoted on flat Ni$_3$Ga/glassy
carbon surfaces, which instead favor generation of one-carbon products. These morphological differences may therefore contribute to the product discrimination observed for Ni$_3$Ga thin films on different carbon solid supports.

By synthesizing and testing various forms of Ni$_3$Ga alloy catalysts, it has been shown that, like copper electrodes, significant morphological and solid support influences exist for this nickel-based CO$_2$ electroreduction system. Unsupported Ni$_3$Ga (whose stoichiometry is maintained throughout the bulk and surface) is modestly capable of reducing CO and relatively inactive toward CO$_2$, but synthesizing films of the alloy on HOPG and vitreous carbon results in an electrochemical reactivity profile that differs from that of the bulk material. Under the conditions described, Ni$_3$Ga nanoparticles seem largely inactive toward CO$_2$ reduction. Thin films of Ni$_3$Ga on different carbon solid supports exhibit dissimilar surface morphologies and reaction mechanisms during CO$_2$ electroreduction, utilizing a pathway that is either CO-inclusive or CO-exclusive. It appears that the role of a carbon solid support in dictating CO$_2$ reduction products generated by Ni$_3$Ga is indirect, as the support exerts control over the catalyst morphology and surface composition during synthesis. Morphology then impacts the electrochemical CO$_2$ reduction reaction that occurs at the material’s surface. A summary of electrolysis products obtained using each of the Ni$_3$Ga morphologies studied here is presented in Table 4.3.
Table 4.3. Summary of electrolysis products generated by five morphologies of Ni$_3$Ga exposed to either CO$_2$ or CO in aqueous solution.

<table>
<thead>
<tr>
<th>Morphology</th>
<th>CO$_2$ feedstock</th>
<th>CO feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film/HOPG</td>
<td>Ethane, H$_2$</td>
<td>Ethane, H$_2$</td>
</tr>
<tr>
<td>Thin film/glassy carbon</td>
<td>CO, Formate, Methanol, H$_2$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>Thin film/RVC</td>
<td>CO, Formate, Methanol, H$_2$</td>
<td>H$_2$</td>
</tr>
<tr>
<td>Unsupported bulk</td>
<td>H$_2$</td>
<td>Methanol</td>
</tr>
<tr>
<td>Nanoparticles</td>
<td>H$_2$</td>
<td>H$_2$</td>
</tr>
</tbody>
</table>

By exploiting the Ni$_3$Ga reaction scope and solid support/morphology effect established herein, a single catalytic material was used to perform two complementary tasks, ultimately improving its ability to generate methanol from CO$_2$ starting material. The importance of solid support choice in achieving particular reaction chemistry has been reported for a handful of systems in the past$^{23,45-48}$ and, combined with the data presented for Ni$_3$Ga, such results suggest that the structure of a catalyst and the identity of its solid support, when applicable, should be carefully considered in tandem when designing new, or modifying old, heterogenous electrocatalysts. These and other factors, such as mechanistic pathways discussed in Chapter 5, can theoretically be manipulated to improve outcomes of CO$_2$ electroreduction, even imparting new catalytic behavior to traditionally inactive metals.
4.5 References

(1) Hoshi, N.; Kato, M.; Hori, Y. Electrochemical Reduction of CO\textsubscript{2}, on Single Crystal Electrodes of Silver Ag(111), Ag(100) and Ag (110). Journal of Electroanalytical Chemistry 1997, 440, 283–286.


Chapter 5. Determining Trends in CO₂ Electroreduction Using Transition Metal/Group 13 Spinel Oxides

5.1 Introduction

Despite recent progress in developing novel CO₂ reduction catalysts, including those discussed in Chapters 2–4, the strategic or guided discovery of CO₂-active species has proven challenging, especially when considering prospective intermetallic or alloy catalyst systems. In addition to many promising outcomes realized experimentally,¹–⁴ interest in alloy electrocatalysts has been supported by theoretical studies suggesting that the distinct surface sites provided by multi-metal electrodes can alter CO₂ or reduction intermediate binding energies⁵,⁶ or break scaling relations that help dictate overpotential and selectivity.⁷,⁸ Efforts have therefore been made to develop models and machine learning algorithms to better predict new mixed-metal catalyst species.⁶,⁹,¹⁰ Despite these predictive tools, catalytic systems not hypothesized by models to be active are consistently reported, including the Cr-Ga oxide and Ni₃Al intermetallic systems, as well as the specific stoichiometry Ni₃Ga.¹¹–¹⁴ While implementation of prediction tools allows for quick identification of candidate catalysts, additional experimental groundwork must seek to identify experimental conditions and other factors that will improve multi-metal catalyst prediction, discovery, and tuning efforts.

One knowledge gap with room for experimental exploration in mixed-metal CO₂ reduction involves the influence of the transition metal (TM) and Group 13 (G13) metal in the broad class of heterogeneous TM/G13 electrocatalyst systems identified in recent years. Reports of these systems began with Cu-In alloys² and have expanded to include
the materials discussed in the preceding chapters.\textsuperscript{13–16} The Al- and Ga-inclusive species, in particular, have proven anomalous yet interesting because of their ability to generate multi-carbon products from CO\textsubscript{2}, an outcome previously effected only by copper-based electrocatalysts.\textsuperscript{17} Experimentally determining the impact of either the TM or G13 metal in CO\textsubscript{2} electroreduction would benefit catalyst discovery and tuning efforts, especially concerning the generation of highly reduced carbon-containing products.

One way to begin addressing TM and G13 metal influence would involve systematically combining a successive set of TMs with G13 metals in a constant material structure and then examining the electrocatalytic properties of this series of materials with respect to CO\textsubscript{2} reduction. In other words, by holding constant the structure type and sequentially varying the TM and G13 components, trends in CO\textsubscript{2} reduction activity may be observed. Based on the metals that have been shown to occupy its crystal lattice, a possible structure permitting such an evaluation is the spinel group of materials. Spinels have the generic structure AB\textsubscript{2}X\textsubscript{4}, where A is a 2+ cation, B is a 3+ cation, and X is a chalcogen. While pure ternary spinels have been explored for CO\textsubscript{2} hydrogenation\textsuperscript{18,19} and other high temperature/high pressure CO\textsubscript{2} reactions,\textsuperscript{20–22} their electrocatalytic behavior toward CO\textsubscript{2} reduction has yet to be determined.

In this chapter, a series of TM/G13 spinel thin films (where A = Mn, Fe, Co; B = Al, Ga; and X = O) will be synthesized, characterized, and electrochemically evaluated to determine whether trends in CO\textsubscript{2} reduction are evident. While all six spinels proved to be modest electrocatalysts, notable differences in activity toward CO\textsubscript{2} were observed based on product Faradaic efficiencies and reduction intermediates. The combination of TM and G13 metal in the spinel structure was shown to elicit non-native TM catalytic
activity, which may be attributed, in part, to induced changes in CO binding energies and
related reduction pathways.

5.2 Experimental Methods

5.2.1 Materials

Manganese(II) nitrate hydrate (99.99%), iron(III) nitrate nonahydrate (≥ 99.95%),
cobalt(II) nitrate hexahydrate (≥ 99.0%), aluminum(III) nitrate nonahydrate (99.997%),
gallium(III) nitrate hydrate (99.9%), KHCO₃ (99.7%), sodium formate (99.998%), 1,4-
dioxane (99.8%), and ¹³CO₂ (99 at% ¹³C) were purchased from Sigma-Aldrich, and
K₂SO₄ (ACS grade) was acquired from EMD Chemicals. Ar, CO₂, CO, and 95% Ar/5%
H₂ gases and mixtures were obtained from AirGas. Glassy carbon plates (GLAS11; 25 x
25 x 3 mm; Structure Probe Inc.) were cut in half prior to use. Silver and Loctite Hysol
epoxies were acquired from Epo-Tek and Grainger. All chemicals were used as received.

5.2.2 Spinel Thin Film Synthesis and Characterization

Thin films of TM/G13 spinels were synthesized by adapting a previously reported
drop-casting procedure.¹³,¹⁵ Briefly, aqueous solutions of metal nitrate salts were mixed
in 1:2 TM:G13 ratios, and 0.5-mL samples were drop-casted onto separate glassy carbon
plates. The plates were placed in alumina boats and loaded into a Carbolite Quartz Tube
Furnace, which was ramped at a rate of 3 °C/min using the temperature and flow
conditions listed in Table 5.1. Following cooling of the furnace to room temperature at −3
°C/min, the films exhibited geometric surface areas of ~0.8 cm².
Table 5.1. Furnace conditions employed to synthesize spinel thin films on glassy carbon. The furnace temperature was held for 5 h.

<table>
<thead>
<tr>
<th>Spinel</th>
<th>Temperature (°C)</th>
<th>Flow gas</th>
<th>Film appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnAl₂O₄</td>
<td>700</td>
<td>95% Ar/5% H₂</td>
<td>Silver</td>
</tr>
<tr>
<td>MnGa₂O₄</td>
<td>700</td>
<td>95% Ar/5% H₂</td>
<td>Silver</td>
</tr>
<tr>
<td>FeAl₂O₄</td>
<td>500</td>
<td>95% Ar/5% H₂</td>
<td>Lustrous dark gray</td>
</tr>
<tr>
<td>FeGa₂O₄</td>
<td>400</td>
<td>95% Ar/5% H₂</td>
<td>Black</td>
</tr>
<tr>
<td>CoAl₂O₄</td>
<td>500</td>
<td>Atmosphere</td>
<td>Lustrous teal</td>
</tr>
<tr>
<td>CoGa₂O₄</td>
<td>500</td>
<td>Atmosphere</td>
<td>Dark teal</td>
</tr>
</tbody>
</table>

Thin films were analyzed to confirm bulk and surface compositions. Powder X-ray diffraction was performed with a Bruker D8 Advance diffractometer with 0.083° step size and CuKα radiation following removal of the films from the carbon support.

Scanning electron microscopy images and energy dispersive X-ray spectroscopy data were acquired using a FEI XL30 FEG-SEM coupled with an EVEX EDX detector (5 keV electron beam; 10–15 mm working distance). Surface-specific characterization was achieved using a ThermoFisher K-Alpha X-Ray Photoelectron Spectrometer set to 20 eV pass energy and 50 ms dwell time; data were analyzed using the Thermo Scientific Avantage Data System and CasaXPS software. Characterization data were collected before and after electrolysis. XPS of post-electrolysis electrodes confirmed that surface contamination (i.e., from counter or reference electrode species) did not occur during electrochemical experimentation.

5.2.3 Electrode Preparation and Electrochemical Experimentation

Electrodes were prepared as previously described by fashioning airtight holders for the thin film/glassy carbon working electrodes. Electrochemical experiments were
performed using CH Instruments 760 and 1140 potentiostats. Custom-made, gas-tight electrochemical cells were fitted with a thin film/glassy carbon working electrode, Ag/AgCl reference electrode, and Pt mesh counter electrode housed within a gas dispersion tube. K₂SO₄ (0.1 M; buffered with KHCO₃ to achieve pH > 4 or adjusted with H₂SO₄ to achieve pH < 4 post-CO₂ saturation) was employed as the electrolyte, which was continuously stirred. Prior to typical electrolysis experiments, the electrochemical cell was purged with CO₂ for 20 min. In CO and formate feedstock experiments, initial pH was adjusted following addition of the feedstock. Electrolyses were considered complete following passage of 40 C of charge.

5.2.4 Product Analysis

Gas-phase products in the headspace were detected by gas chromatography. CO was measured using a HP6890 Gas Chromatograph (Molsieve 5A PLOT capillary column) running a 5-min, 60 °C isotherm with He flow gas. H₂ byproduct was measured using an SRI 8610C Gas Chromatograph running a 7-min, 80 °C isotherm with Ar flow gas. Both chromatographs were fitted with Molsieve capillary columns and TCDs.

Liquid-phase products were detected by ¹H-NMR after combining 530 µL electrolyte with 60 µl D₂O and 10 µL 1,4-dioxane internal standard (10 mM). A Bruker Avance III 500 MHz NMR Spectrometer equipped with cryoprobe detector and operated using a custom water suppression method allowed for direct electrolyte sampling. All products were quantified using calibration curves with R² ≥ 0.99. Faradaic efficiencies were calculated based on product quantities and the charge passed in each experiment.
5.3 Results and Discussion

To systematically study the effect of TM and G13 metal choice in heterogeneous, electrocatalytic CO\textsubscript{2} reduction, a series of spinel compounds was selected based on the following criteria. First, their TMs would appear consecutively on the periodic table to facilitate identification of patterns or trends in electrochemical performance. Second, each TM would have the ability to form the spinel structure by incorporating Al and Ga into the trivalent cation site of the crystal lattice, thereby allowing the two most interesting G13 metals in alloy-mediated CO\textsubscript{2} electroreduction to be probed. Based on these requirements, MnAl\textsubscript{2}O\textsubscript{4}, MnGa\textsubscript{2}O\textsubscript{4}, FeAl\textsubscript{2}O\textsubscript{4}, FeGa\textsubscript{2}O\textsubscript{4}, CoAl\textsubscript{2}O\textsubscript{4}, and CoGa\textsubscript{2}O\textsubscript{4} were targeted for synthesis, characterization, and electrocatalytic testing.

5.3.1 Synthesis and Characterization of Spinel Thin Films

To permit facile implementation as working electrodes, thin films of each spinel were synthesized on glassy carbon solid supports using an established drop-casting and furnace reduction method.\textsuperscript{13,15} Various temperature and flow gas conditions were needed during the syntheses to achieve different spinel compositions (see Table 5.1). As shown in Figure 5.1, powder X-ray diffraction (XRD) confirmed that all six target spinels were successfully synthesized and exhibited some combination of polycrystalline and amorphous character. Some spinels have been reported in the literature to demonstrate crystallinity-dependent catalytic behavior, with amorphousness corresponding to improved catalysis,\textsuperscript{23} though such behavior did not translate to the TM/G13 spinel oxides studied here. This was evidenced by similar electrocatalytic activities of related species regardless of crystallinity, especially MnAl\textsubscript{2}O\textsubscript{4} and MnGa\textsubscript{2}O\textsubscript{4} (i.e., the two related species most divergent in their crystallinity), which will be discussed later. In any case, atomic
compositions were further probed by energy-dispersive X-ray spectroscopy (EDX), which supported these bulk material assignments.

**Figure 5.1.** XRD patterns of as-synthesized TM/G13 thin film species on glassy carbon, indicating that (A) MnAl₂O₄, (B) MnGa₂O₄, (C) FeAl₂O₄, (D) FeGa₂O₄, (E) CoAl₂O₄, and (F) CoGa₂O₄ were produced. Reference peaks correspond to PDF patterns as follows: MnAl₂O₄ (00-029-0880); (Mn₀.₈₉Al₀.₁₁)Al₂O₄ (01-076-6585); MnGa₂O₄ (01-072-1521); MnO (01-007-0230); FeAl₂O₄ (01-086-2320); FeGa₂O₄ (01-074-2229); Fe₃O₄ (01-071-6336); CoAl₂O₄ (01-082-2240); CoGa₂O₄ (01-071-6441); γ-Ga₂O₃ (00-020-0426).

X-ray photoelectron spectroscopy (XPS) revealed completely oxidized thin film surfaces, with Mn, Fe, and Co in either the 2+ or 3+ oxidation state²⁴,²⁵ and the G13 metals in their typical 3+ oxidation state. Sample XPS spectra, obtained for the TM/Al spinel variants, are provided in Figure 5.2. Imaging by scanning electron microscopy (SEM) depicted a morphology consisting of platelets, ranging from approximately 10 to 50 μm in width, distributed across the surface of the glassy carbon solid supports (Figure 5.3). These platelets exhibited relatively smooth, slightly concave surfaces, which is morphologically similar to other bimetallic thin films synthesized by this drop-casting and furnace treatment method.¹³,¹⁶
Figure 5.2. XPS analysis of as-synthesized transition metal/Al spinel thin films. MnAl$_2$O$_4$, FeAl$_2$O$_4$, and CoAl$_2$O$_4$ spectra are depicted at the top, middle, and bottom, respectively. Peaks referenced to the adventitious C 1s peak at 284.8 eV (not shown).
5.3.2 Electro catalytic Activity of Spinels Toward CO$_2$ Reduction

Electrochemical CO$_2$ reduction experiments were conducted using each of the spinel thin films on glassy carbon as working electrodes. Electrolyses were performed using two-compartment electrochemical cells with Pt mesh counter and Ag/AgCl reference electrodes in a CO$_2$-saturated, 0.1 M K$_2$SO$_4$ electrolyte (buffered to achieve pH > 4 or acidified for pH < 4). Given that preliminary cyclic voltammetry scans
demonstrated high H$_2$ evolution activity and negligible current density differences under CO$_2$ and Ar environments, the potential window from −1.18 to −1.58 V vs. Ag/AgCl was selected for electrolysis studies in line with the optimized potentials for alternative TM/G13 electrocatalysts.\textsuperscript{2,13,15,16,26}

**Figure 5.4.** Faradaic efficiencies for carbon-containing products generated during potential-dependent electrolysis experiments using spinel thin films on glassy carbon. All experiments were conducted using CO$_2$-saturated, 0.1 M K$_2$SO$_4$ electrolyte (pH 4.5). Error bars represent the standard deviation of at least three trials.

At a first-pass operating potential of −1.38 V vs. Ag/AgCl and pH 4.5, each spinel thin film generated CO, formate, and methanol from CO$_2$ during electroreduction, as confirmed via electrolysis of isotopically labeled $^{13}$CO$_2$. Potential and pH dependence studies were conducted in order to determine conditions for maximizing product yields, and the resulting Faradaic efficiencies are shown in Figures 5.4 and 5.5. No clear trends in product generation based on electrochemical condition could be discerned, especially for products in the liquid phase. However, Mn-based spinels were consistently the most successful at facilitating CO$_2$ reduction, while the Co-based analogs were least effective.
In all cases, summing the products of CO\textsubscript{2} reduction and H\textsubscript{2} evolution accounted for the total charge passed during electrolyses.

**Figure 5.5.** Faradaic efficiencies for carbon-containing products generated during pH-dependent electrolysis experiments using spinel thin films on glassy carbon. All experiments were conducted at an operating potential of −1.38 V vs. Ag/AgCl. Error bars represent the standard deviation of at least three trials.

Maximum Faradaic efficiencies achieved for CO, formate, and methanol are listed in Table 5.2. Methanol, the most highly reduced product in this distribution, was generated at a maximum Faradaic efficiency of 8 ± 1\% using MnGa\textsubscript{2}O\textsubscript{4} at −1.48 V vs. Ag/AgCl. It is also worth noting that at this potential, in the gas phase, the MnGa\textsubscript{2}O\textsubscript{4} thin film studied here generated syngas in a near-3:1 H\textsubscript{2}:CO ratio. CO\textsubscript{2} reduction on Fe and Co spinels predominantly resulted in a CO product, with sub-5\% Faradaic efficiencies calculated for liquid products regardless of electrochemical conditions. In particular, methanol generation mediated by CoAl\textsubscript{2}O\textsubscript{4} and CoGa\textsubscript{2}O\textsubscript{4} was stunted below 1\%.

Control electrochemical experiments were performed with single-metal thin films on glassy carbon synthesized by the same drop-casting and furnace reduction technique.
used to produce the spinels. Analysis by XRD and EDX confirmed that these films were comprised of metals or metal oxides. Significantly, electrolyses conducted using these single-metal films on glassy carbon as working electrodes generated only CO (< 10%) and formate (< 1%); methanol was not detected, suggesting that both metals must be present to achieve a greater-than-two-electron reduction of CO₂.

**Table 5.2.** Maximum carbon-containing product Faradaic efficiencies achieved using each spinel thin film on glassy carbon.

<table>
<thead>
<tr>
<th>Spinel</th>
<th>Faradaic efficiency (%)†</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>MnAl₂O₄</td>
<td>22 ± 3</td>
</tr>
<tr>
<td>MnGa₂O₄</td>
<td>20 ± 2</td>
</tr>
<tr>
<td>FeAl₂O₄</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>FeGa₂O₄</td>
<td>10.0 ± 0.9</td>
</tr>
<tr>
<td>CoAl₂O₄</td>
<td>14 ± 1</td>
</tr>
<tr>
<td>CoGa₂O₄</td>
<td>5.0 ± 0.5</td>
</tr>
</tbody>
</table>

*†*Standard deviation based on the average of three trials using different electrodes.

In order to better understand the electrocatalytic activity of these TM/G13 spinels, experiments were undertaken to determine whether CO or formate might be intermediates in the electrochemical generation of methanol. Experiments were prepared by either purging the electrolyte with CO for 15 min or adding 10 mM sodium formate to the solution, thereby replacing CO₂ as the reactant. Electrolyses were then conducted using each spinel matched with the corresponding optimized conditions (i.e., potential, pH) for methanol production, and ¹H-NMR spectra were obtained to determine whether methanol was present. Ultimately, methanol could be generated from CO using FeAl₂O₄.
(0.92% Faradaic efficiency), FeGa$_2$O$_4$ (0.14%), CoAl$_2$O$_4$ (0.16%), or CoGa$_2$O$_4$ (0.04%) thin films and from formate when using MnAl$_2$O$_4$ (0.68%) or MnGa$_2$O$_4$ (1.2%). This observation will be discussed further in Section 5.3.4.

5.3.3 Post-Electrolysis Materials Characterization

Materials characterization was performed following electrochemical experimentation in order to assess chemical and physical stability of the spinel thin films. XRD and EDX (Table 5.3) confirmed that each film retained its original bulk composition following electrolysis, though overall crystallinity decreased slightly. XPS analysis indicated that surface metals remained oxidized. The only discernible change in surface composition was the reduction of Fe$^{3+}$ to Fe$^{2+}$ on the FeGa$_2$O$_4$ species, making the surface and bulk oxidation states consistent for that particular post-electrolysis sample.

<table>
<thead>
<tr>
<th>Spinel</th>
<th>Transition metal (%)</th>
<th>Group 13 metal (%)</th>
<th>Oxygen (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pre</td>
<td>Post</td>
<td>Pre</td>
</tr>
<tr>
<td>MnAl$_2$O$_4$</td>
<td>14</td>
<td>15</td>
<td>28</td>
</tr>
<tr>
<td>MnGa$_2$O$_4$</td>
<td>14</td>
<td>14</td>
<td>29</td>
</tr>
<tr>
<td>FeAl$_2$O$_4$</td>
<td>14</td>
<td>13</td>
<td>23</td>
</tr>
<tr>
<td>FeGa$_2$O$_4$</td>
<td>15</td>
<td>15</td>
<td>24</td>
</tr>
<tr>
<td>CoAl$_2$O$_4$</td>
<td>15</td>
<td>14</td>
<td>26</td>
</tr>
<tr>
<td>CoGa$_2$O$_4$</td>
<td>16</td>
<td>14</td>
<td>26</td>
</tr>
</tbody>
</table>

$^\dagger$Electrolysis experiments were conducted at $-1.38$ V vs. Ag/AgCl in pH 4.5, 0.1 M K$_2$SO$_4$.

Greater variability was observed in the physical stability of the spinel thin films during electrochemical testing. SEM images of post-electrolysis samples are shown in
Figure 5.6. Physical stability, defined here as the degree to which platelet structures were lost from the glassy carbon surface, generally corresponded to TM identity, with stability increasing in the order of \((\text{CoAl}_2\text{O}_4 \approx \text{CoGa}_2\text{O}_4) < (\text{FeAl}_2\text{O}_4 \approx \text{FeGa}_2\text{O}_4) < (\text{MnAl}_2\text{O}_4 \approx \text{MnGa}_2\text{O}_4)\). The remaining platelets of Mn and Fe spinels tended to retain their original morphologies, while the surfaces of Co analogs appeared rougher after electrolysis.

**Figure 5.6.** SEM images of post-electrolysis spinel thin films on glassy carbon. Panels correspond to (A) MnAl\(_2\)O\(_4\), (B) MnGa\(_2\)O\(_4\), (C) FeAl\(_2\)O\(_4\), (D) FeGa\(_2\)O\(_4\), (E) CoAl\(_2\)O\(_4\), and (F) CoGa\(_2\)O\(_4\). Images obtained using 5 keV electron beam.
**5.3.4 Implications for CO$_2$ Electroreduction**

Based on the results presented here, TM/G13 spinels are modestly active catalysts toward aqueous CO$_2$ electroreduction. Differences in catalytic ability were evident when comparing the spinels having different TM components. Total Faradaic efficiency for carbon-containing products, a measure of CO$_2$ reduction selectivity compared to H$_2$ evolution, was greatest for the Mn spinels, reaching as high as 40% for MnGa$_2$O$_4$. The Co spinels exhibited the lowest CO$_2$ reduction selectivity, with CoGa$_2$O$_4$ recording just 9.5% total Faradaic efficiency for carbon-containing products. This trend is more clearly observed in Table 5.4.

<table>
<thead>
<tr>
<th></th>
<th>MnAl$_2$O$_4$</th>
<th>FeAl$_2$O$_4$</th>
<th>CoAl$_2$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnGa$_2$O$_4$</td>
<td>40%</td>
<td>12.1%</td>
<td>9.5%</td>
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Table 5.4. Total maximum Faradaic efficiencies for carbon-containing products achieved using spinel thin films on glassy carbon.

These clear variations in CO$_2$ reduction activity are not attributed to the differences in physical stability observed by SEM for the spinel series. Co spinels resulted in both poor physical stability and low Faradaic efficiencies for CO$_2$ reduction products, but the H$_2$ evolution activity of the glassy carbon solid support, exposed upon thin film degradation, is relatively low (much like its activity toward CO$_2$ reduction, contributing to its popularity as a support material for CO$_2$ reduction catalysts).$^{27–29}$ In other words, when using an electrocatalytically inactive solid support, a decrease in catalyst surface area should not correspond to a decrease in product Faradaic efficiency.
Thus, the CO₂ reduction and H₂ evolution selectivities observed should be primarily attributed to the catalytic performance of the spinel films themselves, regardless of their physical stabilities.

More interestingly, improvements in spinel reactivity toward CO₂ might correspond to mechanistic routes of electrochemical CO₂ reduction, particularly when considering the production of methanol. Lower overall methanol Faradaic efficiencies were achieved using the Fe and Co spinels, both of which were shown to generate methanol via a CO-inclusive pathway. These spinels also seemed less effective at generating the CO intermediate itself, particularly when compared to the Mn-based analogs. In contrast, the most effective methanol generator in this series, MnGa₂O₄, appears to utilize a formate-dependent route and is also proficient at generating that intermediate, recording the highest Faradaic efficiency for formate (12%) compared to the other spinels in this series.

Accordingly, the biggest impact of TM choice in determining the CO₂ reduction activity of the spinels studied here seems to be the mechanistic route employed to achieve their most highly reduced product. The need to pass through a CO intermediate during CO₂ electroreduction—as was the case for FeAl₂O₄, FeGa₂O₄, CoAl₂O₄, and CoGa₂O₄—is common, especially in the literature describing hydrocarbon and alcohol formation mediated by Cu electrocatalysts.³⁰,³¹ Even so, systems reducing CO₂ to methanol via a CO-dependent pathway tend to achieve low Faradaic efficiencies, or methanol is a minor product. For Cu electrodes, this is likely because it is more energetically difficult to generate *CHO—required for methanol production—from CO than it is to generate *COH, the latter of which leads to the more common copper-induced products methane
and ethylene.\textsuperscript{30,32} Others suggest that nonoptimal OH binding energies could induce poor methanol selectivity on Cu and other metallic species,\textsuperscript{33} though this theory is less developed. These factors may apply to alternative non-spinel TM/G13 materials, which also achieve methanol as a minor product via CO reduction.\textsuperscript{13,16}

Otherwise, the efficacy with which a catalyst material can reduce CO\textsubscript{2} to products via a CO intermediate depends largely on the material’s CO binding energy. Logically, strong CO binders will self-poison if the CO cannot dissociate from the surface. Materials that bind CO weakly, on the other hand, will exhibit kinetic competition between CO dissociation and further reduction. For example, metallic Fe electrodes tend to bind CO strongly and therefore favor H\textsubscript{2} evolution in aqueous electrolytes,\textsuperscript{34} so the Fe spinels studied here must necessarily have a lower CO binding energy that favors further reduction. Conversely, CO binding on MnAl\textsubscript{2}O\textsubscript{4} and MnGa\textsubscript{2}O\textsubscript{4} must be too weak for reduction to outcompete CO dissociation from the surface, which is a likely reason why the CO Faradaic efficiencies on these spinels are much higher than the Fe and Co analogs. As shown here, the Mn spinels instead generate methanol via a formate intermediate. CO\textsubscript{2} electroreduction to methanol via a formate- or formic acid-dependent pathway has been reported, albeit far less frequently than CO pathways. Specifically, Cu-based CO\textsubscript{2} hydrogenation catalysts\textsuperscript{35} and RuO\textsubscript{2}-based CO\textsubscript{2} electroreduction catalysts\textsuperscript{5,36} utilize this alternative route.

Thus, the differences in CO\textsubscript{2} reduction pathways noted for the TM/G13 spinel series might simply be indicative of differences in CO binding energies, as well as whether the original CO\textsubscript{2} reactant is more likely to bind through the C atom (i.e., expected for a CO-dependent pathway) or an O atom (i.e., expected for a formate-
dependent pathway).\textsuperscript{31} In any case, given the methanol Faradaic efficiencies reported here, MnGa\textsubscript{2}O\textsubscript{4} must be more effective at reducing formate than the Fe or Co spinels are at reducing CO. However, methanol Faradaic efficiencies achieved using all spinels decreased when starting with CO or formate feedstocks (i.e., instead of CO\textsubscript{2}), suggesting that intermediate reduction is rate-limiting irrespective of the intermediate invoked in the CO\textsubscript{2} reduction pathway. These results expand the current understanding of what CO\textsubscript{2} electroreduction pathways are employed by TMs and their compounds to achieve methanol as a product, as depicted in Figure 5.7.

\textbf{Figure 5.7.} Summary of heterogeneous, TM-based electrocatalysts capable of reducing CO\textsubscript{2} to methanol via either a CO (peach line) or formate (orange line) intermediate. The spinels studied here (dark blue TMs) expand upon alternative TM catalysts reported in the literature\textsuperscript{13,16,34,36} (light blue TMs) to follow an electrochemical CO\textsubscript{2} $\rightarrow$ CO/formate $\rightarrow$ methanol pathway.

It is, of course, also necessary to address the likely influence of the G13 metal in dictating the CO\textsubscript{2} electroreduction performance of TM/G13 spinels. Given the fact that none of the single-metal thin films could generate methanol in control experiments, it seems clear that addition of Al or Ga to these TM and TM oxides introduces non-native CO\textsubscript{2} reduction activity, perhaps by influencing the intermediate binding energies discussed previously. Using the case of Fe as an example once again, addition of the G13
metal might help to decrease the CO binding energy that would otherwise prohibit further reduction on heterogeneous, Fe-based species. This seems consistent with the Ni$_3$Al catalyst discussed in Chapter 3, which reduces CO$_2$ to alcohols via a CO-dependent pathway$^{13}$ even though pure Ni strongly binds CO and tends to be a poor CO$_2$ electroreduction catalyst.$^{37,38}$ Similarly, by incorporating Al or Ga in the spinel structures studied here, methanol could be generated using the otherwise-inactive first-row transition metals Mn, Fe, and Co.

5.4 Summary and Conclusions

Thin film spinels of sequential TMs and G13 metals were synthesized, characterized, and tested for their ability to facilitate electrochemical CO$_2$ reduction. Supported on glassy carbon, MnAl$_2$O$_4$, MnGa$_2$O$_4$, FeAl$_2$O$_4$, FeGa$_2$O$_4$, CoAl$_2$O$_4$, and CoGa$_2$O$_4$ were modestly active in reducing CO$_2$, generating a combination of CO, formate, and methanol in aqueous electrolyte. These experiments provide the first demonstration of spinel-facilitated CO$_2$ electroreduction, thereby expanding the catalytic profile of spinel oxides.

More importantly, the catalyst candidates tested here can be added to the growing list of traditionally inactive TMs that do accomplish CO$_2$ reduction when paired with the G13 metals Al and Ga. By studying these TM/G13 spinels in series, differences in reactivity toward CO$_2$ and associated reduction intermediates were illuminated. Namely, Mn spinels seemed to generate methanol via a formate-inclusive pathway, whereas Fe and Co spinels achieved the same product via CO reduction. The relative efficacy of these pathways in producing methanol, measured here in terms of methanol Faradaic efficiency, generally accorded with alternative reports using transition metal-based
catalysts; namely, the formate route seems to be more effective, albeit rarer. Regardless, CO binding energies are likely to be one important factor dictating the pathway of CO₂ reduction. Based on the results described here, combining at least some first-row TMs with Al or Ga necessarily adjusts intermediate binding energies compared to that of the TMs or their oxides alone.

It should not be forgotten, however, that the TM/G13 spinels are oxides, and the oxygen content of the materials is a third factor that, based on other CO₂ reduction catalysts comprised of a TM and G13 metal,¹³,¹⁴,¹⁶ likely impacts CO₂ electroreduction activity. Oxides of the individual TMs and G13 metals were briefly examined here and resulted in no methanol formation, thereby overturning the possibility that the non-native, methanol-generating activity could be achieved in the presence of oxides without incorporation of the second metal. Nonetheless, additional experiments are needed in the future to determine the explicit role of oxide components alongside TMs and G13 metals in these and other CO₂ reduction systems. This understanding would help considerably in the further exploration of TM/G13 and TM/G13-oxide systems to elicit new products and pathways for electrochemical CO₂ reduction.

5.5 References


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(27) Benck, J. D.; Pinaud, B. A.; Gorlin, Y.; Jaramillo, T. F. Substrate Selection for Fundamental Studies of Electrocatalysts and Photoelectrodes: Inert Potential


Chapter 6. Conclusions and Outlook

The work presented in this dissertation has explored various aspects of catalyst discovery, tuning, and mechanistic analysis in the field of electrochemical CO$_2$ reduction, particularly emphasizing the development of transition metal/Group 13 (TM/G13) catalyst species. As such, the results have implications for several strategies associated with advancing CO$_2$ electrochemistry from a laboratory-scale research area to an industrially relevant process. For this goal to be achieved, ongoing work in catalyst development must seek to find new ways to generate commercially relevant chemicals using feasible energetic inputs and cheap, scalable reaction conditions.

Part of this catalyst development process involves the discovery of new species having impressive CO$_2$ reactivity profiles. Prior to this work, the only electrocatalysts reported to facilitate carbon-carbon bond formation during CO$_2$ reduction were a variety of copper-based species and the intermetallic system Ni-Ga.$^{1,2}$ Now, two new TM/G13 catalysts have been added to this exclusive list, each providing distinct advantages and future challenges. The Cr$_2$O$_3$/Ga$_2$O$_3$ alloy on glassy carbon generates oxalate, a very appealing chemical from a commercial perspective, at overpotentials approximately 1 V lower than those reported for previous systems.$^{3-5}$ The discovery of this anomalous catalyst is also interesting from a fundamental perspective, as its activity illuminates a new pathway for the two-electron reduction of CO$_2$ to oxalate. The outcome of this study is a record-breaking 59% Faradaic efficiency for oxalate production in aqueous electrolyte, with detailed analysis of surface chemistry lending insight into the catalytic mechanism. Elucidation of additional mechanistic details would likely facilitate more
effective scale-up of this catalytic system to a larger reaction capacity, which is not outside the realm of possibility given its reasonable energetic demands and high Faradaic and catalytic efficiencies. Industrial implementation is also likely to require adaptation as a flow cell reactor, which would improve mass transport and increase the rate of CO₂ conversion.⁶,⁷

On the other hand, the discovery of intermetallic Ni₃Al as a CO₂ reduction catalyst is interesting from a different perspective. Ni₃Al thin films on glassy carbon represent one of the first non-copper electrodes to generate C3 products from CO₂, achieving 1.9% Faradaic efficiency for 1-propanol alongside trace amounts of acetone and additional C1 and C2 products. The low efficiency and substantial overpotential requirements of this catalyst make it far less suited for industrial application, but the system itself introduces the possibility of developing completely novel catalysts (especially intermetallics and other alloys) that will generate carbon chains from CO₂ building blocks. Of course, a lingering question for this and other systems is the exact role of oxides, whether incorporated as part of the bulk material or existing stably on the catalyst surface, as this seems to be a conserved motif considering the various species studied here. Invoking a surface oxide as part of a CO₂ electroreduction mechanism is not unprecedented.⁸,⁹ Understanding the role of oxides in this context could therefore promote strategies to further improve the catalytic activity of TM/G13 compounds.

Beyond catalyst discovery, catalyst tuning is another strategy for enhancing the industrial applicability of CO₂ electroreduction systems. While nanostructuring¹⁰,¹¹ and synthetic derivation techniques¹²–¹⁴ have been widely explored for heterogeneous CO₂ reduction catalysts, experiments with the intermetallic Ni₃Ga system reported here show
that choice of carbon support material can also influence catalytic activity by dictating
catalyst morphology and surface composition, resulting in changes to reduction
pathways, product distributions, and Faradaic efficiencies. Not only can understanding
solid support influence be exploited for catalyst design purposes, but it can also be used
strategically to develop multi-electrode systems, as demonstrated by experiments
combining supported and unsupported Ni$_3$Ga to elicit improved catalytic outcomes.
However, an important question must still be answered regarding the indirect impact of
carbon supports, and it comes from the observation that films synthesized on HOPG
never seem to generate CO at Faradaic efficiencies greater than 1% and, more frequently,
fail to generate detectable CO altogether. This is even the case when the film produces
multi-carbon chemicals via a CO intermediate. Future work determining the reason for
this activity—or lack thereof—on HOPG might provide additional insight to benefit
catalyst tuning efforts.

Finally, recognizing the role or impact of individual metals within multi-metal
electrocatalyst systems can promote more informed choices in experimental and
theoretical catalyst prediction. By analyzing trends in CO$_2$ reduction ability facilitated by
a series of TM/G13 spinel oxides, incorporation of a G13 metal was shown to induce
non-native CO$_2$ electroreduction activity from Mn, Fe, and Co. Additionally, the spinels
employed two different pathways in CO$_2$ reduction to methanol, the most highly reduced
product of this system. Namely, Mn spinels produced methanol more efficiently in a
formate-dependent pathway than Fe and Co spinels did via a CO-dependent route. These
results lend support to assertions that metal alloys can alter the energetics or
configurations of CO$_2$ and intermediate binding on catalyst surfaces,$^{15,16}$ so design and
optimization of catalysts based on these molecular-level factors should realistically improve CO₂ electroreduction prospects.

Ultimately, electrochemical reduction of CO₂ to produce chemical feedstocks is an attractive method for contributing to climate change mitigation, as its ability to generate profitable products creates an incentive for corporate entities to invest in its technologies. The results presented here demonstrate the value of electrocatalyst discovery, tuning, and mechanistic evaluation in lowering energetic requirements and diversifying product portfolios, while simultaneously motivating continuous research on TM/G13 electrocatalysts for CO₂ reduction. These species have now been shown to generate commercially relevant chemicals at competitive efficiencies, selectivities, and overpotentials, lending credibility to the goal of broadly implementing CO₂ reduction systems in society over time.

6.1 References


Appendix

<table>
<thead>
<tr>
<th>Table A1. List of abbreviations.</th>
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<td><strong>Term</strong></td>
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<tr>
<td>3 Cr$_2$O$_3$:1 Ga$_2$O$_3$</td>
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<tr>
<td>Counter electrode</td>
</tr>
<tr>
<td>Cyclic voltammetry</td>
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<td>Faradaic efficiency</td>
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<td>Glassy carbon</td>
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<td>Group 13 metal</td>
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<td>Heteronuclear single quantum correlation</td>
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<td>Highly oriented pyrolytic graphite</td>
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<td>Octadecene</td>
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