Abstract

System-based Approaches for the Enhancement of Catalytic CO₂ Reduction Reactions

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Doctor of Philosophy

Mechanical & Industrial Engineering

University of Toronto

2017

This thesis focusses on the importance of system design, specifically the engineering of gas, liquid and solid catalyst interactions, in enhancing catalytic CO₂ reduction processes. The most impactful contributions of this thesis are: the enhancement of CO₂ production rates via morphology-induced mass transport (Chapter 3); the manipulation of local reaction environments to increase electrochemical CO₂-to-ethylene production in an H-cell configuration (Chapter 4); the design of an abrupt reaction interface adjacent to a gas-liquid interface for high current and selective ethylene production in an alkaline media (Chapter 5); and the creation of a scalable multi-phase photocatalytic reactor (Chapter 6).

While material science and chemistry are essential in the creation and functionality of CO₂ reduction catalysts, the overall system surrounding the solid catalyst plays a similar influential role in determining the overall efficiency, product distribution and production rate. By understanding the complex interactions between a solid catalyst, liquid electrolyte and gas reagents/products, the underlying influences of system engineering on catalyst performance can be extracted and improved. Using this approach catalyst surface morphology is revealed to increase limiting current densities multifold by enhancing the natural mass transport effects of departing CO₂ reduction products. The pH and CO₂ gradients formed at the catalyst’s surface during the reaction similarly influence product selectivity, most notably the ratio between hydrogen, methane and ethylene using copper-based catalysts. Equipped with this understanding, tuning catalyst morphology under differing buffering capacities allowed for traditionally coupled CO₂ limitations and electrode pH to become partially decoupled; ethylene production under ambient conditions then improved significantly as compared to a catalytic system void of such considerations. Expanding on this knowledge CO₂ reduction catalysts were designed to operate in a highly alkaline environment where the reaction onset potential for ethylene formation was found to be reduced to unparalleled levels. The system design, which manipulated a sub-100 nm diffusion interface, similarly led to half-cell power conversion efficiencies substantially higher than previous efforts at significantly improved production rates.
While catalyst nanostructures can enhance reaction performance, heterogeneous photocatalysts can suffer from both a lack of surface area and interaction with reagents versus homogeneously dispersed photocatalysts. Separately, unanchored catalysts are subject to complications which inhibit flow-through processing and require additional mixing. From bare TiO$_2$ nanoparticles a scalable reactor was engineered that provided a 3-D, stable catalyst structure via surface functionalization. The resulting floating catalyst was composed of nanoparticle shells positioned between two fluids resulting in a variety of reactors including water-in-oil emulsions, oil-in-water emulsions and CO$_2$-in-water foams. Textile dyes were degraded in a partially mixed reactor without the need for nanoparticle filtering or full-body mixing, representing a cost and implementation advantage over both nanostructured and nanoparticle approaches.
The journey from start to finish is one that has felt simultaneously instantaneous and endless. Looking back on the innumerable events that have transpired I feel fortunate to have experienced both successes and failures that have led me to this point in time. I could not have gotten here alone, however, and owe gratitude and acknowledgement to the individuals who not only aided in the advancement of my research proper, but kept me inspired to do so on a daily basis.

First, to my supervisor Prof. David Sinton I owe a great deal of my personal growth over the last four years. I was fortunate to be granted a good mix of guidance and independence as I waded through the ins and outs of experiments, paper and grant writing and leadership roles. The most valuable experiences, however, came about during the difficult periods of research where Dave’s calmness and composure righted the ship. In parallel, I would like to thank Prof. Edward Sargent. Although I may occasional wake up with a sense of dread that the monthly conference is hours away, the four years of collaboration with Ted and his group have been so motivating and in the end, fulfilling. I would also like to thank my committee members Prof. Aimi Bazylak and Prof. Hani Naguib for taking the time to meet with me annually and help steer my path towards graduation.

Over the last four years the people who I spent more waking hours with than anyone are my lab mates who undoubtedly deserve recognition for my accomplishments and growth to date, and in the future. Although not exhaustive, I would like to thank Percival Graham, Cao-Thang Dinh, Yuanjie Pang, MD Kibria, Phil de Luna, Ali Seifitokaldani, Reza Nosrati, Jason Riordon, Soumo Mukherjee, Matthew Ooms, Scott Pierebon, Jonathan Edwards, Brian Nguyen, Seven Qi, Pushan Lele, Katarina Neskovic and Evan Karakolis for all of your research help and personal conversations over the last few years. The last two years the Catalysis and MC64 crews were a second family and I hope we will keep in touch and even work together in the future. Thank you for everything.

I would also like to recognize my friends external to the university. Despite never fully knowing what I did on a daily basis and telling me I needed to get a real job someday, they provided a much needed break from my day job, one that I didn’t always give myself. My family also provided both an escape and overwhelming support and one of the hardest parts has been living away from them for so long. I would sincerely like to thank my mom, Nancy, for getting me where I am today. While the list of reasons is too long to recite here, in the end I owe all of my work ethic, tenacity and principles to her. Thank you John, Cyndy and Matt for being awesome as well, I hope I have made you as proud of me as you have me with each of your accomplishments.

Finally, I would like to acknowledge my girlfriend Sarah Marchionda. It has been a long road to get here and you were endlessly positive every step of the way. You helped to dampen the natural lows of failed experiments,
paper rejections and self-doubt while making sure we celebrated both the big and small accomplishments along the way. Who knows exactly what the world has in store for us, but I am looking forward to heading down that road together.
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Chapter 1.
Foreword

1.1 Motivation

Our society as we know it relies on converting environmental and chemical energy sources into the electricity that lights our cities at night and the fuels that transport us and our goods around the globe. The abundance of energy at our disposal has increased the leisure time of the average person and allowed for vast improvements in the quality of life and advancements in science and technology. A previously unforeseen consequence of our heavy use of carbon-based fuels, however, is the current issue of global climate change. Given the great implications that climate change will have on our current way of life, technological advancements are required that both reduce our current dependence on carbon-based fuel sources and replace our energy-dense fuels with carbon-neutral equivalents. Given the expansiveness of the problem at hand, multiple technologies that economically drive change will be required to take us through this energy transition. This thesis focuses on the advancement of two of these future technologies: electrocatalytic and photocatalytic devices that convert CO\textsubscript{2} into various carbon-based fuels using readily-available energy sources.

Given the chemical stability of CO\textsubscript{2} molecules, energy is required to convert the waste gas back into a useful compound. In photocatalytic processes this energy is provided via irradiation either from direct sunlight or an artificially created replacement. In electrocatalytic reactions the input energy is provided in the form of electricity. In both scenarios, however, the overall energy efficiency of the conversion process is greatly tied to the catalyst on which the CO\textsubscript{2} molecule is converted.\textsuperscript{1,2} A great deal of research has then been undertaken in materials science and chemistry to identify and categorize different catalysts both experimentally and through numerical approaches such as Density Functional Theory (DFT) and molecular dynamics. The result has been a plethora of different catalysts with increasingly lower onset potentials and higher product selectivities.

A caveat of purely catalyst discovery research, however, is that while a catalytic surface may have been nano-engineered for a specific reaction, the surrounding reaction environment generally is not and is subject to reaction-driven changes which can easily shift away from optimal operating conditions. As has recently been emphasized in literature these reaction-driven changes play a large role in the reaction intermediates leading to higher value multi-carbon products such as ethylene and ethanol. Further, due to the limited solubility of CO\textsubscript{2} within aqueous electrolytes, additional engineering of electrolyte-catalyst interactions is needed to supply enough reagent to achieve meaningful production rates and maintain the higher efficiencies achieved at lower currents. While a materials-focused research pathway has been crucial for rapid catalyst advancement, even greater opportunities exist by simultaneously controlling the local reaction environment via system design.
The objective of this thesis was then to explore the under examined mass transport and reaction kinetic aspects of the \( \text{CO}_2 \) reduction field and enable performance gains through this fresh perspective. The \( \text{CO}_2 \) conversion process is more intertwined than currently emphasized in literature and warrants a full examination of the local reaction environment and the reaction-driven changes that take place during \( \text{CO}_2 \) reduction.

1.2 Thesis Contributions

This thesis is focused on system-based approaches for the enhancement of catalytic \( \text{CO}_2 \) reduction reactions. The thesis is divided into five core chapters described below which explores the impact of the local reaction environment on the catalytic conversion of \( \text{CO}_2 \) into various products. After a brief introduction to existing literature in Chapter 2, the following chapters describe progressive advancements in understanding and improving electrochemical \( \text{CO}_2 \) reduction from a mass transport and reaction kinetics perspective. In Chapter 3 the role of the diffusion layer next to catalyst is expanded to include reaction and morphology-driven changes, which plays a large role in \( \text{CO}_2 \) limiting current densities and energy efficiency. The lessons learned are extended to multi-product \( \text{CO}_2 \) reduction processes in Chapter 4 with a focus on copper-oxide derived catalysts. The limits of these catalysts in an H-cell environment are tested by modifying catalyst morphology, operating conditions and electrochemical surface area to simultaneously promote ethylene selectivity and current density. The approaches presented in Chapters 3 and 4 allow for catalyst performance to be better analyzed from a non-material perspective, highlighting important and previously undiscussed factors in the field affecting the reaction process. Aside from emphasizing the importance of the local reaction environment, however, these papers highlight the fundamental problems in the field with (a) testing catalysts in an extremely sensitive reaction environment, and (b) performing \( \text{CO}_2 \) reduction with ample, rather than excess, \( \text{CO}_2 \). The efforts then lead directly to the approach taken in Chapter 5 where catalysts are deposited on a gas-diffusion layer and operated in a flow-cell environment. Shown within this final work is a culmination of knowledge gained from the previous chapters resulting in the advancement of all performance metrics, underlining the importance of designing catalysts in harmony with the surrounding reaction environment. Clear from Chapter 5 is the necessity for the \( \text{CO}_2 \) reduction field to move to such an operating environment for both catalyst discovery purposes and designing practical \( \text{CO}_2 \) electrolyzers for the future.

1.2.1 Chapter Overviews

Chapter 2 – Background

The introduction of this thesis summarizes relevant literature and concepts for the electrocatalytic and photocatalytic conversion of \( \text{CO}_2 \). Emphasis is applied to how \( \text{CO}_2 \) mass transport, catalyst-electrolyte dynamics and system configurations impact key performance metrics of conversion including current density, selectivity and energy efficiency.

Chapter 3 – Nanomorphology-enhanced Gas-evolution Intensifies \( \text{CO}_2 \) Reduction Electrochemistry
This work describes the impact of electrode morphology on the maximum attainable \( \text{CO}_2 \) reduction current density of a catalyst. Specifically, it is found that sharper nanostructures can reduce the bubble release diameter of product gases evolved during an electrochemical reaction, greatly reducing the diffusion layer thickness and increasing the flux of \( \text{CO}_2 \) to the electrode’s surface. The experimental observations led to the formation of an electrochemical model accounting for the effects of mass transport from gas-evolution which can be used to better analyze experimental performance metrics of individual catalysts. This work has been published in *ACS Sustainable Chemistry and Engineering*\(^3\).

Chapter 4 – Joint Tuning of Nanostructured Cu Oxide Morphology and Local Electrolyte Programs High-Rate \( \text{CO}_2 \) Reduction to \( \text{C}_2\text{H}_4 \)

This chapter investigates the coupled effects of electrochemical ethylene formation on a Cu oxide electrode within an aqueous electrode. Specifically, the effects of electrode morphology, current density and electrolyte concentration on \( \text{CO}_2 \) availability and local pH are assessed using the electrochemical model developed in Chapter 3. The fundamental limitations of achieving high ethylene production rates on Cu-oxide derived electrodes within fully aqueous systems is addressed. The findings led to implementation of the flow cell directions in the Sinton and Sargent labs and the work presented in Chapter 5. This work has been published in *Green Chemistry*\(^4\).

Chapter 5 – Abrupt Fluid-Solid Interface for High Performance \( \text{CO}_2 \) Electroreduction to Ethylene

This work utilizes mass transport and DFT modeling to develop an experimental reactor structure that allows for \( \text{CO}_2 \) reduction to occur at high current densities and C2 product selectivity. An abrupt reaction interface of evaporated copper nanoparticles provides simultaneously high \( \text{CO}_2 \) and \( \text{OH}^- \) concentration locally at the catalyst surface. Combined, the elevated concentrations reduce hydrogen, methane and CO production by decreasing protonation pathways as well as reducing the energy barriers of reaction intermediates on the C2 product pathway. This work has been submitted as a letter to *Nature* and forms the foundation of a provisional U.S. patent\(^5\).

Chapter 6 – Self-assembled Nanoparticle-stabilized Photocatalytic Reactors

This chapter describes the design and testing of several emulsions and foams stabilized by photocatalytic nanoparticles. Positioning nanoparticles at a three-phase interface allows for a larger reactive surface and compartmentalizing of reactants. The reactor structure was found to be effective in the continuous degradation of aqueous pollutants due to their ability to be preferentially distributed throughout an aqueous medium. This work has been published in *Nanoscale*\(^6\).
1.2.2 Supplementary Contributions

The following supplementary contributions include papers that I contributed to as co-author and have been submitted for publication. These contributions are not discussed within the manuscript but are included here for completeness.

- **A penalty on photosynthetic growth in fluctuating light**
  - Under Review: Scientific Reports
  - Authors: Percival Graham, Brian Nguyen, Thomas Burdyny, David Sinton

- **An interconversion and storage system for solar, electrical, and hydrogen energy employing narrowband redox bracketing**
  - Submitted: Nature Communications
  - Authors: Cao-Thang Dinh, F. Pelayo García de Arquer, Ankit Jain, Xueli Zheng, Bo Zhang, Thomas Burdyny, Min Liu, Yuanjie Pang, Oleksandr Voznyy, Sjoerd Hoogland, David Sinton, Edward H. Sargent

- **Core/Shell-Vacancy Engineering Promotes Carbon Protonation for Efficient Multi-Carbon Alcohols Electrosynthesis**
  - Submitted: Nature Catalysis
  - Authors: Taotao Zhuang, Zhiqin Liang, Ali Seifitokaldani, Yi Li, Phil De Luna, Thomas Burdyny, Fei Meng, Rafael Quintero-Bermudez, Cao Thang Dinh, Min Liu, Miao Zhong, Fanglin Che, Bo Zhang, Peining Chen, Xueli Zheng, Bangjiao Ye, David Sinton, Shuhong Yu, Edward H. Sargent
Chapter 2.

Background

2.1 Overview of Electrochemical CO\textsubscript{2} Reduction

The electrochemical reduction of CO\textsubscript{2} fundamentally requires four components as shown in Figure 2-1: 1) a negative electrode (aka cathode) that is capable of directly or indirectly converting CO\textsubscript{2} into another molecule, 2) a positive electrode (aka anode) that is capable of sufficiently providing a counter reaction that provides both protons and electrons to the cathode, 3) an electrolyte that is conductive enough to shuttle protons from the anode to the cathode, 4) a voltage source that, by providing a sufficient potential, shuttles electrons from the anode surface to the cathode surface through an external circuit. An ion exchange membrane is also typically positioned in the electrolyte between the anode and cathode to prevent products formed at the anode and cathode from reacting on the opposite surface. Finally, a Ag/AgCl reference electrode is generally placed in the catholyte to control the working potential of the cathode.

Imperative to the reaction is a steady supply of CO\textsubscript{2} to the cathode surface. Several system configurations and operating condition have been created to facilitate CO\textsubscript{2} transport within an electrochemical system, some of which are generalized in Figure 2-1. Two of these four configurations are known as H-Cell setups and have been favored for their simplicity and ease of quickly testing catalysts. The majority of catalysts presented in literature feature H-Cell setups due to the large volume of electrolyte, mechanical mixing, commercial availability and easy-to-use 3-electrode electrochemical setups.\textsuperscript{7–10} The other two common setups are Flow-Cell configurations as shown in Figure 2-1 c and d which pump electrolyte past the cathode and anode. These setups, while more complicated than H-Cells, allow for reduced ohmic losses and finer control over mass transport at the catalyst's surface.\textsuperscript{11,12}

The configurations in Figure 2-1 can also vary by the type of electrode used which affects the supply of CO\textsubscript{2} to the catalyst surface. For the majority of CO\textsubscript{2} reduction catalysts in literature that are deposited on top of a glassy carbon or carbon paper substrate (Figure 2-1 a and c), the CO\textsubscript{2} reagent travels from the bulk electrolyte across a liquid diffusion layer to the catalyst surface. Alternatively, a gas diffusion electrode can be used which allows CO\textsubscript{2} gas to flow through the back of a hydrophobic carbon layer directly to a CO\textsubscript{2} reduction catalyst in the electrolyte (Figure 2-1 b and d). The formed hydrophobic-hydrophilic interface then greatly shortens the diffusion pathway of CO\textsubscript{2} molecules and increases electrolyte flexibility. In a flow-cell the majority of gaseous products will diffuse back into CO\textsubscript{2} gas stream while liquid products will enter the electrolyte.
Figure 2-1 | Electrochemical CO₂ reduction performed in H-cell (a, b) and Flow-Cell (c, d) configurations. Essential components are the 1) cathode, 2) anode, 3) electrolyte and 4) voltage source. The dashed line represents the ion exchange membrane. Configurations (b) and (d) utilize gas diffusion electrodes.

Reduction products created from electrochemical CO₂ conversion largely depend on the catalytic material used and range from single carbon molecules like carbon monoxide (CO)\(^{13-15}\), formate (HCOOH)\(^{16-18}\) and methane (CH\(_4\))\(^{19,20}\) to multi-carbon bonds such as ethylene (C\(_2\)H\(_4\))\(^{21-23}\) and ethanol (EtOH)\(^{24}\). Similarly almost all known catalysts are capable of producing hydrogen (H\(_2\)) which is generally an unwanted, competing reaction. This thesis will focus on the current state-of-the-art catalysts and systems for the major reduction products produced in literature. These products and their thermodynamic reduction potentials are nicely summarized by Kortlever et al. by Equation 2.1 and Table 2-1. As conversion of CO₂ requires both protons (H\(^+\)) and electrons (e\(^-\)), the reaction further results in an increased pH at the reaction interface.

\[ k \, CO_2 + n(H^+ + e^-) \rightarrow \text{Products} + m \, H_2O \]  

(2.1)
Table 2-1 | Stoichiometric requirements and thermodynamic half-reaction potentials for the primary electrochemical CO2 reduction products. Adapted with permission from [25]. Copyright © 2015 American Chemical Society.

<table>
<thead>
<tr>
<th>Reduction Product</th>
<th>k</th>
<th>n</th>
<th>m</th>
<th>$E^\circ$ (V versus RHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon Monoxide, CO</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>-0.10</td>
</tr>
<tr>
<td>Formic Acid, HCOOH</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>-0.20</td>
</tr>
<tr>
<td>Methanol, CH$_3$OH</td>
<td>1</td>
<td>6</td>
<td>1</td>
<td>0.02</td>
</tr>
<tr>
<td>Methane, CH$_4$</td>
<td>1</td>
<td>8</td>
<td>2</td>
<td>0.17</td>
</tr>
<tr>
<td>Ethanol, CH$_3$CH$_2$OH</td>
<td>2</td>
<td>12</td>
<td>3</td>
<td>0.09</td>
</tr>
<tr>
<td>Ethylene, C$_2$H$_4$</td>
<td>2</td>
<td>12</td>
<td>4</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Materials for CO$_2$ reduction can be classified into several groups as recently reviewed by Lu et al. who separated catalysts in literature into metallic, non-metallic and molecular groupings as shown in Figure 2-2. A large majority of cathodes are constructed from Group 11 transition metals Au, Ag and Cu. Use of these materials have resulted in many of the highest reported figures of merit for the products in Table 2-1. Newer catalysts made from bimetallic systems and even non-metallic structures have also shown unique CO$_2$ conversion performance and are a large avenue of future research with the potential to both replace precious metals and create more complex products. Even when using similar base materials to form catalysts, however, performance varies widely depending on the system configuration, morphology, oxidation state and system operating conditions which affect numerous parts of CO$_2$ conversion.

Figure 2-2 | Major CO$_2$ reduction catalyst classifications and specific materials for different reduction products. Reprinted from [26] with permission from Elsevier. Copyright © 2016 Elsevier Ltd.
An important consideration for CO$_2$ electrolyzers is also the operating and capital costs of such a device. While these are primarily a factor of device efficiency, operating conditions and system configuration, the quantity and complexity of catalysts is an important cost consideration. Additionally, catalysts which may perform well and be stable at lower currents on a specific substrate in an H-cell environment, may not be directly transferable to a higher current, flow-cell configuration needed in a commercial system.

### 2.2 Performance Metrics

When evaluating CO$_2$ reduction catalysts, engineers and scientists rely on key performance metrics to gauge progress both within the lab and against reports in literature. While testing conditions and reported values are not as standardized across the field as solar-cell efficiencies, commonly reported performance metrics include geometric current density, overpotential, Faradaic efficiency and stability. Overall the metrics can be used to identify the current state-of-the-art technology, as well as how close a given catalyst is to the parameters required for a commercial system. Below is a brief description of each metric.

#### 2.2.1 Current Density

The rate that products are created within electrochemical reactions is most frequently reported as geometric current density, denoted by $j$. Unlike photocatalytic systems which report in units of mass produced per unit time and mass of catalyst, current density is a function of the total applied current divided by the planar area of active catalyst. The total current density measured accounts for all formed reaction products (CO, HCOOH, CH$_4$, H$_2$, etc.) and any catalyst surface reductions that occur. Within a CO$_2$ electrolyzer the capital cost of a unit is directly proportional the geometric current density. The size of the fluid flow channels, ion exchange membranes, anode materials, gaskets and end plates all scale with the cathode active area and higher current densities are then absolutely necessary for making a practical CO$_2$ electrolyzer. While the target current density depends on electricity price and the product created, minimum production rates of over 100 mA cm$^{-2}$ are suggested for commercial electrolyzer designs to make capital costs minimal versus operating costs.$^{31,32}$ The current density can also be described using the electrochemically active surface area rather than the geometric area to account for the explicit activity of the catalyst.

#### 2.2.2 Faradaic Efficiency

As multiple electrochemical reactions are possible on a single catalyst surface, an important parameter in CO$_2$ reduction is the Faradaic Efficiency (FE), also known as selectivity. This parameter can be used to describe the percentage of current distributed to different reaction products. An ideal catalyst would minimize all competing reactions such that only a singular, target product is produced. The FE is then defined as:

$$FE_{Prod} = \frac{j_{Prod}}{j_{Total}}$$

(2.2)
2.2.3 Overpotential and Onset Potential

The overpotential in CO₂ reduction systems is the difference between the applied potential (E) and the thermodynamic potential of a half-reaction (E° in Table 2-1). The onset potential of CO₂ reduction products is the applied cathode voltage where products are first detected. Ideally the onset potential occurs at the thermodynamic potential but even using the most active catalysts an activation barrier must be overcome. To increase the current density to meaningful limits the overpotential is then increased past the onset potential. The change in current with applied overpotential is described by the Tafel slope and quantifies the kinetics of the electrochemical reaction. While increasing overpotential increases production rates, the overall energetic efficiency of the reaction decreases as further voltage is applied. Coupled with Faradaic Efficiency, the half-cell power conversion efficiency (PCE) for a CO₂ reduction reaction with an ideal water-splitting anode (1.23 V vs RHE) can then be defined as:

\[
PCE_{Prod} = \frac{(1.23 \ V-E)}{(1.23 \ V-E)FE_{Prod}} \tag{2.3}
\]

2.2.4 Stability

Reaction stability is one of the least studied aspects in literature but one of the most important for industry. As commercial catalysts need to last for thousands of hours to be cost-effective and reliable, the applied voltage, current density and selectivity of the electrolyzer should remain constant during extended and cyclical operation. Unfortunately high stability is difficult to achieve due to the number of mechanical, chemical and electrochemical failures that can occur. It is common for designed nanostructures to mechanically break-off, catalysts to dissolve and redeposit elsewhere and for impurities in the electrolyte to contaminate the reduction catalyst. Nevertheless stability is an important design consideration for catalysts which show promise in other performance metrics.

2.3 Catalytic Materials and Structures

An extremely large effort has been applied across disciplines to identify and produce catalysts that efficiently reduce CO₂ to a wide variety of products. Reaction performance has been experimentally shown to be influenced by numerous factors including material, morphology, oxidation state and surface vacancies among others. Due to the complexity of CO₂ conversion, particularly to multi-carbon products requiring over 12 electron transfer steps, significant effort is further required to characterize and model newly developed catalysts and identify the most likely factors contributing to the observed performance gains. These include classical material characterization techniques such as X-ray photon spectroscopy, Ramen spectroscopy and X-ray diffraction and modeling efforts such as Density Functional Theory, which are typically required in parallel. Several recent reviews summarize heterogeneous catalysts for CO₂ reduction in much greater detail than will be discussed here and this subsection acts only to familiarize the reader with some of the overarching material factors affecting electrocatalytic CO₂ reduction.
A large majority of CO₂ reduction catalysts are metallic, deposited onto carbon paper or glassy carbon and tested in an H-cell environment. Specific nanostructures can be created through the direct electrodeposition or reduction of metal salts onto a substrate, or formed separately through wet-chemical methods and mechanically deposited in a secondary step. The former has a parameter space that can result in vastly different nanostructures by varying metal salt concentration, deposition voltage, deposition time and stir rate. This approach has resulted in a number of high-performing catalysts including gold nanoneedles (Figure 2-3a) which has one of the highest CO Faradaic efficiencies, lowest overpotentials and best Tafel slopes of 42 mV dec⁻¹ for electrochemical CO₂ reduction.¹⁴ The increased activity is linked to the sharp radius of the nanofeatures which increases the local electric field and concentrates cations. This in turn locally concentrates the CO₂ reactant. Other examples of possible electrodeposited structures include copper nanowires³⁴ and zinc dendritic structures³⁵ which show both selectivity and efficiency advantages versus planar equivalents. Various morphologies are also able to expose different material facets, edges and corners which are quoted as influencing CO₂ reduction and H₂ evolution processes differently.³⁶ Advanced nanoparticle synthesis techniques, which have a much higher degree of control than electrodeposited structures, have subsequently created a wide variety of precise nanoparticles sizes and features to reach product selectivities of over 90% and energy efficiencies over 60% for CO production (Figure 2-3b).³⁷⁻³⁹

![Figure 2-3](image)

Figure 2-3 | Examples of different catalyst properties affecting CO₂ reduction performance. (a) Modeling and SEM of a Au nanoneedle. The sharp radius results in a high electric field and potassium ion concentration. Reprinted by permission from Macmillan Publishers Ltd: [14]. Copyright © 2016. (b) Density of adsorption sites (yellow, light orange, dark orange, or red symbols for (111), (001), edge, or corner on-top sites, respectively) on closed-shell cuboctahedral Au clusters vs the cluster diameter. The weight fraction of Au bulk atoms is marked with gray dots. Reprinted with permission from [39]. Copyright © 2013 American Chemical Society. (c) Summary of hydrocarbon selectivity of plasma-treated Cu foils. From left to right, the insets show SEM images of the low surface area H₂ plasma-treated metallic Cu foil, the O₂ 20W 2 min plasma-treated Cu foil with optimal ethylene selectivity, and the high surface area nanoneedles on the O₂ 100W 10 min oxidized sample after the reaction (500 nm scale bars). Reproduced from [23]. CC BY 4.0, Copyright © 2016, Rights Managed by Nature Publishing Group.

For the production of multi-carbon products such as ethylene, ethanol and n-propanol, copper is almost exclusively the only catalyst capable of performing the CO-CO bonding step needed to reach these products. The capacity to form so many different bonds and compounds, however, comes with an inherent lack of product selectivity. For most Cu-based systems a wide mix of CO, HCOOH, CH₄, C₂H₄, EtOH and H₂ can be produced at any given time.²⁵ DFT studies point to the effects of surface modifications to promote or suppress the energy
barriers of different reaction intermediates and influence selectivity. For multi-carbon products the most successful surface modification has been varying the oxidation state of deposited copper catalysts.\textsuperscript{9,40–43} During the electrochemical reaction the oxide-layer will be reduced to bare metal with an altered surface state that changes the reaction barriers of CH\textsubscript{4} and C\textsubscript{2}H\textsubscript{4}. The resulting surface can produce high C\textsubscript{2}H\textsubscript{4} selectivities with Mistry et al. reaching 60\% on a plasma-oxidized copper surface (Figure 2-3c) at a half-cell power conversion efficiency of 33\%.\textsuperscript{23} Several DFT and characterization studies have been performed to try to isolate the reasons for the change in performance with a recent study pointing to a non-reduced subsurface-oxide layer effectively altering the oxidation state of a layer of copper atoms at the surface.\textsuperscript{44,45} Recently metal-free catalysts have also produced some C\textsubscript{2}+ reduction products with Wu et al. reaching FE’s of 45\% on N-doped graphene quantum dots.\textsuperscript{46}

This section has provided a brief snapshot of CO\textsubscript{2} reduction catalysts and important factors that will be discussed further in later chapters of this thesis. Although not exhaustively covered here, a wide variety of catalysts are possible and have been tested for CO\textsubscript{2} reduction with accompanying detailed modeling and characterizations of individual reaction pathways. Next in focus is the infrastructure surrounding CO\textsubscript{2} reduction catalyst.

2.4 System Designs for CO\textsubscript{2} Reduction

The previous section showed examples of finely-tuned catalysts that allow for high CO\textsubscript{2} reduction selectivities and low reaction onset potentials. In each case the characteristics of the material play an important role in improving the underlying reaction kinetics. Equally important is a system configuration capable of supplying ample reagent and keeping the reaction environment maintained at optimal conditions for the catalytic reaction to take place. In the absence of such design even the best performing catalysts suffer from low CO\textsubscript{2} current densities and narrow operating conditions. This section provides examples of different system configurations that have been used for CO\textsubscript{2} reduction.

The following configurations all share the components described in Section 2.1 including a cathode, anode, electrolyte and voltage source, but can vary widely in their implementation. One category of systems pressurizes the electrolyte to greatly increase the dissolved CO\textsubscript{2} available for reaction. Using a configuration fundamentally similar to that of Figure 2-1a, Hara et al. used an autoclave to pressurize the CO\textsubscript{2} headspace and electrolyte surrounding a piece of copper wire up to 60 atm showing that a wide range of reduction products can be evolved depending on the system pressure, current density and stir rate. A remarkable CO selectivity of 86\% was achieved at 260 mA cm\textsuperscript{-2} at a cathode potential of -0.78 V vs RHE after iR correction, on par with some of the best nanostructured catalysts at much higher currents. This approach was mimicked by Hashiba et al. who went to pressures of up to 9.5 atm in a combinatorial study about important operating parameters that also included temperature and stirring rate (Figure 2-4a).\textsuperscript{47} Taking the same concept but with improved fluid control, Dufek et al. pressurized a K\textsubscript{2}SO\textsubscript{4} electrolyte up to 18.5 atm (Figure 2-4b).\textsuperscript{48} A direct correlation between
pressure and CO selectivity was shown for a silver electrode, reaching current densities as high as 350 mA cm$^{-2}$ at Faradaic efficiencies of 92%.

An alternative to pressurizing the liquid electrolytes which produces a similar result, is the use of gas-diffusion electrodes and three-phase reaction interfaces. In this case a gas-liquid interface is positioned close to the catalytic material resulting in a much shorter diffusion pathway for dissolved CO$_2$ than the hydrodynamic boundary layer of an electrolyte. While the maximum solubility of CO$_2$ is not increased with this approach, CO$_2$...
current densities similar to pressurized systems are achievable. One of the first instances of gas-diffusion electrodes for CO$_2$ reduction was by Cook et al. in 1989 for methane and ethylene production on copper electrodes in 1 M KOH. A schematic representation of the reaction environment is shown in Figure 2-4c. By pressing a copper gauze onto a Teflon-treated carbon support a hydrophilic-hydrophobic interface was established. The three-phase interface helped to reach ethylene selectivities of 69% at total currents as high as 400 mA cm$^{-2}$ when run at 2°C. Instead of using a carbon support Ogura et al. formed a three-phase reaction interface by placing a piece of copper mesh onto a glass filter Figure 2-4d. Coating the outside of the copper mesh in CuCl prior to the experiment resulted in the deposition of copper nanostructures onto the mesh, producing a reported ethylene selectivity of ~70%. Currents in this case were held to ~15 mA cm$^{-2}$, however.

Two recent adaptations by Ma et al. (Figure 2-4e) and Reller et al. (Figure 2-4f) took similar overall approaches but with much more efficient catalysts. Ma et al. were subsequently able to reach half-cell power conversion efficiencies of 23% at partial ethylene currents of 150 mA cm$^{-2}$ and a potential of -0.58 V vs RHE. This operating potential is below the onset potential of most nanostructured catalysts at much higher currents, highlighting the benefits of system design on conversion efficiency. Work within the same group has applied gas diffusion technology to CO production while varying other system parameters such as catalyst deposition procedures, electrolyte cations and anode materials. Finally, tin has been deposited onto gas-diffusion layers for formate production by Kopljar et al. (Figure 2-4g) and Castillo et al. The efficiency of Kopljar et al. system was improved by increasing catalyst loading and active surface area, reaching maximum currents of 200 mA cm$^{-2}$ at 90% selectivities.

In a departure from the majority of CO$_2$ reduction systems, Li et al. adapted an approach from PEM fuel cells by depositing both the anode and cathode onto a bipolar membrane. The cathode again functions as a gas-diffusion electrode but the electrolyte is provided by a humid CO$_2$ gas stream. Lower CO selectivities are seen as compared to other system configurations but the demonstration of new approaches is promising.

The various electrochemical CO$_2$ reduction systems presented here demonstrate that (a) industrially relevant current densities can be obtained using a variety of system configurations and operating conditions and (b) substantial gains in product selectivity and efficiency can be achieved using relatively simple catalytic materials by enhancing the local reaction environment with system design.

2.5 Catalyst-System Interactions

The previous two sections gave examples of novel CO$_2$ reduction catalysts and system configurations that resulted in impressive or unique reaction performance. In reality the two avenues of research are not as distinct as described here, or as often quoted in literature, due to the combined influences of catalyst morphology, operating conditions and system configurations on the local environment in the vicinity of the catalyst. In this section the specific interactions taking place between the solid catalyst, CO$_2$ reagent and liquid electrolyte are put into focus from both a theoretical and applied point of view. The influence of the local reaction environment as driven by the reaction itself is first summarized using reaction-diffusion models. The implications of these
catalyst-system interactions on limiting current density and product selectivity are then addressed through specific examples.

2.5.1 Diffusion-Reaction Modeling

Adjacent to a CO\textsubscript{2} reduction catalyst is a region of electrolyte known as the diffusion layer. In this region the concentration of CO\textsubscript{2}, hydroxide and other ions making up the electrolyte differs from that of the bulk electrolyte concentration. At the surface of the catalyst both CO\textsubscript{2} and protons are consumed as gas and liquid products are produced. The rate of these changes is directly dependent on the current density and product selectivity as shown in Figure 2-5a. Even at low current densities large changes in the local reaction environment occur, limiting most ambient pressure H-cell experiments to currents of less than 30 mA cm\textsuperscript{-2} before the CO\textsubscript{2} available for the reaction becomes fully depleted. The thickness of this diffusion layer is related to mass transport within the entire system and moderates the impact of these reaction-driven changes as illustrated in Figure 2-5b.

Figure 2-5 | Schematic illustrating the changes in CO\textsubscript{2} and pH next to a CO\textsubscript{2} reduction catalyst in a system where CO\textsubscript{2} is supplied from the bulk electrolyte. Shown are the trends in concentrations from (a) increasing CO\textsubscript{2} reduction current density and (b) varying boundary layer thicknesses as a function of mass transport.

There have been numerous papers focused on modeling the diffusion-reaction region for CO\textsubscript{2} reduction applications with the first comprehensive model developed by Gupta et al.\textsuperscript{56} In this paper the modeled electrolyte was potassium bicarbonate. This is the most commonly used electrolyte for CO\textsubscript{2} reduction applications due to its capacity as a pH buffer. It is shown by Gupta et al. that increasing the electrolyte concentration lowers the reaction-induced surface pH at the electrode which both prevents CO\textsubscript{2} from being neutralized and allows for the partial regeneration of CO\textsubscript{2} from bicarbonate, increasing the limiting CO\textsubscript{2} reduction current density. In an interesting article Chen et al. also showed the hypothetical performance gains possible if the bicarbonate-CO\textsubscript{2} equilibrium rates could be greatly enhanced, similar to the effects of carbonic anhydrase in biological systems.\textsuperscript{57}

Researchers at the Joint Center for Artificial Photosynthesis have greatly expanded on the work by Gupta et al. in several papers, adding in the effects of ion migration, salting out and polarization losses.\textsuperscript{58–61} These models allow for experimental electrode kinetics to be inputted into an electrochemical model such that voltage
vs current curves can be approximated with Nernstein losses induced at the electrode. Even further extensions to these models discuss the potential buffering effects of different cations at the electrode due to variations in cation hydrolysis. Similar to experimental results this model predicts the superior reaction kinetics of heavier cations like Cs\(^+\) over Na\(^+\) or Li\(^+\).\(^{62}\) Several researchers have also utilized these models in conjunction with experimental data to create new understanding about observed variations product selectivity.\(^8\)

While the developed CO\(_2\) reduction reaction-diffusion models have provided insights into catalyst-system interactions, several limitations exist. The primary shortfall is the difficulty in fully pairing mass transport models with an experimental system. As these models are 1-dimensional, and require the product selectivity and current density to be inputted, more complex, non-planar catalysts are modeled less accurately. Additionally all models used to date require the thickness of the mass transport layer to be prescribed. The transport thickness can be measured for a non-reacting system that is magnetically stirred,\(^{47}\) but a large number of papers indicate that product gas evolution is a larger driver of diffusion thickness than mechanical mixing.\(^{63}\) Further, product gas evolution is a function of the reaction current density implying that the diffusion layer thickness is a varying parameter rather than a fixed one. A number of researchers have addressed the effect of gas evolution on boundary layer thickness in other systems, but it has yet to incorporated specifically into CO\(_2\) reduction models where the reagent is much more limited than in the case of H\(_2\) evolution.\(^{64-66}\) Finally, although modeling of CO\(_2\) diffusion has advanced greatly in the case of catalysts fully-immersed in electrolytes (Figure 2-1 a and c), little efforts have gone into modeling the CO\(_2\) availability of catalysts deposited on gas-diffusion layers (Figure 2-1 b and d). While CO\(_2\) availability is known to be much greater due to the shorter electrolyte diffusion pathway of gas-diffusion electrodes, the dynamics of this configuration has only been explored by a couple of research groups.\(^{50,67}\)

2.5.2 Effect of the Local Reaction Environment on Catalytic Performance
A conclusion from both experimental and modeling efforts is that the local reaction environment has a significant impact on catalytic performance. The two most influential molecules affecting performance are CO\(_2\) and hydroxide as indicated in Figure 2-5. As a reaction current is induced, both the CO\(_2\) and hydroxide concentrations in the immediate electrode vicinity vary by orders of magnitude from the initial conditions and the bulk electrolyte.

Within an aqueous liquid electrolyte under ambient temperature and pressure, the solubility of CO\(_2\) is limited to 33 mM at low salt concentrations. With a modest liquid diffusion thickness next to the catalyst of 100 \(\mu\)m, CO\(_2\) reduction current densities are then limited to less than 30 mA cm\(^{-2}\) at high Faradaic Efficiencies,\(^{58,68}\) an order of magnitude lower than that needed for industrial application.\(^{31}\) While this CO\(_2\) limitation has experimentally been shown to vary slightly with electrolyte concentration, cations, electrode size, morphology, stirring speed and product selectivity, the fundamental limitation remains. As currents are increased and a reaction system becomes mass transport limited, concentration polarization losses increase making the system less efficient. The reduced availability of CO\(_2\) molecules further results in an increase in the
proportion of competing reactions, namely H₂ evolution, which lowers the target product selectivity. Products requiring a higher surface coverage of adsorbed intermediates, like multi-carbon reduction products that form via CO-CO coupling, have also been linked to higher CO₂ concentrations and CO* surface coverage.⁶⁹

The concept that CO₂ is important for CO₂ reduction is not novel or ignored in literature, however, as many authors operating in CO₂ limited régimes note that at a certain current density performance decreases due to mass transport. What is evident from literature though, is that significant gains are possible by instead operating in a local environment where the availability of CO₂ is plentiful, rather than sufficient. In a number of studies where the partial pressure of CO₂ is varied, large increases in the maximum current are seen as CO₂ is elevated as can be expected. More importantly however, even at non-limiting current densities the reduction selectivity to CO₂ products is much higher and generally achieved at much lower overpotentials. Some examples of the effect of partial pressure on current, selectivity and overpotential are shown in Figure 2-6.

Using a similar system configuration to that described in Figure 2-4g, Kim et al. varied the concentration of CO₂ behind a silver catalyst deposited on a gas-diffusion electrode (Figure 2-6a). The gas-diffusion layer allowed for CO₂ reduction to occur at feed concentrations as low as 10% but the Tafel slope for CO production and Faradaic efficiency were greatly increased at higher CO₂ partial pressures. Using a similar setup with gaseous CO₂ flowing through a gas diffusion electrode, Dufek et al. pressurized both the gas and liquid streams to 18 atm (Figure 2-6b). At atmospheric pressure CO selectivity was limited to 10% but increased to over 90% at 18.5 atm, reaching total current densities of 350 mA cm⁻² at elevated temperatures. When investigating multi-carbon products Kas et al. concluded that the increased local CO₂ concentration increased ethylene selectivities by increasing CO surface coverage, leading to further CO-CO coupling and reduced methane selectivities. This reasoning also helped to explain the increase in observed CO production as compared to lower pressures due to an increased CO desorption rate (Figure 2-6c). Lastly, in a combinatorial study testing the effects of stirring speed, temperature and pressure, Hashiba et al. found H₂ evolution to be greatly suppressed at higher pressures. While the maximum methane selectivity was not increased with pressure, current densities reached 240 mA cm⁻² without the use of gas-diffusion electrodes (Figure 2-6d). Although the number of papers utilizing the above methods to increase the quantity of CO₂ in the local reaction environment is relatively small, the benefit to the overall conversion process is shown to be significant.

Another environmental factor affecting performance is the local hydroxide concentration. As current density is increased the local pH can be quickly driven to values of 10-12 (Figure 2-5a), which can negatively impact the local concentration of CO₂. Several other papers report the impact of pH on CO₂ reduction selectivity. While this effect has been seen in formate production, the most recent example has been seen for the oxide-derived copper catalysts discussed earlier. At a pH of 7 the mixed oxidation states of the oxide-derived copper surface has similar onset potentials for C₂H₄ and CH₄. As the local pH increases, however, the onset potential of CH₄ is shifted by over 250 mV to higher overpotentials while the kinetics for C₂H₄ are slightly improved.⁷⁰,⁷¹ The high C₂H₄ selectivity of this catalyst is then a combined factor of the surface characteristics and the local
Figure 2-6 | Experimental reports highlighting the effects of CO₂ partial pressure on current, selectivity and overpotential. (a) Faradaic efficiency for CO and H₂, and partial current density of CO, and H₂ as a function of CO₂ concentration, ranging from 10 to 100% (v/v) using N₂ for dilution at four different cell potentials. N = 4 for each data point. Reprinted from [72] with permission from Elsevier. Copyright © 2015 Elsevier Ltd. (b) Impact of pressure on CO FE* at 225 mA cm⁻² at 21 °C and 60 °C. CO₂ flow rate 85 mL min⁻¹ through the gas-diffusion electrode, catholyte 0.5 M K₂SO₄. Republished with permission from [48]. Copyright 2003, The Electrochemical Society. (c) Faradaic efficiencies as a function of CO₂ pressure. FE as a function of time, pressure and electrolyte concentration (applied potential for all: -1.8 V vs. Ag/AgCl). Reproduced from [8] with permission from WILEY. Copyright © 2015 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim (d) Effect of current density on the Faradaic efficiency of H₂ (light blue circles), CH₄ (red triangles), and other products (gray squares) at 1.3 atm, 4 atm, and 9 atm. In these experiments, the stirring speed and temperature were 500 rpm and 25 °C, respectively. Reprinted with permission from [47]. Copyright © 2016 American Chemical Society.

reaction environment which can be altered by both changes in operating parameters and system configuration. Interestingly, a high enough current density then needs to be applied to the electrode to create a high local pH environment without being so high as to also deplete the CO₂ necessary for the reaction (Figure 2-5). To achieve this balance almost every promising oxide-derived copper paper uses a low buffering capacity of 0.1 M KHCO₃ rather than a more buffered electrolyte; while this may be good for C₂H₄ selectivity, it greatly compromises both current density and energetic efficiency by intentionally operating in a CO₂-strained condition.

2.6 Summary

This chapter provided an overview of topics and literature that will be further discussed and extended in this thesis. The major theme addressed in this introduction is the importance of both novel catalysts and system design in increasing the primary performance metrics of CO₂ reduction. Large improvements in efficiency and
selectivity have been made by creating increasingly nanostructured and engineered catalysts. Identical gains in selectivity and current density have been made by micromanaging the local reaction environment surrounding simple catalysts. In the few examples where the two approaches have been combined, the most promising overall result have been achieved highlighting the necessity of further research in this area.
Chapter 3.

Nanomorphology-enhanced gas-evolution intensifies CO2 reduction electrochemistry

This chapter was published as a journal article in *ACS Sustainable Chemistry and Engineering* and reprinted with permission from [3]. Copyright © 2017 American Chemical Society. The candidate was the first author in this work and played the primary role in designing the research, performing the experiments, analyzing the data, and writing the paper. Additional authors for the work include Dr. Percival J. Graham, Dr. Yuanjie Pang, Dr. Cao-Thang Dinh, Dr. Min Liu, Prof. Edward Sargent and Prof. David Sinton. Their contributions were central to the publication of this work and are gratefully acknowledged and appreciated.

3.1 Introduction

The electrochemical conversion of CO2 into fuels, both gaseous and liquid, is an emerging approach to mitigate fossil fuel based carbon emissions. Competing reactions, poor surface binding energies, low reactant solubility and electrode stability all limit system performance and are major obstacles preventing electrochemical CO2 reduction from widespread adoption.31,73,74 To advance the field two distinct approaches have been adopted in literature: 1) improving electrode kinetics, for instance through nanostructured electrodes with low activation potentials, high selectivity and high Tafel slopes; and 2) improving mass transport, such as increasing long-range CO2 flux using pressurization, flow or gas diffusion electrodes.48,55 The field has advanced greatly in improving reaction kinetics while further gains remain available in understanding and improving CO2 transport to electrodes. Additionally, as electrocatalytic kinetics improve, transport limitations become more significant and ultimately limit performance.

Recent electrocatalysts for the CO2 reduction reaction (CO2RR) report high Tafel slopes and lower activation overpotentials when converting CO2 into CO, HCOOH and multi-carbon products. In each case performance advancements are attributed to engineered surface mechanisms. These strategies range from high energy surface structures that improve CO2 surface binding energies38,39; oxide-derived materials that preferentially bind CO2/CO7,23,75; and sharp morphologies resulting in field-induced reagent concentration.14 As current is increased, however, the overpotential needed to further boost current density steadily increases due to pH gradients formed at the electrode and a decrease in the local concentration of CO2.30,76 At even higher currents, the CO2 concentration at the electrode becomes depleted due to both consumption of CO2 in the electrochemical reaction and unfavourable local pH conditions, limiting the maximum current density of CO2 conversion. This limit cannot be overcome via CO2 electrokinetics at the electrode surface. Increasing system pressure48,77 and fluid flow78 via devices are often quoted as a means to improve current density and selectivity in state-of-the-art electrodes. Understanding the mass transport dynamics at play in experimental systems is essential,
however, due to the direct influence of mass transport on observed catalyst performance. As an example the limiting current density of state-of-the-art electrodes has been experimentally shown to be enhanced by different surface morphologies (e.g. ~ 5 mA cm\(^{-2}\) for a flat Ag metallic surface\(^{15}\), ~15 mA cm\(^{-2}\) for Au-oxide nanoparticles\(^{7}\), ~55 mA cm\(^{-2}\) for Au nanoneedles\(^{14}\)). Additionally, Rosen et al. reported a shift in the limiting current from ~10 mA cm\(^{-2}\) to ~35 mA cm\(^{-2}\) when switching from Ag nanoparticles to a nanoporous Ag structure under the same testing conditions.\(^{79}\) These differences imply a significant impact of the electrode surface itself on the flux of CO\(_2\) from the bulk to the electrode, although the exact mechanisms are unclear. There is a need to better understand the complex interactions between the catalyst and the surrounding fluid such that experimental results can be better interpreted and, more importantly, future CO\(_2\) reduction systems can be designed to reach higher currents.

To gain a more in-depth understanding of catalyst/electrolyte interactions several studies have investigated the dynamics of CO\(_2\) and ion concentrations within a prescribed fluid diffusion layer at an electrode surface (~10 – 1000 µm).\(^{56,57,76,80,81}\) These studies allowed for the performance impacts of pH and CO\(_2\) gradients, electrolyte concentration and temperature to be explored, identifying that significant overpotential losses and CO\(_2\) depletion occurs at relatively low current densities. The diffusion thickness which controls the limiting current density, however, is assumed to be a fixed value independent of operating conditions and electrode morphology. In parallel, other efforts have shown that mass transport due to gas-evolution is a primary driver of the diffusion thickness with transport increasing with current density and bubble release frequency.\(^{64,65,82,83}\) Hydrogen evolution applications have subsequently utilized gas-evolution and electrode morphology to increase the physical stability of electrodes by reducing the residence time of formed hydrogen bubbles\(^{84}\) while also increasing efficiencies by increasing active area and reducing ohmic drops and hysteresis at larger currents.\(^{85–88}\) Applying these lessons to CO\(_2\) reduction applications, the morphology of a CO\(_2\) reduction catalyst can be similarly manipulated to enhance gas-evolution mass transport and increase the maximum intensity of CO\(_2\) reduction electrochemistry. By combining existing CO\(_2\) electrochemical models with gas-evolution theory and experimental observations a more complete model can be developed which accounts for the interconnected factors governing CO\(_2\) reduction, illuminating existing and future experimental results.

In short, rapid recent advancements in catalyst performance coupled with low CO\(_2\) solubility demand that transport limitations within CO\(_2\) reduction systems be better understood and addressed. Herein we combine experimental observations with a mathematical model to quantify the role that catalyst nanomorphology plays in significantly enhancing mass transport for CO\(_2\) reduction to CO and increasing the intensity at which the reaction can occur. Experimentally we visualize gas-evolution on established electrocatalyst electrode morphologies - nanoneedles, nanorods and nanoparticles - and use the resulting observations to obtain a volume-averaged gas-evolution diameter for the surface. Combined with an electrochemical model accounting for mass transport from gas-evolution we compare our predicted findings with experimental results from Au nanoneedles and a similarly selective nanoparticle catalyst, emphasizing the influence of morphology-enhanced gas-evolution on the limiting current of experimental systems. Using this new perspective we discuss
the impacts of electrode kinetics and CO₂ availability on product selectivity and partial currents as operating currents are varied. Finally, we extend our new interpretation of CO₂ reduction modelling to multi-carbon (C2) products to identify existing mass transport limited performance and suggest an alternative experimental approach for achieving both high ethylene selectivity and low current densities on a copper catalyst.

3.2 Modeling Section

To model the performance of an electrochemical CO₂ reduction reaction it is necessary to take into account the combined effects of the electrode kinetics of the catalyst and the catalyst’s interaction with the electrolyte. The electrode kinetics are modelled using the Butler-Volmer equation and experimentally obtained parameters for CO₂ reduction and hydrogen evolution (see Supplementary Information). The electrolyte/catalyst interactions are modelled as a 1-D diffusion system as discussed in the following sections.

3.2.1 Calculation of the diffusion thickness

As reactants (both CO₂ and H⁺) are consumed at a catalyst’s surface during an electrochemical reaction the concentration of molecules in the electrolyte will vary from that of the bulk. The concentration gradient is characterized by a diffusion layer adjacent to the electrode whose thickness directly correlates to the reaction’s limiting current density and polarization losses. In previous electrochemical models for CO₂ reduction the diffusion layer thickness is prescribed as a specific value independent of current density or electrode morphology. Here we approximate the thickness of the diffusion layer as a function of operating parameters, allowing it vary with current density.

In a 1-D planar system the thickness of the diffusion layer is equal to the diffusivity of the species of interest, Dᵢ, divided by the mass transfer coefficient, kₘ, present in the system:

\[ \delta_i = \frac{D_i}{k_m} \]  (3.1)

The mass transfer coefficient can be found by accounting for the combined effects of the two primary mass transfer mechanisms present in the system: convective bulk flow and bubble-induced momentum from gas-evolution.

\[ k_m = k_{conv} + k_{bubble} \]  (3.2)

Mass transfer effects for convective flow can be found using the well-known correlation for flow over a flat plate where the average mass transfer coefficient calculated from the Sherwood number is:

\[ k_{conv} = \frac{ShD_i}{L} = \frac{0.664D_i}{L} Re_L^{0.5} Sc^{0.333} \]  (3.3)
where the characteristic length, \( L \), is the length of the electrode in direction of flow. The Reynold’s number can be approximated from the stirring or flow conditions of the electrolyte.

For gas-evolution, several mechanisms contribute to the replenishment of reactant at the electrode surface including bubble growth, break-off and wake flow. A number of numerical correlations have been created to describe these mass transfer processes using a combined mathematical and empirical approach. Collectively, however, these correlations are in relative agreement as described by Vogt et al. To describe the effects of bubble break off where fluid immediately replaces the departing bubble, \( Sh_1 \), we use the Roušar correlation and to describe the combined effects of bubble growth and wake flow, \( Sh_2 \), we use Vogt’s correlation for low electrode bubble coverage (\( \Theta < 0.5 \)):

\[
Sh_1 = \frac{12}{\pi} Re_G^{0.5} Sc^{0.5} \Theta^{0.5}
\]

\[
Sh_2 = \frac{2}{\sqrt{5}} Re_G^{0.5} Sc^{0.34} \left(1 - \frac{\sqrt{2} R_a}{3 R} \Theta^{0.5}\right) (1 + \Theta)
\]

where \( \Theta \) represents the fraction of the electrode area shielded by bubbles during a bubble’s residence time and thus not available for reactions. The ratio \( R_a/R \) in Eq. 3.5 represents the ratio of inactive electrode area below a nucleated bubble as it grows. The Reynold’s and Schmidt numbers for gas-evolution are described as:

\[
Re_G = \frac{\dot{V}_{gas}}{A} \frac{d_b}{v}
\]

\[
Sc = \frac{v}{D}
\]

For gas-evolution the bubble departure diameter, \( d_b \), acts as the characteristic length scale while \( v \) is the kinematic viscosity of the electrolyte. The volume flux from gas-evolution (\( \dot{V}_{gas}/A \)) represents the effective gas velocity and is defined as:

\[
\frac{\dot{V}_{gas}}{A} = j_{evolved} \frac{RT}{n_F \rho}
\]

where pressure, \( P \), and temperature, \( T \), are generally known during experiments and the gas-evolving current, \( j_{evolved} \), is the sum of all currents which form products that depart in the gaseous phase.

As described by Vogt the mass transport effects from bubble break-off and growth/wake flow occur simultaneously and compete with one another. These can thus be combined into a single Sherwood number from which the overall mass transfer coefficient from gas-evolution can be extracted:

\[
Sh_{bubble} = (Sh_1^2 + Sh_2^2)^{0.5}
\]
\[ K_{\text{bubble}} = \frac{2h_{\text{bubble}}D_i}{d_b} \]  

For our analysis we assume that the bubble coverage, \( \theta \), is a constant 25% while \( R_s/\pi \) is assumed to be 0.75.\textsuperscript{64} It is worth noting that the mathematically derived Sherwood numbers in Eq. 3.4-3.5 assumed a flat electrode and a bubble contact angle of 90\(^\circ\). As nanostructured electrodes have a much higher electrochemically active surface area and are generally hydrophilic, the mass transfer coefficient calculated here is conservative, under-predicting most CO\(_2\) reduction electrodes due to the reduced fraction of inactive surface where bubbles contact the electrode surface.

From Eqs. 3.1-3.10 the thickness of the diffusion layer can be calculated as a function of the gas-evolving current density, bubble departure diameter, pressure and fluid flow velocity. The bubble departure diameter is an experimentally determined quantity which depends upon the morphology and wettability of a catalyst's surface.

3.2.2 Numerical modeling of the diffusion layer

With the diffusion layer thickness calculated as a function of operating conditions, the concentrations of reactants within the diffusion layer can be approximated using the Nernst-Planck equation.\textsuperscript{56,76,80} Here we utilize a similar approach to Gupta et al. assuming that the bulk electrolyte remains saturated with CO\(_2\) during the reaction and the effects of migration are negligible.

We first account for the chemical equilibrium formed between CO\(_2\), HCO\(_3\)^-\(,\ CO_3^{2-}\), OH\(^-\) and H\(^+\) in an aqueous solution governed by the following equations:

\begin{align*}
CO_2(aq) & \rightleftharpoons CO_2(g) \\
CO_2(aq) + OH^- & \rightleftharpoons HC\text{O}_3^- \\
HC\text{O}_3^- + OH^- & \rightleftharpoons CO_3^{2-} + H_2O \\
H_2O & \rightleftharpoons H^+ + OH^- 
\end{align*}

whose respective equilibrium constants \( K_0, K_1, K_2 \) and \( K_w \) are determined as functions of temperature and salinity as described in the Supplemental Information. From these equations the bulk concentrations of each component can be found for different electrolyte concentrations, temperatures and operating pressures. The “salting out” effect of CO\(_2\) due to the addition of NaHCO\(_3\) and KHCO\(_3\) is also accounted for as described by Eqs. (S3.5)-(S3.7).

Conservation of mass can then be applied within the diffusion layer bounded by the catalyst surface \((x = 0)\) and the bulk electrolyte \((x = \delta)\) resulting in the following governing equations\textsuperscript{56}: 
\[
\frac{\partial [CO_2]}{\partial t} = D_{CO_2} \frac{\partial^2 [CO_2]}{\partial x^2} - [CO_2][OH^-]k_{1f} + [HCO_3^-]k_{1r} \tag{3.15}
\]

\[
\frac{\partial [HCO_3^-]}{\partial t} = D_{HC} \frac{\partial^2 [HCO_3^-]}{\partial x^2} + [CO_2][OH^-]k_{1f} - [HCO_3^-][OH^-]k_{1r} - [HCO_3^-][OH^-]k_{2f} + [CO_3^{2-}]k_{2r} \tag{3.16}
\]

\[
\frac{\partial [CO_3^{2-}]}{\partial t} = D_{CO_3^{2-}} \frac{\partial^2 [CO_3^{2-}]}{\partial x^2} + [HCO_3^-][OH^-]k_{2f} - [CO_3^{2-}]k_{2r} \tag{3.17}
\]

\[
\frac{\partial [OH^-]}{\partial t} = D_{OH^-} \frac{\partial^2 [OH^-]}{\partial x^2} - [CO_2][OH^-]k_{1f} + [HCO_3^-]k_{1r} - [HCO_3^-][OH^-]k_{2f} + [CO_3^{2-}]k_{2r} \tag{3.18}
\]

with the diffusion coefficients, \(D_i\), and equilibrium rate constants (\(k_{1f}, k_{1r}, k_{2f}, k_{2r}\)) found in Supplementary Information. At the catalyst surface the flux of \(CO_2\) and \(OH^-\) are proportional to the \(CO_2\) reduction current density and total current density, respectively. At the edge of the Nernst diffusion layer the concentrations of each species equal the bulk concentrations as determined from the equilibrium expressions in Eqs. 3.11-3.14. The concentration of each species in diffusion layer can then be solved by prescribing a current density and Faradaic efficiency.

### 3.2.3 Modelling electrochemical \(CO_2\) reduction

From the steady-state concentrations of \(CO_2\) and \(OH^-\) at the catalyst surface found using Eqs. 3.11-3.18 the polarization overpotentials resulting from pH gradients and the depletion of \(CO_2\) reactant are post-calculated as follows:

\[
\phi_{PH} = \frac{2.303RT}{F} \left( \log ([OH^-]_{x=\delta}) - \log ([OH^-]_{x=0}) \right) \tag{3.19}
\]

\[
\phi_{CO_2} = \frac{RT}{nF} \log \left( \frac{[CO_2]_{x=\delta}}{[CO_2]_{x=0}} \right) \tag{3.20}
\]

where \(R\) is the universal gas constant, \(F\) is Faraday’s constant and \(n\) is the number of electrons required for the \(CO_2\) reduction reaction. On the gold catalyst used in this paper only \(CO_2\) reduction to CO and hydrogen evolution are assumed to take place which are both two electron processes:

\[
2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{3.21}
\]

\[
CO_2(aq) + H_2O + 2e^- \rightarrow CO + 2OH^- \tag{3.22}
\]

The overpotential losses can then be added to the previously obtained Butler-Volmer curves for \(CO_2\) reduction to CO and hydrogen evolution to predict the voltage vs. current curve for the cathodic reaction.
During the reaction both CO and H\textsubscript{2} evolution are present with both contributing to the evolved gas in Eq. 8 and subsequently the diffusion thickness and polarization losses. Modelling the electrochemical reaction from the Tafel curves without prescribing a Faradaic efficiency then requires an iterative process as the polarization losses are post-calculated and the effects of CO\textsubscript{2} depletion only affect the CO\textsubscript{2} evolution reaction. To that end an initial Faradaic efficiency is assumed and the simulation run to gain an initial estimation of the polarization losses. From the resulting overpotentials a new Faradic efficiency is calculated and the simulation is re-run until the iterated value converges. At convergence the applied electrode potentials for CO\textsubscript{2} reduction and H\textsubscript{2} evolution are equal and the partial current densities sum to the prescribed total. Finally, the limiting current density for CO\textsubscript{2}RR is determined to be the effective current density where the concentration of CO\textsubscript{2} at the electrode surface is equal to the rate at which it is generated by bicarbonate equilibrium.

### 3.3 Results and Discussion

#### 3.3.1 Influence of gas-evolution on mass transport and CO\textsubscript{2} reduction intensity

Mass transport in electrochemical CO\textsubscript{2} reduction systems is imperative given the low solubility of CO\textsubscript{2} in aqueous systems and the large increase in currents needed to reach industrially relevant currents. Within aqueous electrochemical systems gas-evolution is known to be a primary driver of transport but depends on factors such as current density, bubble dynamics and wettability among others. Here we utilize mass transfer relations for gas-evolution and convective flow to estimate an effective diffusion layer thickness (Nernst diffusion layer) which can be used in a broader electrochemical CO\textsubscript{2} reduction model for predicting CO\textsubscript{2} reduction performance.

Using Eqs. 3.1-3.10 we calculate the expected diffusion thickness for various monodisperse bubble departure diameters and currents from gas products (gas-evolving currents) as seen in Figure 3-1a. Since most aqueous systems are stirred, the approximated diffusion layer for a stirred beaker at ~500 rpm is also shown.
assuming a local flow velocity of $1 \text{ cm s}^{-1}$ and electrode width of $0.5 \text{ cm}$. Figure 3-1a implies that the effective mass transport at the electrode due to bubble growth and departure is much greater than a moderately stirred beaker, particularly at current densities $> 10 \text{ mA cm}^{-2}$ where the diffusion thickness for even large bubbles is half that of a stirred beaker alone. As departure diameter is decreased the number and frequency of bubbles on a catalyst’s surface increases resulting in a boost in mass transport. An increase in the gas-evolving current further decreases the diffusion thickness as observed experimentally elsewhere. 

Previous CO$_2$ reduction models have utilized a fixed diffusion layer rather than accounting for the large variability that occurs as current density and bubble departure diameters are altered.

The effects of altering the bulk CO$_2$ concentration are observed in Figure 3-1b by varying the total and partial pressure of CO$_2$ assuming an electrode selectivity of 100% towards CO. While all three curves are proportional the absolute current densities are very different owing to the increased dissolved CO$_2$ at higher pressures. Observing the 1 atm curve we can see that overcoming the commonly seen limiting currents of $\sim 20 \text{ mA cm}^{-2}$ requires diffusion thicknesses of less than 50µm. Reaching these thicknesses would then require either a significant increase in forced convection or enhanced product release from the catalyst surface. Figure 3-1b also shows that pressure and mass transport have an additive effect on CO$_2$ availability and hence the maximum CO$_2$ reduction intensity while highlighting the need for pure CO$_2$ inputs even in high mass transport cases.

Given the importance of selectivity on performance, the impacts of Faradaic efficiency are also analyzed for a catalyst capable of producing CO and H$_2$. As shown in Figure 3-1c as H$_2$ evolution is increased the maximum intensity for CO production subsequently increases following from the increase in evolved gases. The relative impact of bubble diameters also indicates that only small bubbles diameters are expected to greatly increase the absolute CO$_2$ reaction intensity.

Although mass transport from gas-evolution has been studied both experimentally and numerically, several limitations exist when applying the derived relations to experimental catalysts. For instance the Sherwood numbers in Eqs. 3.4-3.5 generally assume a horizontal, flat electrode in a stagnant reactor. Directionality and convective flow both effect gas-evolution dynamics but variations versus stagnant conditions are generally considered minimal in low flow conditions ($< 0.1 \text{ m s}^{-1}$) versus the overall transport mechanism. Electrode bubble coverage is another assumption which factors into both the derivation and use of Eqs. 3.4-3.5 and varies between 0.1 and 0.3 for the current densities of interest. While mass transport from gas-evolution is greatly reduced for lower values of bubble coverage Vogt found the approximation to under-predict experimental findings as bubble coverage tends towards zero. These combined factors reflect some uncertainty but the overall calculated magnitude of the mass transfer coefficient remains similar to that predicted in Figure 1 for various operating conditions.
3.3.2 Nanomorphology-enhanced mass transport

Nanomorphology has been effective in improving electrode kinetics and reducing the overpotentials needed to convert CO\textsubscript{2} at low currents via a number of surface based approaches. To maintain record efficiency and selectivity at higher currents, however, the long-range flux of CO\textsubscript{2} to the electrode must be increased. As the reduction of CO\textsubscript{2} into CO necessarily results in gas-evolution – which in turn promotes dissolved CO\textsubscript{2} flux – enhancement of this phenomenon by manipulating nanomorphology provides a secondary means for the catalyst surface to influence reaction rates.

To assess the influence of nanomorphology on mass transport we first visualized CO gas-evolution using a dark field microscope for three different electrode morphologies shown in Figure 3-2a-c: Au nanoneedles, nanorods and nanoparticles. The nanoneedles had a noticeably smaller bubble departure diameter with a mean diameter of 23 \( \mu \)m based upon the volume-averaged bubble diameter (Figure 3-2d and Supplementary Video). Under otherwise similar conditions, bubbles on the nanorod and nanoparticle surfaces had average release diameters of 31 \( \mu \)m and 97 \( \mu \)m, respectively (Supplementary Video). In the case of nanoneedles and nanorods a large number of small bubble trains emanated from the surface with some larger bubbles seen in the nanorod case which increased the overall diameter. For the nanoparticles, however, bubbles resided on the surface for much longer times allowing for growth via diffusion. Exposed carbon paper in areas where the catalyst was removed showed the greatest bubble release diameters as expected from the reduced wettability versus gold. Through their structure, nanoneedles reduce the bubble contact diameter decreasing the forces adhering it to
the surface, and the increased agitation promotes bubble detachment. The effervescent generation of small bubbles from the nanoneedles (Figure 3-2) provides improved transport as quantified by the small diffusion thickness (Figure 3-1) and intensified CO₂ reduction. While the volume-averaged bubble diameter can be used in Eqs. 3.4-3.10 to calculate an effective diffusion layer thickness it is accurate only for monodisperse or narrow bubble distribution. For bimodal or flatter distributions a collective mass transfer coefficient should instead be calculated using a weighted average of the mass transfer coefficients of bubble sub-populations. As detailed in the Supporting Information, including measured bubble size distributions resulted in variations of only 5% in terms of diffusion thickness for nanoneedles and particles (details in the Supporting Information).

Using our varying-diffusion-layer electrochemical model (Eqs. 3.1-3.22), we predict the performance of Au nanoneedles and a similarly selective nanoparticle CO₂RR catalyst with a flatter morphology. We chose Au-oxide nanoparticles as an appropriate fair point of comparison due to the similar product, high selectivity, good Tafel slope and defined microstructure. The electrode kinetics of each morphology are separated from transport related effects by using the experimentally determined Tafel slopes and exchange current densities (see

Figure 3-3 | Comparison between predicted and experimental steady-state current versus voltage curves for assumed bubble departure diameters of 20, 50 and 100 µm highlighting the impact of morphology on limiting current density and polarization losses. a) Performance of Au nanoneedles in 0.5 M KHCO₃, b) Performance of Au-oxide nanoparticles in 0.5 M NaHCO₃.
Inputting the system operating conditions into our 1D model, we can then simulate the expected overpotentials and polarization losses for a range of current densities and average bubble size in the system (see Modelling Section for details). The Faradaic efficiency of CO and H₂ evolution are calculated in the model by accounting for the combined effects of the electrode kinetics, electrolyte conditions and polarization losses. Figure 3-3a and b show the predicted CO partial current density versus overpotential for three different bubble departure diameters with the experimental results overlaid. Also included is the CO evolution Tafel curve (no losses) for reference. For the Au-oxide nanoparticles an inputted mean bubble diameter of 100 µm in our simulation best matched the experimental limiting current density of 15 mA cm⁻², comparing well with our experimentally observed bubble diameters on Au nanoparticles (Figure 3-2d) and similar to that reported elsewhere on a Pt catalyst. For nanoneedles, the curve simulated using a 20 µm bubble diameter was needed to boost the limiting current to > 50 mA cm⁻², giving a similar result to the observed bubble diameter from Figure 3-2d. In both cases the partial CO current slowly increases after temporarily plateauing as hydrogen evolution provides the further mass transport needed to supply additional CO₂.

Together, these results show the importance of morphology-dependent gas-evolution dynamics on experimental CO₂ reduction performance and their importance in modelling electrochemical systems.

In Figure 3-4 we illustrate how electrode nanomorphology can increase long-range transport by influencing gas-evolution, resulting in a four-fold increase in limiting current density of CO production for nanoneedles over nanoparticles. Similar to what has been found in heat transfer analyses along a surface, the enhanced mass transport stems from a reduction in the departure diameter of bubbles from the electrode surface. Designing electrodes that provide this level of mixing can then be more efficient and potentially forego high-velocity forced fluid flow that would otherwise be necessary to provide sufficient CO₂ to a surface. Further pairing the above passive approach for increasing current density with a pressurized system a high current density and product purity system may also be possible as an alternative to gas diffusion electrodes which limit product purity in the effluent stream and have poorer catalyst flexibility.

Figure 3-4 | a) Electrochemical cell for CO₂ reduction showing either a flatter or a sharper nanostructured electrode (scale bar is 20 µm). b) Schematic depicting the influence of electrode morphology on bubble departure diameter and the resulting thickness of the diffusion boundary layer. Fresh electrolyte fills the region previously occupied by nucleated bubbles on the electrode’s surface.
From both Figure 3-3a and b it is also possible to see the effect that mass transport has on polarization losses in the system, particularly as the current approaches the limiting value. These losses become inevitable as CO$_2$ concentration decreases and supports the findings of Chen et al.$^{57}$ regarding the importance of operating electrochemical CO$_2$ reduction cells at 80 – 90% of their maximum current density. It is important to note that differences in electrode morphology in turn result in large differences in the overall electrochemically active surface area (ECSA) which impacts both electrode kinetics and the current density normalized by the ECSA.$^{14}$

In addressing the limiting CO2RR current density of the electrode, however, the geometric current density is of primary importance as the flux of CO$_2$ to the catalyst is dependent on the planar area of the electrode rather than the specific surface area of catalyst.

Further optimization of electrode morphology for mass transport purposes is also possible as exhibited by bubble trains as small as 10 µm in portions of the nanoneedle and nanorods electrodes (Figure 3-2g). Facilitating bubble departure could be accomplished, for instance, using a more organized needle structure or even including non-participating structures which promote bubble nucleation and detachment. Increasing electrode wettability would achieve a similar result but changes to the surface would simultaneously impact electrode kinetics. Finally, adding a non-ionic surfactant to the liquid at close to the critical micelle concentration can lower the surface tension of water from $\sim$72 mN m$^{-1}$ closer to $\sim$33 mN m$^{-1}$, enough to aid in the release of bubbles from the surface at a smaller diameters.$^{95–97}$ As confirmation, by adding 0.8 times the CMC of Triton X-100 to the electrolyte we were able to reduce the residence time of bubbles by over half with an average departure diameter from the catalyst surface of 40 µm (Figure 3-7 and Supplementary Video), indicating another route to higher CO$_2$ mass transport via gas evolution.

### 3.3.3 Effect of CO2 availability on CO2 reduction selectivity

Selectivity towards specific CO$_2$ reduction products (CO, HCOOH, C$_2$H$_4$, etc.) over H$_2$ evolution has been the central subject of numerous theoretical$^{25,98,99}$ and experimental$^{35,100}$ works. These efforts explore direct conversion kinetics but leave out CO$_2$ availability as a driver of CO$_2$RR selectivity, and the corresponding impact of mass transport as current increases.

Using nanoneedles, we identify the contributing factors of CO$_2$ availability towards selectivity. From the reported Tafel slope the ideal CO$_2$RR curve for the FIRC needles is shown in Figure 3-5a. Also using the experimental results, we extract the HER (Hydrogen Evolution Reaction) Tafel curve and plot within the same figure (see Modelling Section). Alongside these ideal curves are the predicted polarization losses from pH gradients and CO$_2$ depletion (denoted by $\phi$) assuming a volume averaged bubble departure diameter of 20 µm. As current density increases these losses steadily increase proportional to the OH$^-$ and CO$_2$ concentration at the electrode. It is important to note that the overpotential due to a pH gradient ($\phi_{pH}$) at the electrode surface is a function of the total current density and affects both reaction products. The total and partial current densities for CO and H$_2$ are then plotted in Figure 3-5b next to experimental data. Finally the selectivity towards CO as
well as the electrode CO$_2$ concentration for a range of overpotentials are plotted in Figure 3-5c, agreeing well with the Au needle experimental data.$^{14}$

Three interesting conclusions can be made from the plots in Figure 3-5. Firstly, as long as the Tafel slope of CO$_2$RR is greater than that of HER and the activation overpotential is lower, the high Faradaic efficiency of CO

![Butler-Volmer curves for CO$_2$RR and HER for gold nanoneedles with CO$_2$ saturated 0.5 KHCO$_3$. Inset shows more favorable HER kinetics at low overpotentials. Dashed lines indicate the addition of polarization overpotentials ($\phi$) for a 20 µm bubble departure diameter. b) Partial and total simulated current densities. c) Selectivity and CO$_2$ availability of the catalyst for CO$_2$RR using the loss adjusted CO$_2$RR and HER curves in a). Red experimental data is from Au nanoneedles$^{14}$ in 0.5 M KHCO$_3$.](image)
production is maintained provided ample CO$_2$ is supplied to the electrode. Concentration polarization losses are then kept small until $\sim$45 mA cm$^{-2}$ where selectivity slowly begins to decrease. Secondly, as H$_2$ evolution increases at higher overpotentials the thickness of the diffusion layer continues to decrease due to additional gas generation and mass transport, as seen in Figure 3-1a and Figure 3-8. The partial current density of CO then sees a small rise at higher voltages instead of plateauing, albeit at lower FE. Without transport increasing with gas-evolution the absolute CO partial current would remain constant after the limiting current. Finally, the poor CO Faradaic efficiency below 0.2 V is the result of more favourable H$_2$ evolution even though H$_2$ evolution kinetics are worse at higher overpotentials (highlighted inset in Figure 3-5a). This widely seen trend is due to the 0.10 V lower activation potential for H$_2$ evolution ($E^{\circ}_{H2} = 0$ V versus $E^{\circ}_{CO2} = -0.10$ V RHE).

The analysis here can be applied to any mixture of gas and liquid CO$_2$RR products and can be used to determine losses and the limiting current density even when a large number of products are present (eg. on a copper electrode). The greatest CO$_2$RR current densities will be seen at higher volumes and ratios of gas products as described by Figure 1a and b. Systems with purely liquid CO$_2$RR products have shown lower current densities than gaseous products (eg 5 – 10 mA cm$^{-2}$ for formate), implying that performance suffers in the absence of bubble-induced transport.

### 3.3.4 High intensity production of C2 products

Here we extend the experiment-validated idea of a variable diffusion layer and current-dependent mass transport to C2 reduction products in an effort guide future experiments towards both high product selectivity and current density. To date both experimental and modelling efforts have shown the importance of a high local electrode pH on ethylene (C$_2$H$_4$) selectivity due to the pH-dependent pathway for methane production allowing for high Faradaic efficiencies to be achieved on copper electrodes using low buffering capacities (0.1 M) and increased system pressures.$^{8,41,101}$ Operating at too high a pH, however, shifts carbonate equilibrium away from CO$_2$. As a consequence, while lower electrolyte buffering capacities results in high ethylene selectivities the ethylene partial current is constrained at higher currents due to a shortage of CO$_2$. Rather than operating at a high local pH the local environment of the catalyst should be regulated to achieve both the desired ethylene selectivity and current density. In Figure 6 we briefly show the sensitivity of common operating conditions (buffering, pressure, mass transport) on the local pH and CO$_2$ availability versus a standard operating condition (0.1 M KHCO$_3$, 1 atm) using our model accounting for current dependent mass transport.

For simplicity we assume a Faradaic Efficiency distribution of 40% ethylene, 40% hydrogen and 20% liquid HCOOH in all cases though the exact ratio of methane/ethylene would change with current and pH. A bubble departure diameter of 100 µm is assumed to represent a typical electrode surface while a baseline convective flow from stirring is also assumed as before (500 rpm, Figure 3-1a). The effects of buffering capacity and pressure on CO$_2$ solubility and carbonate equilibrium are again taken into account in the Supporting Information. Termination of a line indicates the point where no CO$_2$ is present at the catalyst surface which in all cases happened close to a pH of 12.
Observing the curves in Figure 3-6 the relative impacts of changing each operating condition on the maximum current density and pH can be seen. First, systems with low buffering capacity will reach high pH values at overall lower current densities allowing for higher ethylene/methane ratios to be produced at low currents. The penalty with this approach, however, is the CO\textsubscript{2} at the electrode being depleted at modest currents of ~ 40 mA cm\textsuperscript{-2}. The maximum ethylene partial current is then limited to less than 16 mA cm\textsuperscript{-2} as has been obtained experimentally\textsuperscript{8,41}. As the buffer is increased to 0.2 M the current needed to reach higher local pH increases, implying that more methane will be produced at lower currents. Higher total currents, however, are possible as compared to the more weakly buffered case. When the electrolyte concentration is brought back to 0.1 M and the pressure increased to 3 atm a similar initial trend exists as in the 1 atm case. Due to the increased CO\textsubscript{2} concentration at higher pressures, however, the system remains buffered and is allowed to reach total currents of over 65 mA cm\textsuperscript{-2} before depleting all available CO\textsubscript{2}. It is worth noting that the increase in current over the 1 atm case is only 25 mA cm\textsuperscript{-2} showing the necessity of either further buffering or mass transport to ensure that the 3-fold larger initial CO\textsubscript{2} concentration is fully-utilized for ethylene production. Finally we see that in the case of enhanced mass transport from a smaller bubble diameter of 20 µm, maximum currents of over 100 mA cm\textsuperscript{-2} are possible even at a low electrolyte concentrations. Each of the proposed approaches is a demonstration of how higher ethylene partial currents can be reached by preventing the local electrode pH from getting so high that CO\textsubscript{2} is lost to a shift in the carbonate equilibrium. Controlling pH with sufficient combinations of electrolyte, pressure and mass transport then provides an avenue to both high ethylene selectivity and current density. These results highlight the importance of combining modelling and experimental efforts to ensure that the best operating and testing conditions are identified to maximize performance.

Figure 3-6 | Local electrode pH as a function of current density for various electrolyte KHCO\textsubscript{3} concentrations, pressures and bubble departure diameters. Selectivity fixed as 40 % C\textsubscript{2}H\textsubscript{4}, 40 % H\textsubscript{2} and 20 % HCOOH. The termination of a line indicates that CO\textsubscript{2} has been fully depleted.
3.4 Conclusions

Widespread application of CO₂ reduction will necessitate high current densities and progress in both electrode kinetics and mass transport. These are linked by the low solubility of CO₂ in aqueous media and the importance of process conditions on measured performance. In addition to influencing reaction rates and local reactant concentration, we show that the morphology of nanostructured electrodes can also enhance long-range CO₂ transport via their influence on gas-evolution, effectively extending the reach of the nanostructure into solution.

This is supported by an electrochemical model which deviates from previous CO₂RR efforts with the inclusion of bubble-induced mass transport via a variable diffusion layer thickness. This relatively straightforward approach replicated trends observed experimentally, most notably differences in limiting currents achieved with different electrode morphologies. A more complete understanding of the transport mechanisms affecting the selectivity and current densities of experimental electrodes and their results is then enabled as compared to previous trends. Application to gas, liquid or combinations of products can help to guide experiments towards more promising operating conditions as well as interpreting existing results. The complexity of the model would need further enhancement for scenarios where factors such as surface poisoning affect product composition but could be incorporated into the underlying electrode kinetics. One instance of this involves CO surface poisoning which can either promote or delay hydrogen evolution at lower voltages.

Collectively, this work illustrates how electrode morphologies influence not only short-range reaction and concentration effects but long-range CO₂ transport, and provides a framework for quantifying the impacts of operating parameters and electrode kinetics on product selectivity and efficiency.

3.5 Supplementary Information

3.5.1 Butler-Volmer Equations

The electrode kinetics of the carbon monoxide and hydrogen evolution reactions are modelled using the Butler-Volmer equation. For comparisons to experimental data the charge transfer coefficient (α, c,i) and exchange current densities (i₀,i) are extracted from the experimentally obtained Tafel slopes for each reaction and inserted into the following two equations to determine the current as a function of applied potential.

\[ i_{c,H_2} = i_{0,H_2} \exp \left( \frac{2α_{c,H_2}F}{RT} (V_{app} - E_{0,H_2}) \right) \]  \hspace{1cm} (3.51)

\[ i_{c,CO_2} = i_{0,H_2} \exp \left( \frac{2α_{c,CO_2}F}{RT} (V_{app} - E_{0,CO_2}) \right) \]  \hspace{1cm} (3.52)

The extracted electrode kinetics from Liu et al. and Chen et al. used in the manuscript are seen below in Table 3-1. In both cases the experimental Tafel slope for CO production was reported and the exchange current density found by fitting the Butler-Volmer equation to the experimental data using the reported electrochemically active surface area to scale the relation in the case of the Au nanoneedles. The hydrogen evolution kinetics were similarly extracted by fitting the hydrogen partial current densities at low current
densities (< 1 mA cm$^{-2}$). Use of these parameters helps to separately extract mass transport related performance from that of electrode kinetics.

Table 3-1 | Experimental data for the CO2RR and HER reaction kinetics

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Reaction</th>
<th>Tafel Slope (mV dec$^{-1}$)</th>
<th>$E_{0,i}$ (V vs RHE)</th>
<th>$i_{0,i}$ (A m$^{-2}$)</th>
<th>$\alpha_{cl}$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au Nanoneedles$^{34}$</td>
<td>CO Evolution</td>
<td>42</td>
<td>-0.10</td>
<td>0.0094</td>
<td>0.6115</td>
</tr>
<tr>
<td></td>
<td>H$_2$ Evolution</td>
<td>110</td>
<td>0</td>
<td>0.026</td>
<td>0.2335</td>
</tr>
<tr>
<td>Au-oxide Nanoparticles$^{7}$</td>
<td>CO Evolution</td>
<td>56</td>
<td>-0.10</td>
<td>0.014</td>
<td>0.4586</td>
</tr>
<tr>
<td></td>
<td>H$_2$ Evolution</td>
<td>110</td>
<td>0</td>
<td>0.0078</td>
<td>0.2335</td>
</tr>
</tbody>
</table>

3.5.2 CO$_2$ Solubility in an Electrolyte Solution

Assuming CO$_2$ acts as an ideal gas the solubility of CO$_2$ in pure water can be found using Henry’s Law:

$$[C_{O_2}]_{aq,0} = K_0[C_{O_2}]_g$$  \hspace{1cm} (3.53)

where the coefficient, $K_0$, for CO$_2$ can be found as a function of temperature$^{103}$ as:

$$\ln(K_0) = 93.4517 \left( \frac{100}{T} \right) - 60.2409 + 23.3585 \ln \left( \frac{T}{100} \right)$$  \hspace{1cm} (3.54)

In an electrolytic salt solution, however, the solubility of CO$_2$ will be reduced versus that of a pure water solution due to the “salting out” effect as described by the Sechenov Equation$^{104}$:

$$\log \left( \frac{[C_{O_2}]_{aq}}{[C_{O_2}]_{aq,0}} \right) = K_S C_S$$  \hspace{1cm} (3.55)

where $K_S$ represents the Sechenov constant and $C_S$ is the molar concentration of the electrolyte solution. The Sechenov constant is a function of the specific ions in solution as well as the dissolved gas, in this case CO$_2$. Using the work presented by Weisenberger et al. the effects of common cations (Na$^+$, K$^+$, Li$^+$, Rb$^+$, Cs$^+$) and anions (HCO$_3^-$ and CO$_3^{2-}$) on CO$_2$ solubility can be found using the following sets of equations and the specific parameters for each component as seen in Table 3-2.

$$K_S = \Sigma (h_{ion} + h_G)$$  \hspace{1cm} (3.56)

$$h_G = h_{G,0} + h_T (T - 298.15)$$  \hspace{1cm} (3.57)

Table 3-2 | Parameters used to find the Sechenov constant in NaHCO$_3$ and KHCO$_3$ solutions

<table>
<thead>
<tr>
<th>Ion</th>
<th>$h_{ion}$</th>
</tr>
</thead>
</table>
As stated in the main text the reduction in CO$_2$ solubility in a 0.5 M NaHCO$_3$ solution versus pure water at 298 K is 18.4% using Eqs. S5-S7, which is non-negligible.

3.5.3 Carbonate Equilibrium Constants

In an aqueous system CO$_2$, HCO$_3^-$, CO$_3^{2-}$, OH$^-$ and H$^+$ form an equilibrium in solution which tends towards carbonate in alkaline solutions, bicarbonate in neutral solutions and CO$_2$ in acidic solutions as described by Eqs. 3.11-3.14 in the main text. We have ignored the effects of H$_2$CO$_3$ due the small concentration versus dissolved CO$_2$.

Miller et al.\textsuperscript{105} described the equilibrium constants for the two bicarbonate reactions (Eqs. 3.12 and 3.13) as a function of temperature and salinity where $K_1^*$ and $K_2^*$ are defined as:

\[
K_1^* = \frac{[\text{HCO}_3^-][\text{H}^*]}{[\text{CO}_2]} \quad (3.58)
\]

\[
K_2^* = \frac{[\text{H}^*][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (3.59)
\]

The logarithmic equilibrium constants are then described by Eqs. S10-S13:

\[
pK_{101}^* = pK_{01}^* + 13.419 \cdot S^{0.5} + 0.0331 \cdot S - 5.33 \times 10^{-5} \cdot S^2 - \left(\frac{530.123 \cdot S^{0.5} + 6.103 \cdot S}{T}\right) - 2.070 \cdot S^{0.5} \ln(T) \quad (3.510)
\]

\[
pK_{01}^* = -126.340 + \frac{5320.813}{T} + 19.5682 \ln(T) \quad (3.511)
\]

\[
pK_{202}^* = pK_{02}^* + 21.089 \cdot S^{0.5} + 0.125 \cdot S - 3.687 \times 10^{-4} \cdot S^2 - \left(\frac{772.483 \cdot S^{0.5} + 20.051 \cdot S}{T}\right) - 3.334 \cdot S^{0.5} \ln(T) \quad (3.512)
\]
\[ pK_{02}^* = -90.183 + \frac{5143.692}{T} + 14.613 \ln(T) \] (3.S13)

In our system we use the equivalent OH\(^-\) equilibrium where \( K_1 \) and \( K_2 \) can then be defined as:

\[ K_1 = \frac{[\text{HCO}_3^-]}{[\text{OH}^-][\text{CO}_2]} = \frac{K_1^*}{K_w} \]  (3.S14)

\[ K_2 = \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-][\text{OH}^-]} = \frac{K_2^*}{K_w} \]  (3.S15)

with the water dissociation constant is defined in Eq. S16 assuming a constant value of \( 1 \times 10^{-14} \):

\[ K_w = [H^+][OH^-] = 1 \times 10^{-14} \]  (3.S16)

Finally, in Eqs. S17-18 the salinity is calculated as a function of the electrolyte’s ionic strength:

\[ I = 0.5 \sum_{i=1}^{n} c_i z_i^2 \]  (3.S17)

\[ S = 1000 \frac{I}{19.92 + 1.0049 I} \]  (3.S18)

From the above set of equations the bulk concentrations of all components in a bicarbonate buffer are found. The forward and backward reaction rates used within the diffusion layer governing equations can also be found and for a 0.5 M solution at 298 K are reported below in Table 3.3.

Table 3.3 | Reaction rate constants for bicarbonate equilibrium at 0.5 M electrolyte concentrations and 298 K

<table>
<thead>
<tr>
<th>Reaction Constants</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_{1f} )</td>
<td>2.23 \times 10^3</td>
</tr>
<tr>
<td>( k_{1r} )</td>
<td>1.72 \times 10^{-5}</td>
</tr>
<tr>
<td>( k_{2f} )</td>
<td>6 \times 10^9</td>
</tr>
<tr>
<td>( k_{2r} )</td>
<td>7.06 \times 10^4</td>
</tr>
</tbody>
</table>

3.5.4 Measurement of bubble release diameters

3.5.4.1 Experimental setup

To characterize the bubble release diameters from electrode surfaces with different nanomorphologies, the electrochemical operation of several Au nanostructures were observed under a dark field microscope. The Au electrodes were positioned within a petri dish containing 0.5 M KHCO\(_3\) directly below an upright microscope which also contained platinum foil which functioned as an anode and a Ag/AgCl reference electrode. The electrode was operated in a slightly inclined position to visualize individual bubbles being released from the surface. A fixed voltage was then applied between the anode and cathode causing the nucleation and release of product gases on the electrode’s surface which could then be recorded using the microscope camera and
subsequently measured afterwards. The Au nanostructures (nanoparticles, nanorods and nanoneedles) used were deposited on carbon paper substrates as described by Min et al. Specific differences in release diameters due to electrode orientation and coalescence are outside the scope of this study and readers are directed elsewhere for more in-depth experimental and theoretical studies. Finally, due to the needed stability to visualize bubble formation and release, the electrolyte was not stirred during operation.

3.5.4.2 Measurement

Using videos obtained during gas evolution the diameter of bubbles released from the electrode surface were measured using ImageJ software. Bubbles that did not originate in the frame were not included in our counting while coalescence from bubbles rising from below were also excluded due to their unknown growth since initial release. In the case of constant bubble trains an average bubble size was discerned from the first five bubbles following which a counter was used to determine the overall number of bubbles released in a given timeframe. Using this criteria the bubble departure diameters for nanoneedle, nanorods and nanoparticle surfaces were determined using the videos taken using the microscope.

From the distribution of diameters the volume weighted bubble diameter was extracted and can be used as the average bubble release diameter in our simulation. Weighting according to volume is needed as the product gas volume is proportional to current density. The volume weighted diameter is subsequently larger than that of the average measured. For the nanoneedles, nanorods and nanoparticles measured the volume weighted average diameters were then 23, 31 and 97 µm using the data in Figure 3-2d.

For a more accurate representation of mass transport effects, particularly for polydisperse bubble distributions, the mass transport coefficient can be calculated by weighting the effects of several sub-populations (subscripted by $i$) by their contribution to the total volume of evolved gases. Using this approach Eqs. 9-10 from the manuscript then become:

$$Sh_{\text{bubble},i} = Sh_{\text{bubble}}(d_i) = \left(Sh_{1,i}^2 + Sh_{2,i}^2 \right)^{0.5}$$

$$k_{\text{bubble}} = \frac{D_{CO}}{\sum \frac{V_i}{V_t} \frac{Sh_{\text{bubble},i}}{d_i}}$$

where $V_i/V_t$ is found from the experimental distribution. Using sub-populations of 5 µm increments and the data in Figure 2g the calculated mass transport coefficient using the two above approaches varies by less than 5% in the case of nanoneedles and nanoparticles. For the nanorods, however, the weighted sub-population approach predicts a 10-20% lower mass transport coefficient depending on the chosen current density displaying the need for the weighted approach in the case of bimodal distributions.
Figure 3-7 | Comparative bubble departure diameters for Au nanoparticles on a carbon paper substrate a) without surfactant and b) with Triton X-100 surfactant at 0.8 CMC.

Figure 3-8 | Predicted current density for Au nanoneedles in a 0.5 KHCO₃ electrolyte at 1 atm overlaid with a) electrode local pH, and b) boundary layer thickness for a bubble departure diameter of 20 µm.
Chapter 4.

Joint Tuning of Nanostructured Cu-Oxide Morphology and Local Electrolyte Program High-Rate CO2 Reduction to C2H4

This chapter has been published as a communication in *Green Chemistry.* The candidate was a co-first author in this work and played a primary role in designing the research, performing the experiments, analyzing the data, and writing the paper. The other co-first author Dr. Yuanjie Pang performed the initial experiments leading to the work, analyzed the data and assisted in writing the manuscript. Additional authors for the work include Dr. Cao-Thanh Dinh, Dr. Md Golam Kibria, Dr. Min Liu, Dr. James Zhangming Fan, Prof. Edward Sargent and Prof. David Sinton. Their contributions were central to the publication of this work and are gratefully acknowledged and appreciated.

4.1 Introduction

Electrocatalytic reduction of carbon dioxide (CO2) to produce valuable carbon-based fuels and feedstocks is an important step in utilizing intermittent renewable energy. As compared to promising photocatalytic CO2 reduction, the electrocatalytic approach is attractive due to its higher throughput and energy conversion efficiencies, despite requiring an external energy source. Several carbon-based compounds can currently be produced via the electrocatalytic CO2 reduction reaction (CO2RR) including carbon monoxide, methane, formates, methanol, and ethylene. Among these products ethylene (C2H4) benefits from a large existing global market and price point compared to other one- and two-carbon products. To date, copper (Cu), Cu-based materials and N-doped carbon are the only known catalysts that can produce C2H4 with encouraging efficiencies.

Significant research efforts have focused on increasing the Faradaic efficiency (FE) of C2H4 on Cu-based catalysts via material-based mechanisms. The use of an oxide-derived Cu catalyst has recently proven to have superior reaction kinetics for C2H4 production with multiple authors reporting FE’s greater than 40%. The record FE of 60%, however, belongs to a plasma-activated Cu oxide-derived surface configuration. Nanostructure engineering of Cu metal offers an additional path to high C2H4 FE. Various surface morphologies have been devised using Cu-based catalysts including nanoparticles, nanocubes, and nanowires with the highest FE for C2H4 reaching 41%.

In addition to varying catalyst design, both experimental and theoretical research has pointed to the reaction environment as a primary factor in C2H4 selectivity on oxide-derived Cu. Most notable is the local pH at the electrode surface which varies as a function of current density and buffering capacity. On a Cu-oxide
derived catalyst a higher local pH has been shown to inhibit the surface protonation pathway of adsorbed CO towards methane (CH$_4$), resulting in an increase in CO-CO coupling leading to C$_2+$ product formation.$^{25,117}$ A way to locally influence local pH is confinement which has also been shown to influence selectivity with both shallow nanopores$^{118}$ and deeper micropores$^{119,120}$ enhancing C$_2$H$_4$ and ethane (C$_2$H$_6$) formation, in addition to maintaining high concentrations of reaction intermediates within the pores. Similar mass transport manipulations on the microscale were also meticulously studied in the context of CO formation where H$_2$ formation was suppressed via diffusional gradients, albeit at low current densities < 1 mA cm$^{-2}$. Confined structures, however, simultaneously restrict transport of CO$_2$ reagent from the bulk electrolyte limiting the use of this approach for attaining higher currents.

Despite increases in selectivity and understanding the underlying mechanisms of C$_2$H$_4$ production via CO$_2$RR, maximum C$_2$H$_4$ production rates under ambient conditions (1 atm, 298 K) have been limited to low partial current densities (<15 mA cm$^{-2}$). Reaching higher C$_2$H$_4$ partial currents requires more than increasing the mass transport of CO$_2$, however, due to competing CH$_4$ and H$_2$ production, both of which increase significantly with overpotential. Using a simplified supporting model and a roughened electrode Kas et al. began to address the entangled reaction processes by manipulating pressure and electrolyte buffering to preferentially switch selectivity between CH$_4$ and C$_2$H$_6$. $^8$ Interestingly the C$_2$H$_4$/CH$_4$ ratio was increased by two separate means, i) by using low buffering concentrations to increase local pH and suppress CH$_4$, and ii) by oversupplying CO$_2$ using high pressure to increase CO surface coverage, promoting CO dimerization$^{122}$ and C$_2$H$_4$ formation. Similarly Varela et al. varied electrolyte concentration on a mechanically polished electrode surface finding that while H$_2$ and CH$_4$ formation increase with buffering, the C$_2$H$_4$ production rate remains relatively constant indicating the increased proton availability promotes competing reactions while maintaining C$_2$H$_4$. $^{123}$ In parallel, Xiao et al. identified onset potentials for both C$_2$H$_4$ and CH$_4$ on Cu (111) at different pH values. While the onset potentials for each product were equal at a pH of 7, the onset potential for CH$_4$ was suppressed by ~250 mV at a pH of 12, suggesting that CO$_2$RR can be driven towards C2 products only over a narrow range of operating potentials.$^{71}$ These findings are similarly supported by the experimental findings of Schouten et al.$^{101}$ and highlight the numerous contributing factors that must be taken into account to simultaneously improve C$_2$H$_4$ selectivity and current density on oxide-derived Cu catalysts.

Here we assess the importance of varying electrode surface area, morphology and CO$_2$ availability in concert with electrolyte concentration to increase C$_2$H$_4$ partial current densities on oxide-derived Cu. A primary focus is to promote C$_2$H$_4$ selectivity by operating within local environments that suppress the primary competing CO$_2$RR product, CH$_4$, which both consumes CO$_2$ reagent and reduces overall C$_2$H$_4$ selectivity. Where possible the Cu-oxide derived electrodes should then be operated in a narrow potential window immediately after the onset of C$_2$H$_4$ production with the surrounding microenvironment at an elevated local pH. Using an updated electrochemical model accounting for surface mass transport as guidance for our experiments, we operate several electrode morphologies within the expected overpotential window for C$_2$H$_4$ production and
show a shift in the peak C\textsubscript{2}H\textsubscript{4} selectivity towards higher overall current densities. The impact of buffering on CO\textsubscript{2} availability is also addressed. Finally, the opportunities and fundamental limitations of C\textsubscript{2}H\textsubscript{4} production on Cu-oxide derived catalysts in fully aqueous systems is discussed.

4.2 Results and Discussion

To create electrodes with varying active surface areas but similar surface characteristics we first electrodeposited thin Cu layers onto a cleaned Cu foil surface. Operating in Galvanostatic mode with a current density of 3 A cm\textsuperscript{-2} thin micro-porous foams were formed as the result of simultaneous Cu deposition and H\textsubscript{2} evolution.\textsuperscript{124} Four types of porous Cu structures were deposited using this method, with deposition durations of 2 s (Porous1), 4 s (Porous2), 8 s (Porous3) and 16 s (Porous4). A bare Cu foil surface (Flat) was also used in testing. Following the deposition process all five samples were oxidized using a wet-chemical etching technique to provide a uniformly oxidized surface (see Experimental Section). SEM images of the samples after wet-oxidation can be seen in Figure 4-1 a-e with varying levels of roughness and porosity. The formed oxide layer is reduced to bare Cu at the beginning of the CO\textsubscript{2} reduction process, giving an oxide-derived Cu reaction surface. The reduction of Cu oxides to a complete or major metallic state during CO\textsubscript{2}RR, and the resultant high selectivity of the oxide-derived Cu, is previously investigated and explained.\textsuperscript{23,75,125,126} Further details about the electrode deposition and oxidization process can be found in the Experimental Section while SEM images of each electrode as electrodeposited, after wet-oxidation and after 30 min of CO\textsubscript{2}RR can be found in Figure 4-6 of the Supplementary Information.

Prior to CO\textsubscript{2} reduction we characterized the bulk mass transport properties from gas evolution on each catalyst to aid in our analysis of the experimental results (see Supplementary Information).\textsuperscript{3} The mass transport properties of a particular surface are important as they influence both the availability of CO\textsubscript{2} reagent and the energetic efficiency of the reaction. The latter is important as enhanced mass transport can reduce the

![Figure 4-1](image-url) | (a-e) SEM Images of five different electrodeposited Cu electrodes that have undergone a wet-chemical oxidation process. Scale bars are equivalent to 20 \(\mu\)m, inset scale bar in (a) is 3 \(\mu\)m. (f-j) Images of gas product bubbling during CO\textsubscript{2}RR on various Cu electrodes taken using a dark field optical microscope. Scale bars are equivalent to 200 \(\mu\)m. Below each bubble image is a histogram showing the distribution of bubble diameters.
overpotentials needed to reach higher current densities allowing for CH4 to be suppressed over a larger current range during C2H4 production. Using a dark field microscope we observed gas evolution from each morphology and measured the diameters of the released bubbles in order to calculate the bubble-induced mass transport in each case. At current densities over 10 mA cm−2 bubble-induced mass transport dominates over the effects of moderately a stirred beaker resulting in a varying diffusion layer thickness that can be approximated using the bubble size distribution from a gas-evolving electrode. This addition represents the primary modeling deviation from the widely utilized model by Gupta et al.56,63 The measured bubble-size distributions are shown in Figure 4-1 f-j in addition to still images of the gas evolution on each structure. By pairing these results with the diffusion layer modeling aspects of other established models,56,58,59 the local pH and CO2 concentration at the electrode surface is approximated as a function of current density and product selectivity. Using a prescribed selectivity distribution of 50% H2, 30% C2H4, 10% CH4, 5% HCOOH and 5% EtOH the predicted mass transport kinetics of each morphology can be compared by predicting the local CO2 concentration as a function of current density as shown in Figure 4-2. The Porous2 sample provides the greatest mass transport while the Flat, Porous1 and Porous4 samples result in the worst.

As a baseline for comparison to our porous samples we first performed reduction experiments on our Flat Cu sample (see Experimental Section for details). The FE’s of C2H4 for several currents were obtained in KHCO3 concentrations of 0.1 M, 0.2 M, 0.3 M and 0.5 M and are plotted in Figure 4-3a. As shown in Figure 4-3a-b the C2H4 selectivity decreases with increased buffering concentration while CH4 selectivity increases as has been similarly demonstrated elsewhere.8,123 It is important to note that despite a drop in C2H4 selectivity the overall production rate remains relatively constant (see Figure 4-7). Using our model accounting for mass transport on the flat electrode we predicted the local pH and CO2 concentration in Figures 3d and e using the same prescribed selectivity as in Figure 4-2 and compared the results against our experimental operating voltages.

At 0.1 M KHCO3 the potentials at which both CH4 and C2H4 were detected is -1.1 V vs RHE at low overall current densities (Figure 4-8). As the local electrode pH increases with current density we then expect the onset

Figure 4-3 | (a) Ethylene selectivity versus current density for various KHCO₃ concentrations on a flat oxide-derived Cu catalyst. (b) Methane selectivity versus current density for various KHCO₃ concentrations on a flat oxide-derived Cu catalyst. (c) Applied potential for each current density and electrolyte concentration. Predicted (d) local electrode pH and (e) local electrode CO₂ concentration using a diffusion based model and variable-diffusion thickness. The inputted selectivities used to calculate the gas evolved from the electrode and electrons consumed for (d) and (e) are 50% H₂, 30% C₂H₄, 10% CH₄, 5% HCOOH and 5% EtOH.

potential of CH₄ to shift to higher overpotentials while the onset potential of C₂H₄ remains fixed. As current is increased, however, we observe both CH₄ and C₂H₄ production increasing towards a peak selectivity. As seen in Figure 4-8, however, as the total current approaches 50 mA cm⁻² the C₂H₄ partial current density remains relatively constant while CH₄ production greatly decreases. Observing Figure 4-3d the drop in CH₄ corresponds to the predicted local pH of 12 at an operating potential of -1.4 V, 300 mV greater than our observed C₂H₄ onset potential of -1.1 V. These results indicate that while CH₄ may be partially suppressed at higher current densities for the Flat electrode at 0.1 M KHCO₃, the operating potentials needed to obtain a higher local pH (via current density) is misaligned with what would be required to achieve a significant ratio of C₂H₄/CH₄. In the elevated electrolyte concentrations our simulations show that the current densities needed to reach high local pH conditions also do not sufficiently align with the required applied potentials to meaningfully suppress CH₄ production. Furthermore, as seen in Figure 4-3c, higher buffering concentrations result in overall more active catalysts for both H₂ and CH₄ formation due to an increased concentration of proton donors. Higher buffering further lowers polarization losses due to pH gradients contributing to more efficient overall reactions.

Of additional interest is the predicted local CO₂ concentration of the Flat samples as a function of current density and buffering capacity. As seen in Figure 4-3e at 0.1 M KHCO₃ concentrations the system is expected to become CO₂ limited at 90 mA cm⁻² for the prescribed selectivity distribution; at higher KHCO₃ concentrations this limiting CO₂:RR current density increases. The simulation results in Figure 4-3e then indicate that the
Availability of CO₂ is significantly affected by the higher local pH present within the diffusion region at higher currents, despite the relatively slow hydration kinetics of the CO₂ to bicarbonate reaction. Thus while low electrolyte concentrations have experimentally allowed for favorable C₂H₄/CH₄ ratios, the findings highlight the necessity of increased buffering concentrations to also obtain significantly higher current densities in fully aqueous reaction systems.

Learning from the limitations of our Flat catalyst, a more energetically efficient catalyst can be used to better align the local electrode pH with the onset potential of C₂H₄. A similar set of experiments to the Flat sample were then undertaken on our electrodeposited oxide-derived Porous catalysts with increased surface roughness and mass transport characteristics. Similar to the Flat sample experiments, gas is collected after 30 minutes of CO₂ reduction, but the selectivity towards C₂H₄ is maintained for at least 45 minutes (a sample test is shown in Figure 4-9). The operating potential also remains stable at the applied current density while minimal change in the morphology is observed before and after CO₂RR (Figure 4-6). As seen in Figure 4-4a each of the porous structures result in the peak C₂H₄ selectivity shifting to greater overall current densities. The ratio of C₂H₄/CH₄ product formation similarly increases with Cu deposition time as seen in Figure 4-4d with each sample showing multi-fold increases over the Flat sample. The increase is attributed to the decreased overpotentials needed to reach higher currents as seen in Figure 4-10 resulting in a higher local pH closer to the
 Joint Tuning of Nanostructured Cu-Oxide Morphology and Local Electrolyte Program High-Rate CO₂ Reduction to C₂H₄

onset potential of C₂H₄. As the onset potential of CH₄ production is shifted to higher overpotentials with increasing local pH, electrodes with larger roughness and porosity also allow for favorable C₂H₄ formation over a broader current density range as shown in Figure 4-4d. While the Porous 3 and 4 structures exhibit high C₂H₄/CH₄ ratios, the overall C₂H₄ selectivity and current density is low. Similar to the Flat structure we hypothesize this may be due to poor CO₂ availability in the Porous 3 and 4 samples at currents above 50 mA cm⁻² as calculated from our mass transport model (Figure 4-2). Additionally, while our modeling analysis assumes a rough planar electrode, the CO₂ concentration within deeper pores would likely be lower than our predicted value due to a larger overall diffusion thickness from the bottom of the cavity. Thus while higher surface areas from porous materials are shown to be desirable from an energetic efficiency and C₂H₄/CH₄ perspective, they should be balanced with sufficient mass transport to supply the necessary reagent to maintain higher CO₂RR currents. The chosen nanostructures then greatly affect the local reaction environment through both morphology induced mass transport and surface area resulting in the variations of FE’s achieved.

Observing the Porous 2 sample, a partial C₂H₄ current of 23 mA cm⁻² is achieved (Figure 4-4b). We attribute the higher selectivity and partial current to the increased mass transport which allows a higher local CO₂ concentration to be maintained at the electrode as current is increased. As shown by Kas et al. when increasing system pressure, increased CO₂ availability subsequently increases CO surface coverage. With greater surface coverage of CO the maximum formation rate of C₂H₄ would then be expected to increase,¹²²,¹²⁷ highlighting the importance of maintaining ample CO₂ concentration at the electrode surface. For all samples the overall partial C₂H₄ current eventually saturates at higher overpotentials as shown in Figure 4-4b while the selectivity begins to decrease.

From the results of our experiments in 0.1 M KHCO₃ and our modeling results in Figure 4-3 d and e, the electrolyte concentration plays a large role in local pH and CO₂ availability which in turn impacts C₂H₄ production. Previously for the Flat sample increasing buffering resulted in decreased C₂H₄ formation due to a misalignment between the local pH and the onset potential of C₂H₄. For our more electrochemically active Porous samples, however, higher total current densities are possible at lower overpotentials potentially allowing for high buffering capacities to be used, thereby increasing current densities where CO₂ is predicted to become limited. Each of the electrodes were subsequently run at an elevated KHCO₃ concentration of 0.2 M with increased overall current densities. The resulting C₂H₄ selectivity curves shown in Figure 4-5a mimic a similar overall trend as the 0.1 M KHCO₃ tests in Figure 4-4a, with the peak selectivity again shifting further to higher current densities in order of increasing deposition time. In the higher buffering environment three of the five samples also reach a C₂H₄ selectivity of ~30% with the Porous 2 and 3 samples achieving a high partial C₂H₄ current of 35 mA cm⁻². The best performance, however, belongs to a Porous2 sample operated in 0.2 M KHCO₃ electrolyte concentration using a total current density of 120 mA cm⁻², achieving an FE for C₂H₄ of 29.7% and a jC₂H₄ of 35.6 mA cm⁻², a 3.4-fold increase in C₂H₄ current density as compared to the Flat sample. Additionally all Porous samples exceed their peak partial C₂H₄ current density as compared to the 0.1 M
buffering case as seen in Figure 4-5c. The increase in partial C\textsubscript{2}H\textsubscript{4} current is in contrast to our Flat sample and the findings of Varela et al. where the higher buffering is expected to increase the availability of proton donors, increasing reaction kinetics for H\textsubscript{2} and CH\textsubscript{4} formation, but not C\textsubscript{2}H\textsubscript{4}. We conclude the increased CO\textsubscript{2} availability from the higher electrolyte concentration also increases CO surface coverage increasing CO-CO dimerization and C\textsubscript{2}H\textsubscript{4} currents, similar to that found when increasing CO\textsubscript{2} partial pressure by Kas et al. Finally, as shown by the simulation in Figure 4-3d, the additional buffering capacity also requires a higher current density to reach a higher local pH which explains the observed shift in peak C\textsubscript{2}H\textsubscript{4} selectivity to higher current densities.

From our results several important trends are extracted. The first is in regards to the importance of increasing surface roughness to drive CO\textsubscript{2} product formation towards C2 products rather than CH\textsubscript{4}. Under both 0.1 M and 0.2 M electrolyte concentrations higher C\textsubscript{2}H\textsubscript{4}/CH\textsubscript{4} ratios were obtained with increasing electrode roughness and porosity as higher currents are observed at lower overpotentials. Heightened local pH values can then occur closer to the observed onset potential of C\textsubscript{2}H\textsubscript{4} suppressing CH\textsubscript{4}. Secondly, our experimental and modeling results indicate that CO\textsubscript{2} limitations occur as a result of operating under high local pH conditions, affecting maximum CO\textsubscript{2}:RR production rates. While surface-derived mass transport effects can partially mitigate pH-driven CO\textsubscript{2} limitations, as illustrated by the performance of the Porous 2 sample, substantial increases in C\textsubscript{2}H\textsubscript{4} current densities requires an increase in the electrolyte buffering capacity. Finally, while higher electrolyte concentrations are fundamentally needed to achieve higher efficiencies and production rates of C\textsubscript{2}H\textsubscript{4}, increasing the concentration of HCO\textsubscript{3}\textsuperscript{-} can provide too strong a buffering affect to take advantage of separating the onset potentials of C\textsubscript{2}H\textsubscript{4} and CH\textsubscript{4}. Additionally, the increased proton availability can facilitate competing H\textsubscript{2} and CH\textsubscript{4} reactions.

Maximizing the performance of C\textsubscript{2}H\textsubscript{4} production on oxide-derived Cu then requires a number of contending factors to be taken into consideration including operating potential, CO\textsubscript{2} availability and catalyst activity. Under aqueous H-cell configurations C\textsubscript{2}H\textsubscript{4} production will then always be confined to a narrow operating region where C\textsubscript{2}H\textsubscript{4} is most favorable before either competing reactions take over or the CO\textsubscript{2} reagent is depleted by
consumption or pH-driven conversion into carbonate. For efficient C₂H₄ production it is then necessary to design catalysts and systems that enable decoupling of these underlying factors to provide further degrees of freedom to increase selectivity and current density concurrently. Catalytically this requires further pH-independent separation of C₂H₄ and CH₄ onset potentials through material design and a better understanding of individual reaction mechanisms through theoretical studies. System-based approaches, such as flow cell devices, can also be used which allows for catalysts to operate in a high pH media with ample CO₂, providing a much broader current range where optimal reaction conditions can exist.²¹,²²

4.3 Conclusions

In this work we assessed the potential of increasing the partial current density of C₂H₄ on oxide-derived Cu within an H-cell configuration. By creating electrodes with varying surface areas and mass transport properties we were able to increase the C₂H₄ partial current to 35 mA cm⁻² on our Porous 2 sample, a 3.4-fold increase over the Flat comparison. Highlighted by our experiments are the fundamental constraints of C₂H₄ production on a Cu-oxide derived catalyst due to the coupled effects of the applied potential on current density and local pH. When poorly aligned, low C₂H₄/CH₄ ratios are observed while operating under high local pH conditions are shown to additionally constrain CO₂ availability, hindering maximum current densities. We hope the combined material and mass transport analysis presented aids in disentangling the competing influences of CO₂ reduction on Cu-based catalysts and that similar methods can be used in the testing of newly discovered catalysts in the future.

4.4 Experimental Section

Cu foil substrates with a 99.9% purity were purchased from Sigma Aldrich. Cu foil was cleaned prior to wet oxidation or electrodeposition. The sample was first sonicated in 3 M HCl for 10 minutes, and then sonicated in isopropanol for 10 minutes. The samples were rinsed with deionized water and dried in a flowing nitrogen gas stream following each of the cleaning steps. All samples used in this work had a working area of 0.09 cm².

Electrodeposition of a Cu foam structure was performed as described previously.¹²⁸ Briefly, a two-electrode system in an 80 mL beaker was used for the deposition process. The working electrode (substrate for deposition) and the counter electrode were both Cu foil (99.9% purity, Sigma Aldrich). A precursor solution that consists of 0.2 M CuSO₄, 0.7 M H₂SO₄, and 1.2 M (NH₄)₂SO₄ was used. An electrochemical workstation (Autolab PGSTAT204) running in Galvanostatic mode at a current density of 3 A cm⁻² was used for the deposition, and deposition duration was varied and specified accordingly in the main text.

Wet oxidation of the Cu samples was performed as follows. Cleaned flat Cu foils or electrodeposited Cu foam samples were immersed into an oxidant solution consisting of 60 mM HCl (Sigma Aldrich) and 60 mM H₂O₂ (Sigma Aldrich) without stirring for 60 seconds. The samples were immediately rinsed in deionized water and dried again in a flowing nitrogen gas stream.
The composition of the nanoparticles formed on the Cu foil substrate after wet-oxidation were observed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) in Figure 4-11 a and b, respectively. The samples show a Cu 2p3/2 peak at 932.2 eV, and a O 1s peak at 531.3 eV, matching the peak positions for Cu(I) oxide. The XRD pattern of the sample after wet-oxidation shows primarily Cu(I) oxide present on the Cu substrate with minor amounts of Cu(II) oxides also present.

An Autolab PGSTAT204 electrochemical workstation was used for all electrochemical processes described in this work with new samples used for each data point. The electrochemical workstation was run in Galvanostatic mode at various current densities and product gases were collected after running for 30 min at the prescribed current. Gas product detection was performed using a Perkin Elmer Clarus 680 gas chromatography system.

All CO\textsubscript{2} reduction experiments were performed in a three-electrode system connected to the electrochemical workstation (Autolab PGSTAT204). An Ag/AgCl (with saturated KCl as the filling solution) and platinum foil were used as reference and counter electrodes, respectively. Electrode potentials were converted to the reversible hydrogen electrode (RHE) reference scale using \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197V + 0.0591\times \text{pH} \). The KHCO\textsubscript{3} electrolytes with concentrations 0.1M, 0.2 M, 0.3 M and 0.5 M saturated with CO\textsubscript{2} have pH values of 6.8, 6.9, 7.0 and 7.2, respectively. The experiments were performed in a gas-tight two-compartment H-cell separated by an ion exchange membrane (Nafion117). 30 mL of electrolyte was used in both the anode and cathode sides, and the gas phase headspace in both the anode and cathode sides was approximately 20 mL. The electrolyte in the cathodic compartment was stirred at a rate of 500 r.p.m. during electrolysis. CO\textsubscript{2} gas (99.99%, Praxair) was delivered into the cathodic compartment at a rate of 20.00 standard cubic centimeters per minute (s.c.c.m.) and was routed into a gas chromatograph (PerkinElmer Clarus 680). The gas chromatograph was equipped with a Molecular Sieve 5A capillary column and a packed Carboxen-1000 column. Argon (Linde, 99.999%) was used as the carrier gas. The gas chromatograph columns led directly to a thermal conductivity detector to quantify hydrogen, and a flame ionization detector equipped with a methanizer to quantify methane and ethylene.

Bubble release diameters were determined by visual observation of gas evolution from each of the three primary electrode surfaces: flat copper, oxidized Cu with short deposition time and oxidized copper with longer deposition (Cu foam structure). Bubble diameters were recorded at the time of release from a horizontal electrode surface witnessed from above using a dark-field microscope similar to our previous publication.\textsuperscript{3}

4.5 Supplementary Information

4.5.1 Modeling of the Diffusion Region and Surface Mass Transport

The modeling results throughout the manuscript were performed as detailed in our previous manuscript\textsuperscript{3} and are briefly summarized here. All simulations were performed in 1D in MATLAB. The diffusion region consisted
of a left-hand boundary \((x = 0 \mu m)\) consisting of the electrode surface and a right-hand boundary at the edge of the diffusion layer \((x = \delta)\) where the concentrations of all aqueous components are assumed to be equal to their bulk concentrations depending on the concentration of electrolyte used.

The thickness of the diffusion layer, \(\delta\), was determined as described previously where the thickness varies depending on the electrode current density, product selectivity and the size distribution of product bubbles evolving from the electrode. Taken into account gas evolution is needed as the mass transport invoked by bubble growth and departure is larger than that of a stirred beaker at even moderate electrode current densities. Within the simulation, current densities are prescribed and the bubble size distribution is taken directly from the experimentally measured values for each electrode shown in Figure 4-1 f-j. The diffusion thickness can then be calculated as a function of current density, selectivity and electrode choice and results in the variations between electrodes observed in Figure 4-2.

The diffusion region itself was modeled similar to other sources with the exception of the varying diffusion thickness. Taken into account are the interactions between \(\text{CO}_2\) and the carbonate electrolyte, ‘salting out’ effects of \(\text{CO}_2\) in a salt solution, \(\text{OH}\) generation at the electrode surface and \(\text{CO}_2\) consumption at the electrode as a function of current density. The following equations are subsequently solved to determine the local \(\text{pH}\) and \(\text{CO}_2\) concentration at the electrode’s surface:

\[
\frac{\partial [\text{CO}_2]}{\partial t} = D_{\text{CO}_2} \frac{\partial^2 [\text{CO}_2]}{\partial x^2} - [\text{CO}_2][\text{OH}^-]k_{1f} + [\text{HCO}_3^-]k_{1r} \tag{4.51}
\]

\[
\frac{\partial [\text{HCO}_3^-]}{\partial t} = D_{\text{HCO}_3^-} \frac{\partial^2 [\text{HCO}_3^-]}{\partial x^2} + [\text{CO}_2][\text{OH}^-]k_{1f} - [\text{HCO}_3^-][\text{OH}^-]k_{1r} - [\text{HCO}_3^-][\text{OH}^-]k_{2f} + [\text{CO}_3^{2-}]k_{2r} \tag{4.52}
\]

\[
\frac{\partial [\text{CO}_3^{2-}]}{\partial t} = D_{\text{CO}_3^{2-}} \frac{\partial^2 [\text{CO}_3^{2-}]}{\partial x^2} + [\text{HCO}_3^-][\text{OH}^-]k_{2f} - [\text{CO}_3^{2-}]k_{2r} \tag{4.53}
\]

\[
\frac{\partial [\text{OH}^-]}{\partial t} = D_{\text{OH}^-} \frac{\partial^2 [\text{OH}^-]}{\partial x^2} - [\text{CO}_2][\text{OH}^-]k_{1f} + [\text{HCO}_3^-]k_{1r} - [\text{HCO}_3^-][\text{OH}^-]k_{2f} + [\text{CO}_3^{2-}]k_{2r} \tag{4.54}
\]

Rate constants of the carbonate equilibrium are calculated as a function of temperature and salinity\(^\text{105}\) while the ‘salting out’ effect is calculated from the Sechenov equation.\(^\text{104}\)

The right-hand boundary conditions set the \(\text{CO}_2\), \(\text{HCO}_3^-\), \(\text{CO}_3^{2-}\) and \(\text{OH}^-\) concentrations equal to their bulk concentrations, depending on the \(\text{KHCO}_3\) concentration used in the experiments. This assumes the H-cell beaker is well mixed with saturated \(\text{CO}_2\) at the 500 rpm stirring speed and \(\text{CO}_2\) headspace as described in the Experimental Section.

At the left boundary the flux of \(\text{CO}_2\) and \(\text{OH}^-\) were fixed to the applied current density and chosen selectivity. The local \(\text{pH}\) at the electrode then increases with the applied current density while the amount of \(\text{CO}_2\) consumed increases.
Figure 4-6 | SEM images of Cu-based catalysts. (a-c) Flat samples. (d-o) Samples based on electrodeposition of porous Cu structures with various deposition duration of 2 s (d-f), 4 s (g-i), 8 s (j-l), and 16 s (n-o). Panels (a, d, g, j, and n) show samples before wet-oxidation; Panels (b, e, h, k, and l) show samples after wet-oxidation; Panels (b, e, h, k, and l) show samples after CO₂RR for 30 minutes. All scale bars represent 20 μm.

Figure 4-7 | Ethylene production rate versus total current density at 0.1 M, 0.2 M, 0.3 M and 0.5 M KHCO₃ concentrations for the Flat electrode.

Figure 4-8 | Ethylene production rate versus total current density at 0.1 M, 0.2 M, 0.3 M and 0.5 M KHCO₃ concentrations for the Flat electrode.
JOINT TUNING OF NANOSTRUCTURED Cu-OXIDE MORPHOLOGY AND LOCAL ELECTROLYTE PROGRAM HIGH-RATE CO2 REDUCTION TO C2H4

Figure 4-9 | Stability test of the electrocatalyst tested using Sample Porous 2, 0.1 M KHCO₃, 50 mA cm² total current.

Figure 4-10 | Total current density versus applied potential for 0.1 M KHCO₃ concentrations for the Porous electrode samples.

Figure 4-11 | Characterization of the chemical composition of the wet-oxidated sample. (a) XPS spectra of the Cu 2p and O 1s orbitals of the wet-oxidated Cu foil, showing existence of Cu₂O on the surface. (b) XRD pattern of the wet-oxidated Cu foil, showing signals from the Cu substrate and a surface layer of various forms of Cu oxides, with a majority of Cu₂O and a minority of other types of oxides. The sample shows a Cu 2p₃/₂ peak at 932.2 eV, and a O 1s peak at 531.3 eV, matching the peak positions for Cu(1) oxide.¹²⁹
Chapter 5.

Abrupt Fluid-Solid Interface for High Performance CO₂ Electroreduction to Ethylene

This chapter has been submitted as a letter in *Nature* and forms the basis of a provisional US patent. The candidate was a co-first author in this work and played a primary role in designing the research and experiments, modeling the reaction environment, analyzing the data, and writing the paper. The other co-first authors Dr. Cao-Thang Dinh, Dr. Ali Seifotokaldani and Dr. Md Golam Kibria played equally pivotal roles by performing and designing the experiments and models, creating the catalyst, analyzing the data and writing the paper. Additional authors for the work include Dr. Amirreza Kiani, Mr. Jonathan P. Edwards, Dr. Oleksandr Bushuyev Dr. Pelayo García de Arquer, Dr. Christine M. Gabardo, Dr. Chengqin Zou, Dr. Rafael Quintero-Bermudez, Dr. Yuanjie Pang, Prof. Edward Sargent and Prof. David Sinton. Their contributions were central to the publication of this work and are gratefully acknowledged and appreciated.

5.1 Overview

The efficient electrochemical conversion of carbon dioxide (CO₂) into valuable carbon-based fuels provides an avenue for the urgently-needed storage of intermittent renewable electricity sources and the net reduction of greenhouse gas emissions. A global community has worked to advance the prospects of producing ethylene - a highly demanded feedstock - from CO₂ electroreduction. Unfortunately, present achievements in power energy conversion, the key factor determining the operational cost; and production rate, which governs the capital cost per unit of energy stored; remain too low to enable the practical application of renewable ethylene production. Here we report the abrupt fluid-solid interface (AFSI) catalyst that enables CO₂ reduction in unprecedentedly high-pH alkaline media. We show that strong alkaline media accelerates the kinetics of CO₂ reduction by lowering the CO-CO coupling energy barrier. Only by developing the AFSI, which uses a sub-100 nm layer of Cu catalyst on a carbon gas diffusion electrode, do we enable the use of ultra-high electrolyte concentrations. Counterintuitively, we find herein a domain of energy materials in which managing a highly planar and thin reaction interface is the necessary design rule for high production and conversion efficiencies. We report as a result an ethylene Faradaic efficiency of 67% at a current density of 275 mA cm⁻² and a potential of -0.54 V versus a Reversible Hydrogen Electrode (RHE). This represents an electricity-to-ethylene power conversion of 44% compared to the best previous 33%. The AFSI enables us to further optimize the reaction environment to achieve an ethylene partial current density of 500 mA cm⁻². This is a fully 3x improvement over the 150 mA cm⁻² in previous reports; yet it is achieved at 1.5x higher energy conversion efficiency. The AFSI catalyst also enables an exceptionally high ethylene mass activity of 17.8 A/mg, more than 50x higher than the best prior report.
5.2 Introduction

The CO₂ reduction reaction (CO₂RR) has reached lower activation overpotentials and increased Faradaic efficiencies via tuning of catalyst nanomorphologies, manipulating oxidation states, and introducing dopants. For CO₂ to ethylene - a precursor desired for polymer production - Cu-oxide derived catalysts have achieved impressive Faradaic efficiencies of 60% by utilizing a pH-dependent shift in the onset potential of methane and operating in a narrow reaction window. Separately, ethylene partial currents of over 150 mA cm⁻² have been achieved at more modest selectivities of 36% and at a potential of -0.58 V versus RHE on bare Cu nanoparticles in a flow cell configuration using alkaline electrolytes. Using CO as a precursor enabled a low onset potential for the formation of C₂ products; however, efficient ethylene generation from CO₂ has not yet been achieved at the low overpotentials.

Despite advancements in individual performance metrics, the field has yet to achieve high power conversion efficiencies at commercially relevant production rates. For example, the best half-cell energy conversion of 33% was achieved at a partial current density of 12 mA cm⁻²; while an impressive ethylene partial current density of 150 mA cm⁻² was combined with a low 23% energy conversion efficiency. Advances in understanding and performance are required to advance CO₂ electrolyzers for widespread application in industry and climate impact.

Here we pursue new insights into the influence of hydroxide on CO-CO coupling and provide a novel interpretation of catalyst-system interactions to advance CO₂RR performance. We show that an abrupt CO₂-catalyst-electrolyte (fluid-solid) reaction interface (AFSI) enables a high production rate and energy conversion efficiency in CO₂ electroreduction to ethylene.

5.3 Results and Discussion

Hydroxide ions (OH) (in both adsorbed and bulk forms) play an important role in electrocatalytic processes such as hydrogen evolution and hydrogen reduction. They affect the reactant concentration and they interact with reaction intermediates, influencing reaction pathways. In CO₂RR, alkaline electrolytes are reported to suppress both methane and hydrogen evolution by reducing proton availability. However, the effect of OH on CO₂RR in strong alkaline media (up to 10 M OH concentration) has been little explored. We show here that this is likely due to the draconian catalyst redesign it mandates to achieve CO₂RR in such conditions.

We hypothesized that the local reaction environment, specifically the prevalence of hydroxide ions in high concentration immediately proximate the electrode surface, influences CO adsorption and CO-CO coupling steps. We posited that these OH ions could directly reduce the energy barrier of ethylene formation on copper (Cu). We used Density Functional Theory (DFT) to assess the impact of hydroxide ions on the individual energy barriers for CO adsorption on Cu (111), (100) and (110) surfaces (see Figure 5-5, Table 5-2 and Table 5-3).
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DFT results (Figure 5-1a and Figure 5-6) reveal that the presence of hydroxide lowers the binding energy of CO on the Cu surface; while it stabilizes the OCCO intermediate. This combination leads to an overall decrease in the CO-CO coupling energy, the crucial rate-limiting step in CO2RR to multiple carbon products. The presence of hydroxide is found to lower the CO-CO coupling energy barrier by as much as 117 meV on Cu (100), the primary active surface, with OH concentrations as low as 2/16 ML (Figure 5-1a and 1b). The energy barrier is further reduced as the OH concentration is increased and the hydroxide ion becomes closer to the adsorbed CO (Figure 5-1b). Hydroxide is found to increase the charge imbalance between carbon atoms in adsorbed OCCO, and then further stabilizes this intermediate by making a stronger dipole attraction within OCCO (Figure 5-6). The same behavior is seen on the other two surfaces, further confirming the critical role of hydroxide in lowering the reaction barrier for multiple carbon products from CO2RR.

To challenge the DFT predictions that hydroxide aids in CO-CO coupling on a copper surface, we measured the kinetics of CO2RR in a flow cell configuration under various bulk KOH electrolyte concentrations. A Cu catalyst was thermally deposited onto the carbon microporous surface of a gas diffusion layer, which allows for
an interface to form between gaseous CO$_2$ and liquid electrolyte adjacent to the Cu catalyst; and therefore for hydroxide and CO$_2$ to co-locate. As the bulk KOH concentration is shifted from 1 M to 10 M, the onset potential for ethylene is reduced from -0.48 V versus RHE to as low as -0.18 V versus RHE at 10 M, only 0.26 V higher than the potential thermodynamically necessary to accomplish CO$_2$-to-ethylene electroreduction. Remarkably, this is the lowest onset for ethylene formation from CO$_2$RR reported (Table 5-1). Further increasing the KOH concentration to 15 M did not significantly reduce the ethylene onset potential (Table 5-4). Interestingly, the onset potential shift of 300 mV when the KOH concentration increases from 1 M to 10 M is much higher than the potential shift due to pH difference (150 mV, see Table 5-4), emphasizing the crucial role of hydroxide in reducing the CO-CO coupling barrier as predicted by DFT.

Tafel analysis (Figure 5-1d) of the Cu catalyst in 1 M and 10 M KOH gives slopes of 150 and 65 mV dec$^{-1}$, respectively. The reduced slope in 10 M KOH further confirms faster CO-CO coupling kinetics in higher hydroxide concentration, in good agreement with DFT predictions (Figure 5-1a and b). The Tafel slope of 65 mV is even smaller than that of CO-CO coupling in CO reduction (110 mV) 75. We conclude that elevated hydroxide concentration at the surface of the catalyst substantially decreases the reaction barrier of the CO-CO coupling reaction.

In light of the important role of hydroxide in CO-CO coupling, we aimed to design a catalyst that would not only allow CO$_2$ to exist in the normally-parasitic concentrated KOH environment; but, would further enable record CO$_2$ reduction currents and selectivity. In a flow cell reactor CO$_2$ and OH can exist concurrently through molecular diffusion of CO$_2$ across a gas-liquid interface, established by depositing a hydrophilic catalyst on top of a hydrophobic gas diffusion layer (Figure 5-2a). At the elevated OH concentrations suggested by DFT and onset potential findings, however, a critical evaluation of these interface kinetics is necessary to design a catalyst capable of overcoming the new problem of low CO$_2$ concentration that now arises.

We modeled the local CO$_2$ concentration within the catalyst layer as a function of electrolyte concentration, catalyst thickness and current density (Figure 5-2b). Of particular interest is the CO$_2$ concentration distribution for a thin (100 nm) versus thick (1 µm) catalyst layer (Figure 5-7). For the thin catalyst the average CO$_2$ concentration across the catalyst in a 5 M electrolyte operating at 250 mA cm$^{-2}$ is 5x higher than that of the thicker catalyst due to reduced opportunity to interact with the electrolyte as CO$_2$ travels to the reaction site. As KOH is increased to 10 M, the thick catalyst layer becomes CO$_2$ depleted at the applied current density. A thin catalyst, which forms an abrupt reaction interface more proximate to the gas-liquid interface, is therefore expected to lead to higher maximum current densities and a simultaneously high surface concentration of CO$_2$ and OH. The predicted local OH concentration also deviates from that of the bulk OH concentration due to partial neutralization with CO$_2$ at low currents and hydroxide generation at higher current densities (Figure 5-2c). Current density then acts as a secondary means of controlling the local OH concentration.
To drive CO$_2$ reduction to ethylene towards high efficiency, current density and selectivity, we sought to implement these reaction conditions and abrupt reaction interface. We used thermal evaporation of Cu onto a gas-diffusion layer to create a homogenously abrupt interface. We used deposition thicknesses of 10 and 25 nm (denoted as AI1 and AI2) and compared with controls comprising of a distributed interface electrode with deposition thickness of 1000 nm (denoted as DI1). The nanoparticle size and surface morphologies were characterized via Scanning Electron Microscopy (SEM) (Figure 5-2d-f). The particle sizes are in the range of 15 to 40 nm. The cross-section STEM images and elemental mapping of 25 nm thickness Cu deposited on the gas diffusion layer (AI2 sample) (Figure 5-8) show an estimated roughness of the electrode of 2 µm with Cu uniformly deposited on the surface of the microporous carbon layer. X-ray photoelectron spectroscopy of all three samples showed the presence of C, Cu, and O (Figure 5-9a and b). The Cu peaks indicated a mixture of metallic Cu and Cu$^{+}$. X-ray diffraction further confirmed the crystalline structure of the samples (Figure 5-9c). The catalyst loadings, analyzed using ICP-MS, were ~11, 28 and 1100 µg cm$^{-2}$ for AI1, AI2 and DI1, respectively.
The CO₂RR activity of the evaporated Cu samples was evaluated in the flow cell using KOH as the electrolyte. For comparison, commercial Cu nanoparticles (particle size smaller than 50 nm) were also deposited on a gas diffusion layer with a loading of 1000 µg cm⁻² using a drop-casting technique (sample DI2, Figure 5-10). Figure 5-3a shows geometric reduction current density as a function of applied potential of the samples under CO₂RR conditions using 10 M KOH. At less negative potentials (> -0.4 V versus RHE), all samples show similar slopes, implying a similar intrinsic activity, though DI1 and DI2 show higher current density compared to AI1 and AI2 due to their higher catalyst loading. At more negative potentials, however, the reaction rates on AI1 and AI2 are higher than those of DI1 and DI2, leading to a similar current density at -0.54 V versus RHE for AI2, DI1 and DI2. We attribute this to the improved CO₂ availability at higher current densities for the abrupt reaction interfaces (AI1 and AI2) compared to the more distributed reaction (DI1 and DI2) as predicted in Figure 5-2.
Analyzing product selectivity in 10 M KOH, all samples show optimal ethylene production in the current range of 225 to 275 mA cm\(^{-2}\) (Figure 5-3b). Notably, both AI1 and AI2 show an ethylene Faradaic efficiency higher than 60% with AI2 peaking at 67% ethylene along with an 11% ethanol and 6% acetate (Figure 5-11 and Figure 5-12). Overall, AI2 shows a record total C2 selectivity of 84% at 275 mA cm\(^{-2}\) and a low potential of -0.54 V versus RHE, corresponding to an energy conversion of 44% for ethylene (See Table 5-1 for detailed calculation). When we run the same catalysts in an H-cell configuration using 0.1 M KHCO\(_3\), all samples show an ethylene FE in the range of 30-35% with DI1 and DI2 showing higher ethylene selectivity (Figure 5-13). The data confirm that the high C2 selectivity of AI2 sample in a flow cell originates from the combination of reaction interface design and strong alkaline electrolyte; rather than the nature of the catalyst itself. The abrupt reaction interface also enables exceptionally high ethylene mass activity of higher than 6.5 A mg\(^{-1}\), more than an order of magnitude higher than in any previous reports\(^{21,134}\) (Figure 5-3c and Table 5-1).
To shift \( \text{CO}_2 \) conversion toward even higher current densities, we lower the KOH concentration to 1 M KOH to increase \( \text{CO}_2 \) availability (Figure 5-2). With the exception of the AI1 sample, both \( \text{CO}_2 \text{RR} \) selectivity and maximum current density improve with decreasing catalyst thickness, with the AI2 sample reaching 90% selectivity for \( \text{CO}_2 \) reduction products at 1 A cm\(^{-2}\), the highest reported \( \text{CO}_2 \) electrolyzer current density (Figure 5-3d). As the physical catalysts are identical, the suppressed hydrogen evolution reaction can be attributed to the increased average \( \text{CO}_2 \) concentration across the electrode enabled by the decreased diffusion distance. To challenge the hypothesis, we reduced the partial pressure of \( \text{CO}_2 \) in the gas phase and showed that at non-limiting \( \text{CO}_2 \) reduction current densities, hydrogen evolution increases (Figure 5-14). Although high current densities can be achieved at low KOH concentrations, the selectivity for ethylene (about 51%, Figure 5-15) is lower than at high KOH concentrations (67%).

To achieve high ethylene current density and selectivity simultaneously, we sought to balance \( \text{CO}_2 \) and OH availability within the electrolyte. In view of our experimental results and mass transport model (Figure 5-2), a high local OH concentration can be accomplished by reducing the bulk KOH concentration and increasing current density, pointing to a strategy to increase ethylene production without sacrificing selectivity. At 500 mA cm\(^{-2}\) in 5.5 M KOH, we achieved an optimal ethylene selectivity of 60% and a total C2 Faradaic efficiency of 81% (Figure 5-16a). At 750 mA cm\(^{-2}\) in 3.5 M KOH ethylene selectivity drops to 52% while the total C2 selectivity remains as high as 80%. Adding 5 M KI to the 3.5 M KOH solution to offset the lost potassium concentration we then reduced the C2 proportion of ethanol and reached an ethylene FE of 66% and C2 selectivity of 82% at 750 mA cm\(^{-2}\) and a potential of -0.66 V versus RHE (Figure 5-4a and Figure 5-16b). These ethylene and C2 partial current densities of 500 and 615 mA cm\(^{-2}\), respectively, far exceed previously reported performance (Table 5-1).

Finally, we extend our concept of an abrupt reaction interface for \( \text{CO}_2 \) reduction in flow cells to \( \text{CO} \) production to prove the ability to adapt our system design to other reduction products. Using evaporated silver on a gas diffusion electrode (see Figure 5-17a and b for SEM characterization, sample AI-Ag) we show in Figure 5-4b and Figure 5-18 that high \( \text{CO} \) selectivity can be obtained while again using an extremely thin layer of the precious metal catalyst. Notably, the abrupt interface catalyst (AI-Ag) shows a \( \text{CO} \) selectivity of higher than 95% at a current density as high as 600 mA cm\(^{-2}\). In contrast, the \( \text{CO} \) selectivity drops to 27% on a distributed Ag sample (DI-Ag, see Figure 5-17c and d for SEM characterization) at the same operating conditions. While the applied overpotential and product selectivities of 95% are on par with more-finely tuned nanostructures in aqueous solutions\(^{141,142}\), a record \( \text{CO} \) partial current density of 565 mA cm\(^{-2}\) is obtained at a potential of -0.83 V versus RHE after iR correction (Figure 5-4b and Figure 5-18), showing suppression of the competing hydrogen evolution reaction. The sample produces \( \text{CO} \) for multiple hours without a drop in selectivity (Figure 5-4c).

### 5.4 Conclusions

The \( \text{C}_2\text{H}_4 \) power conversion efficiency of 44% reported here represents a 1.3x increase over the best reported values in literature. It does so at fully 15x production levels\(^{23}\) compared to the highest-efficiency prior reports.
Similarly, the C2H4 partial current of 500 mA cm\(^{-2}\) represents a 3x improvement over the highest current densities of previous flow cell reports\(^{21}\). Operating in a rarely-investigated experimental régime for CO\(_2\) reduction, we validated a new picture of the role of hydroxide on CO-CO coupling. Pairing this with mass transport modeling at the nanoscale, we designed a counterintuitively-thin catalyst configuration that manipulates the reaction environment of the Cu catalyst under the competing conditions of simultaneously high hydroxide and CO\(_2\) concentrations. This report progresses CO\(_2\) electrolyzer technologies closer to practical performance levels.

5.5 Supplementary Information

5.5.1 DFT Calculations

Vienna \textit{ab initio} Simulation Package (VASP)\(^{143}\) was used to perform all the plane wave density functional theory (DFT) computations. The projected augmented wave (PAW) approach\(^{144,145}\) together with the generalized gradient approximation (GGA) parametrized by Perdew, Burke and Ernzerhof (PBE)\(^{146}\) are employed. Three different crystalline facets, (111), (100) and (110) of the pristine copper are approximated by a 4×4×4 slab in a 20 Å vacuum. Due to the vacuum, dipole corrections are implemented. To resemble the real bulk material and the surface, respectively, two bottom layers are fixed in their positions while the two top layers are free to move due to interaction with the adsorbates. A cut-off energy of 400 eV for the plane wave basis sets and a 4×4×1 Γ-centered Monkhorst-Pack mesh for the k-points sampling in the first Brillouin zone, with a first order Methfessel-Paxton smearing parameter \(\sigma\) of 0.1 eV ensured that the energy convergence criteria is better than 1 meV. The k-points grid is doubled for charge density calculations. The self-consistent field (SCF) convergence criterion is set to \(1 \times 10^{-4}\) eV for electronic iteration and the ionic relaxation continued until the maximum force was less than 0.02 eV/Å. This was updated by the conjugate gradient approach.

Almost all previous literature indicates that the CO-CO coupling is pH independent because no proton participates in the coupling reaction. However, we explicitly investigate the effect of OH on changing the electronic structure and, in turn, the coupling reaction energy. In this work, we explicitly considered OH in our simulations to see how CO bonding and CO-CO coupling energies are affected.

One and two adsorbed carbon monoxides are simulated on all three surfaces with a varying number and proximity of hydroxides. In each case, different rational possible configurations (overall more than 200 configurations) are considered to find the global minima. The CO adsorption energy is calculated as:

\[
E_{\text{adsorption}} = E_{\text{ads}}^{n-OH} - (E_{\text{slab}}^{n-OH} + E_{\text{CO}})
\]  

(5.51)

where, \(E_{\text{ads}}^{n-OH}\) is the electronic structure energy of the adsorbed CO on the catalyst with \(n\) OH ions on the surface, \(E_{\text{slab}}^{n-OH}\) is the energy of the slab without the CO adsorbate but includes \(n\) OH ions, and \(E_{\text{CO}}\) is the CO energy in gas phase without the catalyst. The CO-CO coupling energy barrier is calculated according to the following reaction and the corresponding reaction free energy:
\[ ^\circ OCCO = ^\circ CO + ^\circ CO \]  
\[ E_{C-O CO}^{\text{ coupling barrier}} = E_{OCCO}^{\text{ coupling barrier}} - (E_{CO}^{\text{ coupling barrier}} + E_{CO}^{\text{ coupling barrier}}) \]

In our simulations, 0, 1 and 2 OH are considered on a surface of 16 (4×4) copper atoms, corresponding to 0, 1/16 and 2/16 ML concentrations, respectively. However, in configurations where OH is very close to the adsorbed CO, it is assumed that the OH concentration is even higher and forced to be very close to the adsorbates, and the local minima is calculated in this case. These cases are virtually described by 3/16 and 4/16 ML in Figure 5-1. Otherwise, in 0, 1/16 and 2/16 ML concentrations, the configuration with the global minima energy is the reference for our calculations. This includes all possible configurations for OH as adsorbed on the surface or as being in the vacuum just above the surface. The DFT energy of the optimized configurations with the global minimum energies are tabulated in Table 5-2. CO adsorption energies and the CO-CO coupling energy barriers are also mentioned in Table 5-3.

From Figure 5-1 and the data in Table 5-3, we see that CO-CO coupling energy barrier decreases with increasing OH concentration. It is found that increasing the OH concentration on the slab surface implicitly changes the charge density of the C atoms in adsorbed CO and OCCO, such that CO bonding becomes weaker and CO-CO coupling becomes stronger and more favorable. On the (100) surface, for instance, CO without any OH is adsorbed on the hollow site with four bonds to the surrounding copper ions. However, increasing the OH concentration pushes CO to the bridge site with two folds bonding and weaker binding energy. This bonding becomes even weaker as OH is further added to the surface, such that OH in the vicinity pushes CO to the top site with one fold bonding. The same trend is observed on two other facets. Table 5-2 demonstrates this situation on (100).

In general, we conclude that at higher OH concentrations CO bonding is weaker and this might lead to either more CO in gaseous products and easier CO-CO coupling. Indeed, both are shown under experimental conditions. We calculated the electronic charge density on each ion by Bader charge analysis. As demonstrated in Figure 5-6, we see that increasing the OH concentration, not only decreases the CO-CO coupling energy barrier mentioned in Figure 5-1 and Table 5-3, but also increases the charge difference between two C atoms in coupled carbon monoxides. This increased charge difference, makes a stronger intramolecular dipole and consequently more stable coupling due to the stronger ionic adsorption. The electronic charge distribution and also charge difference between two C atoms in coupled carbon monoxides, i.e. proportional to the dipole magnitude, are demonstrated in Figure 5-6.

### 5.5.2 Modeling of CO₂ diffusion into the liquid electrolyte

The diffusion layer was modeled in MATLAB using the built-in pdepe solver taking into account the interactions between CO₂, OH⁻, HCO₃⁻ and CO₃²⁻. The boundaries for the 1D simulations included a gas-liquid interface at the left boundary (x = 0 µm) and a liquid diffusion boundary layer at the right boundary (x = 500 µm) (see Figure
The catalyst layer extended from the left boundary into the electrolyte a specified distance and porosity. In all simulations, an electrochemical current distribution corresponding to a selectivity of 10% H₂, 10% CO and 80% (EtOH+C₂H₄) was assumed. The choice of selectivity affects the relative amount of CO₂ consumed per electron transferred as well as the H⁺ consumed, and subsequently, OH⁻ generated through water dissociation at the catalyst surface.

The diffusion equations used are adapted from CO₂ reduction modeling in neutral media and take into account carbonate equilibrium reactions, consumption of CO₂ and generation of OH⁻ within the catalyst layer.

\[
\frac{\partial [CO_2]}{\partial t} = D_{CO_2} \frac{\partial^2 [CO_2]}{\partial x^2} - [CO_2][OH^-]k_{1f} + [HCO_3^-]k_{1r} - R_{CO_2} \quad (5.54)
\]

\[
\frac{\partial [HCO_3^-]}{\partial t} = D_{HCO_3} \frac{\partial^2 [HCO_3^-]}{\partial x^2} + [CO_2][OH^-]k_{1f} - [HCO_3^-]k_{1r} - [HCO_3^-][OH^-]k_{2f} + [CO_3^{2-}]k_{2r} \quad (5.55)
\]

\[
\frac{\partial [CO_3^{2-}]}{\partial t} = D_{CO_3^{2-}} \frac{\partial^2 [CO_3^{2-}]}{\partial x^2} + [HCO_3^-][OH^-]k_{2f} - [CO_3^{2-}]k_{2r} \quad (5.56)
\]

\[
\frac{\partial [OH^-]}{\partial t} = D_{OH^-} \frac{\partial^2 [OH^-]}{\partial x^2} - [CO_2][OH^-]k_{1f} + [HCO_3^-]k_{1r} - [HCO_3^-][OH^-]k_{2f} + [CO_3^{2-}]k_{2r} + R_{OH} \quad (5.57)
\]

The consumption of CO₂ and generation of OH⁻ within the catalyst layer is assumed to occur homogeneously throughout such that:

\[
R_{CO_2} = \begin{cases} \frac{F}{n_e H_2} \left( \frac{F_e H_2}{n_e H_2} + \frac{F_e CO}{n_e CO} \right) \frac{\varepsilon}{L_{catalyst}}, & 0 \leq x \leq L_{catalyst} \\ \frac{F}{n_e C_2H_4} \frac{\varepsilon}{L_{catalyst}} & x > L_{catalyst} \end{cases} \quad (5.58)
\]

\[
R_{OH} = \begin{cases} \frac{F}{n_e CO} \frac{\varepsilon}{L_{catalyst}}, & 0 \leq x \leq L_{catalyst} \\ \frac{F}{n_e C_2H_4} \frac{\varepsilon}{L_{catalyst}} & x > L_{catalyst} \end{cases} \quad (5.59)
\]

where the catalyst length, L_{catalyst}, and catalyst porosity, ε, are predefined. A porosity of 60% was chosen in all scenarios. All equilibrium and rate constants are calculated as a function of temperature and salinity as discussed previously.

The left boundary condition for Eq. 1 was set as the solubility limit of CO₂ in a specified bulk KOH concentration assuming a partial pressure of 1 atm and temperature of 298 K at the gas-liquid interface. The maximum solubility of CO₂ in KOH electrolyte was modeled using Henry’s constant and the Sechenov equation to account for ‘salting out’ effects (Figure 5-7b). A no-flux boundary condition was applied for CO₂ at the right-hand boundary. For OH⁻, HCO_3⁻ and CO_3^{2-} no-flux boundary conditions were applied at the left boundary while the concentrations at the right boundary were set to the equilibrium values in the specified bulk KOH concentration.
Simulations were performed by prescribing current density, selectivity, bulk KOH concentration and catalyst layer thickness. The concentration of CO\textsubscript{2} as a function of electrolyte penetration depth from the left-hand boundary could then be found for a variety of inputs as shown in Figure 5-2 and Figure 5-7. Average CO\textsubscript{2} concentrations presented in Figure 5-2 correspond to the average CO\textsubscript{2} concentration across the prescribed catalyst layer thickness. As seen in Figure 5-7c the KOH media is particularly parasitic to CO\textsubscript{2} and is neutralized by OH\textsuperscript{-} well before the 500 µm liquid diffusion boundary.

5.5.3 Material Synthesis

The Freudenberg (Fuel cell Store) gas diffusion layer (GDL) was used as substrate to evaporate Cu (99.99%) and Ag (99.99%) using Angstrom Nexdep Evaporator. The deposition was performed in \(\sim 10^{-5}-10^{-6}\) Torr at 1.5 Å/sec. The thicknesses of the Al1, Al2 and DI1 samples were 10 nm, 25 nm, and 1000 nm, respectively. The thickness of Al-Ag was 50 nm. The DI2 and DI-Ag samples were prepared by drop-casting commercial Cu and Ag nanoparticles (Sigma-Aldrich, particle size smaller than 100 nm). The nanoparticles were first dispersed in a mixture of isopropanol, water and Nafion solution (50 microliter of Nafion solution in 1 mL of 3:1 isopropanol:water mixture). The mixture was then sonicated for 1 hour to produce Cu and Ag nanoparticle inks. The Cu and Ag catalysts were painted on the gas diffusion layer and dried overnight at room temperature. Silver nanoparticles were deposited on gas diffusion layer using the same procedure as for Cu nanoparticles.

5.5.4 Material Characterization

The morphologies of the prepared electrodes were investigated using Scanning Electron Microscopy (SEM) on a Hitachi SU-8230 apparatus and Transmission Electron Microscopy (TEM) on a Hitachi HF-3300 instrument with an acceleration voltage of 200 kV. Cross-sectional elemental mapping was performed using a Hitachi CFE-TEM HF3300, the Cu coated GDL sample was prepared using Hitachi Dual-beam FIB-SEM NB5000. Briefly, a slice (~50-100 nm thick) of Cu coated GDL was cut using Ga-beam and attached with a TEM stage with tungsten deposition and lifted out for subsequent STEM-EDX analysis.

The structural characteristics of the Cu electrodes were measured by powder X-ray diffraction at room temperature on a MiniFlex600 instrument with a copper target (\(\lambda = 1.54056\) Å). The oxidation state and compositions of the samples were studied by X-ray photoelectron spectroscopy (XPS) (model 5600, PerkinElmer). The binding energy data were calibrated with reference to the C 1s signal at 284.5 eV. The Cu loading on the gas diffusion layer was characterized using an inductively coupled plasma optical emission spectrometer (ICP-OES, Agilent Dual-View 720 with a charge-coupled device (CCD) detector for full wavelength coverage between 167 nm and 785 nm).

5.5.5 CO\textsubscript{2} Reduction

Electroreduction for the main figure results were performed in a flow cell configuration consisting of a gas diffusion layer, anion exchange membrane and nickel mesh anode (Figure 5-2a). In both the Abrupt Interface (AI) and Distributed Interface (DI) cases a catalyst was deposited on top of the microporous side of the
Freudenberg gas diffusion layer. The combined catalyst and diffusion layer, anion exchange membrane and nickel anode were then positioned and clamped together using PTFE spacers such that a liquid electrolyte could be introduced into the chambers between the anode and membrane as well as the membrane and the cathode. Gaseous CO₂ could then be passed behind the gas diffusion layer and diffuse into the liquid electrolyte present at the catalyst. In the catholyte stream a port drilled into the PTFE spacer is present for a Ag/AgCl reference electrode to be positioned a specific distance from the working electrode.

All CO₂ reduction experiments were performed using an electrochemical workstation (Autolab PGSTAT302N) with a Ag/AgCl reference (with 3 M KCl as the filling solution). Electrode potentials after iR compensation were rescaled to the reversible hydrogen electrode (RHE) reference by \( E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.197 \text{ V} + 0.0591 \times \text{pH} \). All potentials reported here were obtained by averaging over a timespan of at least 150 s for each applied current. The electrolytes (KOH solution of various concentrations, 100 mL) were circulated through the electrochemical cell using peristaltic pumps. The electrolyte flow was kept at 10 mL min⁻¹. The CO₂ (Linde, 99.99%) flow was kept constant at 50 mL min⁻¹ using a mass flow controller. All CO₂ reduction experiments were performed under galvanostatic mode. The reactions were run for at least 150 s before the gas products were collected for analysis.

The gas products from CO₂RR (CO, H₂, CH₄ and C₂H₄) were analyzed using a gas chromatograph (PerkinElmer Clarus 680) coupled with a thermal conductivity detector (TCD) and a flame ionization detector (FID). The gas chromatograph was equipped with a Molecular Sieve 5A capillary column and a packed Carboxen-1000 column. Argon (Linde, 99.999%) was used as the carrier gas. The liquid products were quantified using Nuclear magnetic resonance spectroscopy (NMR). \(^1\)H NMR spectra of freshly acquired samples were collected on Agilent DD2 500 spectrometer in 10% D₂O using water suppression mode, with Dimethyl sulfoxide (DMSO) as an internal standard. Sixteen second relaxation time between the pulses was used to allow for complete proton relaxation.

The CO₂ reduction experiments using Cu catalysts (AI1, AI2, DI1, DI2) were also performed in an H-cell configuration as controls. The electrolytes for both the cathode and anode in this case were 0.1 KHCO₃. CO₂ gas was bubbled through the catholyte for at least 30 min to saturate the electrolyte with CO₂. The reactions were performed under potentiostatic mode with the potential range of -1.6 to -2 V vs RHE (without iR correction). The CO₂ flow was controlled at 30 mL min⁻¹. The gas and liquid products were analyzed after 1 hour of reaction using gas chromatography and NMR as described above.
Figure 5-5 | Effect of OH on adsorbed OCCO intermediate. Oxidation states (charge density) of the adsorbed OCCO elements and the adjacent copper as calculated by Bader charge analysis. Oxidation states on (100), (110) and (111) facets of copper, without OH, with one and two OH are shown for the most stable configurations.

Figure 5-6 | Effect of OH on CO binding energy and C-C charge difference. (a) CO adsorption energy on (100), (110) and (111) facets of copper at different OH concentrations. (b) Charge differences of two carbons in adsorbed OCCO on three different facets of copper and at different OH concentrations. (c, d) Electron charge density and the optimized configuration of the adsorbed CO with no OH and one OH on Cu(100). (e, f) Electron charge density and the optimized configuration of the adsorbed OCCO with no OH and one OH on Cu(100). The charge difference between two carbons and the induced dipole in presence of OH is shown in (f).
Figure 5-7 | Modeling of the gas-liquid diffusion interface. (a) Schematic of the modeled gas-liquid interface where CO\textsubscript{2} reduction occurs on the red catalyst. (b) Maximum CO\textsubscript{2} solubility in various bulk KOH concentrations due to ‘salting out’ effects. (c) CO\textsubscript{2} diffusion into various KOH concentrations without catalyst or CO\textsubscript{2} reduction \((j = 0 \text{ mA cm}^{-2})\). (d) OH distribution in the liquid diffusion layer at a current of 250 mA cm\(^{-2}\), (e) CO\textsubscript{2} distribution throughout a 1000 nm thick catalyst layer at a current of 250 mA cm\(^{-2}\), (f) CO\textsubscript{2} distribution throughout a 100 nm thick catalyst layer at a current of 250 mA cm\(^{-2}\). Model assumes a selectivity distribution of 10% H\textsubscript{2}, 10% CO and 80% C\textsubscript{2} products, catalyst porosity of 60% and liquid diffusion thickness of 500 \(\mu\text{m}\).

Figure 5-8 | Cross-section characterization of Al2 electrode. Structural and compositional analysis technique using a focused ion beam (FIB) system and scanning transmission electron microscope (STEM). (a) Cross-section STEM of sample Al2. The fill region shows the roughness of the reaction interface where Cu is deposited. Elemental mapping for Carbon (c) and Cu (d) and overlap of all elements (b) on the cross-section mode of Al2. W was used to protect the surface during sample preparation using FIB.
Figure 5-9 | Chemical and physical characterization of Cu catalysts. (a) Cu 2p and (b) O 1s XPS spectra of the samples showing the presence of metallic and oxide phases on the surface of all AI1, AI2 and DI1 samples. (c) XRD diffraction patterns of AI1, AI2 and DI1 samples showing the co-existence of both oxide and metallic phases.

Figure 5-10 | Characterization of DI2 catalysts. (a, b) SEM images showing the size of Cu nanoparticles used in the D12 sample (around 50 nm). (c) Cu 2p and (d) O 1s XPS spectra of the sample showing the presence of oxide phase on the surface of Cu nanoparticle.
Figure 5-11 | Performance of Cu catalysts in 10 M KOH electrolyte. Faradaic efficiency for CO (a); H2 (b) and CH4 (c) on AI1, AI2, DI1, and DI2 catalysts using 10 M KOH electrolyte in the current range of 200 to 300 mA cm−2. (d) Faradaic efficiency for ethanol and acetate on the catalyst at the optimum current density for ethylene: AI1 (250 mA cm−2); AI2 (275 mA cm−2); DI1 and DI2 (225 mA cm−2).

Figure 5-12 | Representative NMR spectra of the liquid products. NMR spectrum of the reaction products obtained upon CO2RR on AI2 sample at current density of 275 mA cm−2 using 10 M KOH electrolyte. (a) full spectrum (largest singlet at 2.71 ppm corresponds to the reference DMSO signal, while noisy part around 4.60 ppm is due to suppressed water signal); (b) magnified portion of the spectrum demonstrating ethanol and acetate product peaks; (c) magnified portion of the spectrum demonstrating the formation of a small amount of formate.
Figure 5-13 | Performance of Cu catalysts in an H-cell configuration. Faradaic efficiencies for gas products in the potential range of -1.6 to -2 V vs RHE (without iR correction) for AI1 (a); AI2 (b); DI1 (c); and DI2 (d). The electrolyte was 0.1 M KHCO₃ for all runs.

Figure 5-14 | Effect of CO₂ concentration on CO₂RR selectivity. CO₂ reduction selectivity on the AI2 sample at CO₂ gas concentration of 25, 50, 75 and 100%.
Figure 5-15 | Performance of the Al2 catalyst in low concentration KOH electrolyte. C2H4 Faradaic efficiency of the Al2 sample in 1 M KOH electrolyte at various current densities.

Figure 5-16 | High performance CO2RR on an abrupt reaction interface sample. (a) Optimal C2 selectivity on the Al2 sample using 10 M KOH (at 275 mA cm⁻²); 5.5 M KOH (at 500 mA cm⁻²); 3.5 M KOH (at 750 mA/cm²). (b) Applied potentials (iR corrected) at different current densities on the Al2 sample using an optimized electrolyte for high C2H4 selectivity: 10 M KOH (at 275 mA cm⁻²); 5.5 M KOH + 4 M KI (at 500 mA/cm²); and 3.5 M KOH + 5 M KI (at 750 mA/cm²). The corresponding C2H4 Faradaic efficiency to Extended Data Figure 12b is shown in Figure 4a of the manuscript.
Figure 5-17 | SEM characterization of Ag catalyst. AI-Ag (a, b) and DI-Ag (c, d).

Figure 5-18 | CO\textsubscript{2}RR performance of the AI-Ag catalyst. (a) CO partial current density and, (b) CO Faradaic efficiency at different potentials. The electrolyte is 2 M KOH.
Table 5-1 | Summary of CO$_2$RR to C$_2$H$_4$ performance on different catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>C$_2$H$_4$ onset potential (V vs RHE)</th>
<th>$J$(C$_2$H$_4$) mA cm$^{-2}$</th>
<th>C$_2$H$_4$ Faradaic efficiency (%)</th>
<th>C$_2$H$_4$ energy conversion (%)$^{(a)}$</th>
<th>C$_2$H$_4$ mass activity (A mg$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma-Oxidized Cu</td>
<td>-0.6</td>
<td>12</td>
<td>60</td>
<td>33</td>
<td>-</td>
<td>Reference$^{23}$</td>
</tr>
<tr>
<td>Plasma-Cu Nanocubes</td>
<td>-0.6</td>
<td>16</td>
<td>40</td>
<td>25</td>
<td>-</td>
<td>Reference$^{53}$</td>
</tr>
<tr>
<td>N-doped graphene dots</td>
<td>-0.45</td>
<td>40</td>
<td>33</td>
<td>18</td>
<td>0.08</td>
<td>Reference$^{46}$</td>
</tr>
<tr>
<td>Cu nanostructure</td>
<td>~ -0.3</td>
<td>100</td>
<td>40</td>
<td>23</td>
<td>0.33</td>
<td>Reference$^{134}$</td>
</tr>
<tr>
<td>Cu nanodendrites</td>
<td></td>
<td>97</td>
<td>55</td>
<td>28</td>
<td>-</td>
<td>Reference$^{22}$</td>
</tr>
<tr>
<td>Cu nanoparticles</td>
<td>-0.36</td>
<td>150</td>
<td>36</td>
<td>23</td>
<td>0.15</td>
<td>Reference$^{21}$</td>
</tr>
<tr>
<td>AFSI-Cu</td>
<td>-0.18</td>
<td>500</td>
<td>66</td>
<td>40</td>
<td>17.8</td>
<td>This work</td>
</tr>
<tr>
<td>AFSI-Cu</td>
<td>-0.18</td>
<td>184</td>
<td>67</td>
<td>44</td>
<td>6.7</td>
<td>This work</td>
</tr>
</tbody>
</table>

(a) C$_2$H$_4$ energy efficiency is calculated for the half-cell (i.e. assuming the overpotential of the oxygen evolution reaction is zero). C$_2$H$_4$ energy efficiency = (1.23 + (-E$_{C2H4}$))$^*$FE(C$_2$H$_4$)/(1.23 + (-E)), where E is the applied potential vs RHE; $E_{C2H4} = 0.08$ V is thermodynamic potential (vs RHE) of CO$_2$ reduction to ethylene; FE(C$_2$H$_4$) is the measured C$_2$H$_4$ Faradaic efficiency in percentage.
Table 5-2 | Ground state energy of the adsorbates on three different facets of the copper

<table>
<thead>
<tr>
<th>Adsorbates</th>
<th>111</th>
<th>100</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-14.767</td>
<td>-14.767</td>
<td>-14.767</td>
</tr>
<tr>
<td>Cu</td>
<td>-247.790</td>
<td>-243.406</td>
<td>-299.709</td>
</tr>
<tr>
<td>Cu-OH</td>
<td>-258.531</td>
<td>-254.334</td>
<td>-310.672</td>
</tr>
<tr>
<td>Cu-2OH</td>
<td>-269.182</td>
<td>-265.208</td>
<td>-321.635</td>
</tr>
<tr>
<td>Cu-CO</td>
<td>-263.479</td>
<td>-259.149</td>
<td>-315.372</td>
</tr>
<tr>
<td>Cu-CO-OH</td>
<td>-274.225</td>
<td>-270.036</td>
<td>-326.168</td>
</tr>
<tr>
<td>Cu-2CO</td>
<td>-279.154</td>
<td>-274.791</td>
<td>-331.114</td>
</tr>
<tr>
<td>Cu-2CO-2OH</td>
<td>-300.390</td>
<td>-296.602</td>
<td>-352.896</td>
</tr>
<tr>
<td>Cu-OCCO</td>
<td>-277.486</td>
<td>-273.830</td>
<td>-329.684</td>
</tr>
<tr>
<td>Cu-OCCO-2OH</td>
<td>-298.934</td>
<td>-295.757</td>
<td>-351.496</td>
</tr>
</tbody>
</table>

Table 5-3 | CO adsorption energy and C-C coupling energy barrier on three different facets of copper at different OH concentrations

<table>
<thead>
<tr>
<th>OH Concentration</th>
<th>CO adsorption energy (eV)</th>
<th>CO-CO coupling energy barrier (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>111</td>
<td>100</td>
</tr>
<tr>
<td>0</td>
<td>-0.922</td>
<td>-0.976</td>
</tr>
<tr>
<td>1/16</td>
<td>-0.927</td>
<td>-0.935</td>
</tr>
<tr>
<td>2/16</td>
<td>-0.936</td>
<td>-0.924</td>
</tr>
<tr>
<td>3/16</td>
<td>-0.686</td>
<td>-0.919</td>
</tr>
<tr>
<td>4/16</td>
<td>-0.556</td>
<td>-0.823</td>
</tr>
</tbody>
</table>
### Table 5-4 | Physical properties of KOH electrolyte and its effect on the $\text{C}_2\text{H}_4$ onset potential and Tafel slope

<table>
<thead>
<tr>
<th>KOH concentration (M)</th>
<th>Resistance (Ω) (a)</th>
<th>Surface pH (b)</th>
<th>$\text{C}_2\text{H}_4$ onset potential (V vs RHE) (c)</th>
<th>Tafel slope (mV per decade) (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.58</td>
<td>12.40</td>
<td>-0.48</td>
<td>150</td>
</tr>
<tr>
<td>5</td>
<td>1.08</td>
<td>14.48</td>
<td>-0.29</td>
<td>112</td>
</tr>
<tr>
<td>10</td>
<td>0.98</td>
<td>14.94</td>
<td>-0.18</td>
<td>65</td>
</tr>
<tr>
<td>15</td>
<td>1.32</td>
<td>15.16</td>
<td>-0.20</td>
<td>95</td>
</tr>
</tbody>
</table>

(a): Measured using electrochemical impedance spectroscopy (EIS); (b) Calculated in the diffusion model taking into account the effect of CO$_2$ gas in the catalyst layer; (c) The potential at which the catalyst shows an ethylene faradaic efficiency of 0.5%; (d) Calculated based on the experimental C$_2$H$_4$ partial current densities.
Chapter 6.

Self-assembled Nanoparticle-Stabilized Photocatalytic Reactors

This chapter was published as a journal article in *Nanoscale* and Reproduced from [6] with permission from The Royal Society of Chemistry. The candidate was the first author in this work and played the primary role in designing the research, performing the experiments, analyzing the data, and writing the paper. Additional authors for the work include Dr. Jason Riordon, Dr. Cao-Thang Dinh, Prof. Edward H. Sargent, and Prof. David Sinton. Their contributions were central to the publication of this work and are gratefully acknowledged and appreciated.

6.1 Introduction

Photocatalysis takes advantage of the solar resource to produce electron-hole pairs that are transferred to an adsorbed species to carry out a desired chemical reaction.\(^{148}\) Nanoparticles and nanostructures play an essential role in advanced photocatalysis processes by presenting multi-functional catalyst surfaces having desirably large areas. Important applications include decontamination of pollutants present in water\(^{149-152}\), sterilization of organic matter\(^{153}\), water-splitting\(^{154,155}\) and solar fuel production from carbon dioxide.\(^{73,156,157}\) Photocatalysis research efforts to date have largely been aimed at developing highly photoactive materials\(^{158}\), and at designing novel nanostructured scaffolds, such as nanorods\(^{159}\), nanotubes\(^{160}\) and thin films\(^{161}\) which facilitate electron-hole pair transport and maximize reagent-photocatalyst interactions. Rapid advances in the performance of nanoscale-engineered photocatalysts now necessitate progress on low-cost, highly scalable reactors and robust strategies to leverage them.

Existing photocatalytic systems include those that use an immobilized photocatalyst and photocatalytic slurry reactors. In immobilized systems, nanostructured photocatalysts are supported on a macroscopic substrate which can be designed to improve charge kinetics and grow unique nanostructures. The fixed structure further permits continuous use of the photocatalysts without the need for particle separation near the output of the reactor. Favourable substrate based charge kinetics, however, are offset by low surface to volume ratios, which limits mass transport of reagents to the photocatalyst surface. Non-planar structures and stronger mixing can negate this issue but become prohibitive at larger scales. In addition, immobilized photocatalysts are susceptible to abrasion and substrate separation in liquid reaction environments.\(^{162,163}\) Further, electrical and thermal deposition of the catalyst onto a substrate, followed by annealing processes between 300°C and 600°C\(^{164}\), requires more energy per unit of catalyst than the mass-production of the base nanostructures by either sol-gel or hydrothermal processes.\(^{165}\)
The use of nanoparticle suspensions in a photocatalytic slurry reactor avoids these issues by directly dispersing mass-produced nanostructures in water. In the suspension approach, it is the dispersion and retention of the photocatalysts, and the associated energy and infrastructure required for mixing and filtering, that limit overall energy conversion and storage performance, as well as compromising cost-effectiveness. In addition, the operating conditions of aqueous suspensions are limited to ranges in which the working photocatalytic nanostructures have sufficiently high zeta potentials to prevent coagulation and a subsequent loss of catalyst surface area. As redox energy levels are pH-dependent, the dispersible range of the material must also align with the thermodynamics of the desired reaction.

The addition of secondary non-photocatalytic materials to reactors has allowed for the creation of flexible and unique means of deploying photocatalysts. Solidified lipid droplets and polystyrene beads have been used as mechanical anchors for TiO$_2$ while photocatalysts deposited onto solid magnetic cores have given particles magnetic properties; all of which have aided in catalyst recovery. Polystyrene microspheres have also acted as an anchor for the growth of ZnO nanowires while subsequent modification of the surface wettability allowed for tunable dispersion in both polar and non-polar media without aggregation. As an alternative to solid substrates, secondary materials have also been used to form emulsions, in which two fluid phases are stabilized by the permanent adsorption of solid particles to the fluid-fluid interface. These particle-stabilized emulsions, or Pickering emulsions, are self-assembling and can last for years. With catalytically-active nanoparticles positioned at the interface, Pickering emulsions can be leveraged for reactant/product separation, as was demonstrated in catalytic biofuel production within a carbon nanotube matrix. Emulsions formed by incorporating nanotube and titanate emulsifiers have been combined with photocatalysts, but the emulsifiers were found to hinder light absorption. In another work, oil-in-water and water-in-oil Pickering emulsions were formed by intercalating organic cations into a layered niobate semiconductor. In all of these reactor strategies, however, photocatalysts must be paired with secondary, non-participating materials for emulsion stabilization or to provide other physical benefits.

In this work, we introduce the Self-assembled Nanoparticle-stabilized Photocatalytic Reactor (SNPR), a photocatalytic reactor comprised only of photocatalysts and fluids. By tuning particle wettability, we permanently adsorb photocatalytic nanoparticles to a fluid-fluid interface which functions as a high surface area substrate. We create oil-in-water emulsions, water-in-oil emulsions and, for the first time, CO$_2$-in-water foams which are readily usable in water decontamination, CO$_2$ reduction and oil-spill remediation applications. By comparing the photoactivity of our SNPR to a fixed-photocatalyst reactor and an aqueous suspension, we demonstrate that the SNPR addresses the limitations of both without the addition of secondary materials. Specifically, the ability to control the distribution of catalyst in the system allows for photocatalyst to be used in high throughput continuous reactors without filters, pumps or risk of environmental contamination. Finally, we quantify photoactivity of individual microreactor droplets, and demonstrate photocatalytic degradation reactions in both the continuous and dispersed phases. Taken together, our results demonstrate the operational benefits and versatility of using a nanoparticle-stabilized photocatalytic reactor for solar energy applications.
6.2 Results and Discussion

6.2.1 Photocatalytic nanoparticle-stabilized emulsions and foams

TiO$_2$ nanoparticles 21 nm in diameter were added to an aqueous mixture containing hexylamine - an amphiphile - and caused the originally hydrophilic TiO$_2$ nanoparticles to exhibit mixed wettability. The suspension was agitated in the presence of either oil, air or CO$_2$, and caused the nanoparticles to adsorb at the fluid interface, creating stable Pickering emulsions and foams (for synthesis, see Experimental Methods). The amphiphile used in this study, hexylamine, features a short carbon chain with an active bonding group compatible with the predominant hydroxyl group on the photocatalyst’s surface. For materials with different surface chemistries the active group on the end of the short carbon-chain amphiphile can be changed to match the material. This method extends readily to other oxide-based materials, nanostructures and combinations of polar and non-polar fluids. Using this approach, photocatalytic nanoparticles were used to stabilize oil-in-water, water-in-oil and CO$_2$-in-water SNPRs (Figure 6-1).

The content of the dispersed and continuous phases was controlled by adjusting the relative volumes of oil and water as well as by adjusting the wettability of the nanoparticles. Since the nanoparticles were originally dispersed in the aqueous phase, an oil-in-water emulsion is initially favoured. To create the reverse scenario, the amphiphile concentration was increased until wettability favoured the oil phase, and nanoparticles transitioned from water to oil. In both cases, once the wetting conditions were established, simple stirring generated the bulk emulsions. The size distribution of a stabilized emulsion follows a log-normal distribution (Figure 6-2a-c). The average drop diameter was increased from 10 µm to 20 µm by decreasing the amphiphile concentration.

![Figure 6-1](image-url) | Self-assembled Nanoparticle-stabilized Photocatalytic Reactors (SNPRs). (a) Schematic of a photocatalytic oil-in-water emulsion process for degrading organic contaminants. (b) A schematic of an oil-in-water emulsion. (c) An oil-in-water emulsion microscope image. (d) An oil-in-water emulsion floating on the surface of water containing methylene blue dye. (e) A schematic of a water-in-oil emulsion. (f) A water-in-oil emulsion microscope image. (g) A water-in-oil emulsion where the oil phase is dyed with Nile red. (h) A schematic of a CO$_2$-in-water foam. (i) A CO$_2$-in-water foam microscope image. (j) An undiluted CO$_2$-in-water foam. Images (c), (f) and (i) use a scale bar length of 50 µm.
concentration tenfold. The result is an all-fluid emulsion and foam reactor stabilized exclusively by photocatalytically-active nanoparticles.

After formation, the oil-in-water emulsions were diluted to remove excess nanoparticles and oil in the continuous phase. Monitoring the diluted emulsions over a three month period showed that the volume of the emulsions remained the same with zero accumulation of nanoparticles in the bottom of the container. Additionally, there was no change observed in the average droplet size or distribution, which indicated a strong resistance to coalescence and destruction of the formed emulsions. Furthermore, affixing nanoparticles to the micro-droplets prevented the permanent coagulation of individual nanostructures over the full range of pH values tested (3 – 11). In contrast, loose nanoparticles in suspension aggregate quickly over time in unfavourable chemical conditions causing a reduction in catalyst surface area over time. While the coagulation and intentional sedimentation of photocatalytic nanostructures can be used as a means of separation, this process requires both time and chemical alteration which has rendered such processes impractical for both batch and continuous operations. Finally, the CO$_2$-in-water foams also showed resistance to gas diffusion into and out of the bubbles as confirmed by the presence of CO$_2$ in the bubbles one week after formation.

A diluted oil-in-water emulsion was dried for 24 hours in air on carbon tape and imaged using a scanning electron microscope (SEM) as shown in Fig. 3. As the water surrounding the droplets evaporated the oil dispersed on the carbon tape, leaving the remaining hollow TiO$_2$ spheres. Some hollow spheres have visible
cracks which are artefacts of the drying process. The TiO$_2$ nanoparticles form a dense photocatalyst layer at the interface (Figure 6-3b).

The SNPRs self-assemble at the microscale, and were readily produced in macroscale quantities by increasing the amount of nanoparticles, amphiphiles and fluids (Figure 6-7). The cost of the amphiphiles needed to form the SNPR is below 1% of the cost of TiO$_2$ photocatalyst (8 µL/g of emulsified TiO$_2$) and the electrical energy input cost of mixing the suspension is negligible (below $0.01/kg of emulsified TiO$_2$). The entire cost of manufacturing the SNPR is then directly proportional to the nanoparticles themselves with no significant structural material or energy inputs. The high stability, suspendability and scalability of the SNPR provides a reactor strategy which is readily applicable to large scale solar photocatalytic applications, such as organic water decontamination, where the unique mechanical system properties can be leveraged to reduce both costs and complexity as compared to existing systems.

6.2.2 Reactor performance in batch and continuous flow conditions

As incident solar energy is widely dispersed, commercial solar photocatalysis will require large areas and reactors that can operate with minimal additional equipment, materials and energy. We tested the performance

![Figure 6-3](image-url)  
Figure 6-3 | (a) SEM images of nanoparticle-stabilized oil-in-water droplets that were dried in air on carbon tape. (b) A dried oil-in-water droplet whose TiO$_2$ shell cracked during the drying process allowing the release of the oil originally contained inside. The scale bars represent 1 µm.
We compare the performance of the SNPR to that of a model fixed-photocatalyst reactor made of sedimented photocatalytic nanoparticles. Each reactor was composed only of photocatalysts and fluids, and was operated in a batch reactor process under the conditions shown in Figure 6-4a. A fixed volume of reactant and catalyst were present and the change in concentration of the reactant was measured over time as it was photocatalytically degraded (Figure 6-4b). Mild surface agitation was sufficient to disperse the SNPR throughout the upper portion of the reactor volume while the sedimented nanoparticles remained stationary. The resulting degradation rate constants were 0.025 s$^{-1}$ and 0.011 s$^{-1}$ for the SNPR and the fixed-photocatalyst reactor, respectively, which represents a 2.2-fold improvement in the reaction rate of the SNPR under otherwise similar conditions. In this scenario the degradation rate of the fixed-photocatalyst reactor was limited by mass transport of methylene blue to the catalyst surface, while the dispersed emulsion avoided this loss. As discussed further in the Experimental Methods, both reactors are also light limited due to the high UV absorption of TiO$_2$, which limits the improvement to the 2.2-fold observed here.

The SNPR was then compared to an aqueous suspension of nanoparticles which has a similar ability to be dispersed among the reactants. In a batch reactor process, when the systems were fully agitated both the nanoparticles and the SNPR were fully dispersed throughout the container (Figure 6-5a.). The subsequent degradation rate of methylene blue was found to be similar in both scenarios while using the same lighting conditions, mass of TiO$_2$ and initial methylene blue concentration (Figure 6-5b). An additional control test was
run with amphiphiles in the aqueous suspension and resulted in an identical reaction rate demonstrating that the amphiphiles are not contributing, or hindering, the reaction as can be the case with other emulsifiers.\textsuperscript{180,181} An alternative to batch reactors, continuous processes are often preferred for large scale energy and environmental operations.\textsuperscript{188} Figure 6-5c provides a schematic of the SNPR and an aqueous suspension operating in continuous mode where methylene blue is continuously injected into the top of the reactor (see Experimental Methods). Each reactor initially contained 200 mg of TiO$_2$. For the aqueous suspension, full dispersion of the photocatalytic nanoparticles required steady magnetic stirring in the bottom of the reactor to prevent sedimentation; however, nanoparticle dispersion resulted in particle loss over time through the outlet stream (Figure 6-8). The measured particle loss rate agrees well with the superimposed exponential decay curve, consistent with continuous outflow of a fully dispersed mixture. With the loss of photocatalyst, the effectiveness of the reactor decreased over time, as quantified by the methylene blue degraded each hour plotted in Figure 6-5d. In the case of the SNPR a small degree of surface agitation was sufficient to disperse the emulsion within the top 50% of the reactor. The photocatalyst-stabilized emulsion was both sufficiently robust, and buoyant, to maintain the lower portion of the reactor effectively nanoparticle-free. The resulting outlet
stream subsequently contained only reaction products, and enabled steady-state operation with no detectable loss of photocatalyst. As quantified in Figure 6-5c, the SNPR continuously degraded, on average, 96% of the dye over 20 hours while the aqueous suspension stopped entirely within the same time frame. In general, the specific rate of degradation of the aqueous suspension depends on flow rate. The flow rate and the mass of the catalyst employed here were selected such that incoming reactant was effectively completely degraded under initial experimental conditions for both cases. Importantly, the slurry reactor is subject to material loss while the SNPR retains the catalyst during operation. In an industrial setting, aqueous suspensions are run through a filter at the output stream, and a certain percentage of nanoparticles are collected and redistributed. Both the increased agitation needed to suspend the nanoparticles and the filtration/aggregation required to subsequently collect them, however, add significantly to process complexity and cost.

As photocatalysts leave the aqueous suspension in the continuous test the decrease in performance (Figure 6-5d) appears to lag behind the loss of particles (Figure 6-8). We attribute lag to two effects. First, starting with 200 mg of TiO$_2$, the photocatalyst was initially in excess and thus early particle loss did not significantly negatively affect performance. Second, the volume of the reactor presents an inherent lag due to dilution, with a timescale on the order of 2 hours ($\tau \sim$ volume / flow rate) (see Experimental Methods). Collectively these results demonstrate the SNPR as a continuous photocatalytic reactor strategy, free of the expense of separation and filtration requirements of aqueous suspensions. Additionally, the reduced energy requirements of surface agitation over stirring of the entire reactor are a benefit that scales with reactor size. The floatability and scalability of the reactor would further enable use in large natural or man-made bodies of open water.

### 6.2.3 Photocatalytic reactions in nanoparticle-stabilized droplets

Droplets are the functional units of this photocatalytic reactor strategy with the fluid interface providing the role of a high surface area substrate. We assessed the photocatalytic properties of individual droplets by imaging the photocatalytic degradation of Nile red and fluorescein dyes. Figure 6-6a shows the degradation of Nile red dye within the oil phase of photocatalyst-stabilized oil-in-water droplets under UV excitation. The three droplets were irradiated over a period of 40 s. Over this period, the dye adsorbed to the photocatalyst and was degraded via the photogenerated charge species present on the surface.

By measuring the degradation rate locally using fluorescence, we quantify several characteristics of these droplet microreactors. First, the average decrease in dye concentration inside a droplet followed first-order reaction kinetics, which is anticipated for the degradation of a single reactant on a photocatalyst (Figure 6-9). Second, as shown in Fig. 6b for a 112 μm diameter droplet, the degradation rate varied along the radius. Specifically, the dye degradation rate was 25% faster at the interface ($r/R = 1$) than at the centre of the droplet ($r/R = 0$) (Figure 6-10). As dye degradation occurs only on the nanoparticle’s surface located at the fluid-fluid interface, the concentration of Nile red within the droplet decreases with radial diffusion within the relatively viscous oil. In the reverse emulsion case, water-in-oil droplets, no radial dependence on the degradation rate
was detected (Figure 6-10). In contrast to the oil case, dye diffusion within the water droplet is much faster (~50 times based on Stokes-Einstein relation), and the concentration profiles are effectively flat. The dependency of droplet radius on degradation rate was also analysed. Figure 6-6c shows the individual degradation rates for a population of droplets with radii varying from 5 – 43 μm. These individual reaction rates correspond well to the plotted inverse relationship expected for the case of uniform nanoparticle distribution on the surface of a droplet. As the radius of a droplet increases, the ratio of catalyst on the surface relative to the volume of dye decreases. In previous studies this is described as an essential parameter for degradation in the dispersed phase. Our ability to fabricate droplets with a diameter as small as 5 µm without the use of light-hindering emulsifiers represents the largest demonstrated catalyst-to-contaminant ratio for this type of system. A typical 10 μm droplet, with a uniform particle surface coverage of 80%, contains on the order of 1 million nanoparticles which represents a catalyst-to-liquid ratio of ~3 wt%. Comparably, this particle concentration is reduced to ~0.4% for a 20 μm droplet. With reference to current photocatalysts and reaction rates, these droplet characteristics indicate that smaller droplets (i) are insignificantly affected by internal concentration gradients in dispersed reactants and (ii) increase the photocatalytic activity in the dispersed phase by maximizing the ratio of photocatalyst to reactant.

6.3 Conclusions

The disperse nature of solar radiation necessitates solar photocatalysis technologies that are functional over large areas. The SNPR presented here uses the self-assembled adsorption of photocatalytic nanoparticles to the fluid-fluid interfaces of droplets to create a reactor that has been shown to be manufactured, and scales to sufficiently large areas (>1 m²), for a cost on par with the nanostructures themselves. This reactor methodology is extendable to different materials, nanostructures and reaction mediums with further enhancements possible by leveraging the self-assembling reactor design.
In photocatalytic operation, the SNPR outperformed both a fixed-photocatalyst reactor and a dispersed aqueous suspension in batch and continuous flow-through processes similar to those that would be used for degrading organic contaminants. By shifting the substrate anchoring the photocatalyst from a solid immobilized structure to a fluid interface it was possible to form a reactor with the efficiency of an aqueous reactor whose distribution within an aqueous medium was also controllable. This substrate-free nature of the fluid SNPRs avoided the mass transfer limitations between photocatalysts and reagents, as well as the uneven light distributions of fixed-photocatalyst reactors. The design further allowed for complete recovery of the catalyst from the supernatant which not only reduces the loss of catalyst, but also avoids the negative impacts of releasing trace nanoparticles into the environment. In summary the SNPR represents an improvement in cost and operational simplicity over existing photocatalytic systems.

Further manipulation and development of the proof of concept reactor also allows for unique photocatalytic efficiency improvements. Firstly, the interfacial forces leveraged here to trap and assemble photocatalysts could be further used to assemble groups of collaborating nanoparticles with, for instance, complementary band gaps or plasmonic resonances\(^\text{190}\). The simplicity of the self-assembling process, coupled with the large available surface area of micro-droplets, would enable sizable quantities of these complex systems to be made at once. Secondly, the internal fluid phase has the potential to contribute to a desired reaction either as a source of reagents, a means to separate products\(^\text{179}\) or to assist with charge kinetics. Thirdly, with the photocatalyst rigidly positioned at the interface, surface functionalization can be done at large scales similar to that done to form Janus particles\(^\text{191}\). Finally, the properties of the emulsion reactor uniquely enable scaling over bodies of water. This approach is readily applicable to industrial reservoirs such as tailings ponds, and potentially applicable to contained areas within larger natural water bodies, the photocatalysis equivalent of aquaculture.

The self-assembled nanoparticle-stabilized photocatalytic reactor is comprised of the bare minimum of fundamental ingredients: photocatalysts and fluids. The approach has benefits over immobilized system in terms of photocatalytic efficiency, and benefits over aqueous suspensions in terms of nanoparticle dispersion and retention. We conclude that SNPRs are a robust and scalable photocatalysis strategy which presents a viable route-to-scale for photocatalytic nanomaterials.

6.4 Experimental Section

6.4.1 Materials

Aeroxide® P25 TiO\(_2\) (d = 21 nm, BET = 35-65 m\(^2\)/g) nanoparticles were donated by Evonik Industries. The amphiphilic surface modifier, hexylamine, was purchased in liquid form from Sigma-Aldrich. Paraffin oil (SG = 0.858 – 0.882, µ = 36.05 cSt @ 40 °C) was purchased from Bio Basic Inc. Sodium hydroxide (1 M) was used to alter solution pH. All pH measurements were taken using an Oakton Acorn pH 5 meter.
6.4.2 Emulsion and foam preparation

The methodology used for producing the emulsions and foam are provided elsewhere. Here, we used a particle concentration roughly 10-fold lower as we were not producing solid structures from the emulsions and foams. The oil-in-water emulsions were prepared by mixing the nanoparticles in water under constant magnetic stirring at a pH of 10.6 (1 g TiO\textsubscript{2}, 4.8 mL deionized water) followed dropwise by the amphiphiles (4 µL hexylamine, 2 mL deionized water) and then paraffin oil (9 mL). For the micro-scale tests the paraffin oil contained Nile red dye (0.021%) while no Nile red is present in the batch or continuous experiments. The suspension was then mixed for 5 min at 5,000 rpm using a stirring rod until the emulsion was formed. Once formed, excess nanoparticles not adsorbed to the oil-water interface were removed by dilution in water. The remaining suspension contained only a floating emulsion ensuring that photocatalytic reactions occurred only at the fluid-fluid interface.

Formation of water-in-oil emulsions followed a similar process. However, additional amphiphiles were required to make the particle's surface sufficiently hydrophobic. Nanoparticles were mixed in water under constant magnetic stirring at a pH of 10.6 (2 g TiO\textsubscript{2}, 11 mL deionized water) followed dropwise by the amphiphiles and fluorescent dye (120 µL hexylamine, 8 mL deionized water, 3 x 10\textsuperscript{-4}\% fluorescein dye) and then paraffin oil (15 mL). The suspension was mixed at 5,000 rpm. Oil-in-water emulsions with diameters between 10 µm and 50 µm were then observed with the phase identified via the fluorescein dye. Further amphiphiles and oil (40 µL hexylamine, 2 mL deionized water, 5 mL paraffin oil) were then added and the suspension re-stirred. The resulting water-in-oil emulsion was confirmed using a fluorescent microscope. Phase separation of excess water was observed in the macroscopic sample. This excess liquid was devoid of nanoparticles indicating that TiO\textsubscript{2} was sufficiently hydrophobic to migrate into the oil phase.

Following a similar approach, air-in-water and CO\textsubscript{2}-in-water foams were formed by dispersing particles in water at a pH of 10.6 (1 g TiO\textsubscript{2}, 6 mL deionized water) followed by amphiphiles dropwise (20 µL hexylamine, 4 mL deionized water). The entire suspension was then stirred at 5,000 rpm for 5 min in the presence of either air or CO\textsubscript{2} to form the gas-in-water foams.

6.4.3 Batch and continuous methylene blue test procedure

The fixed-photocatalyst reactor, aqueous suspension and SNPR batch reactor experiments were performed by dispersing the photocatalyst in water at a pH of 9 (45 mg TiO\textsubscript{2}, 120 mL deionized water) with methylene blue (250 µL of 2.5 mM methylene blue) in a container with a height to diameter aspect ratio of 2.7. The reactors sat in the dark for 2 hours to allow methylene blue (MB) to reach equilibrium adsorption to the catalyst surface. The reactors were then irradiated under 6 parallel 15 W black lights with a peak irradiation wavelength of 365 nm and an intensity of 2.5 mW cm\textsuperscript{2} at the sample's surface, with agitation provided by mixing or a shaker table. Every 20 min a sample was removed, filtered using a 0.22 µm syringe filter and run through a spectrometer.
Prior to the mild agitation tests both an aqueous suspension and the SNPR were agitated via shaker table for 12 hours. After this point the nanoparticles sedimented to the bottom of the reactor to form a fixed-photocatalyst reactor while the emulsion remained dispersed in the top 50% of the reactor. In both cases the same total amount of catalyst is used, however the distribution of catalyst within the reactant is superior in the SNPR case, as compared to the sedimented, fixed photocatalyst reactor. Thus the SNPR avoids the mass transport limitation inherent to the fixed photocatalyst reactor. If mass transport was the only limiting factor, the improvement would be greater than the 2.2-fold observed here, however, light is also limiting in both cases, due to the high rate of UV absorption by TiO$_2$. As a further control, an aqueous suspension containing amphiphiles in the same proportion to TiO$_2$ as the emulsion was run under similar conditions (45 mg TiO$_2$, 120 mL deionized water, 250 µL of 2.5 mM MB, 0.2 µL hexylamine). Specifically, the ratio of amphiphiles to active sites is 0.081 or 8.1 %, given 5 sites/nm$^2$ and a BET = 50 m$^2$/g. No difference in performance was seen indicating that the amphiphiles do not affect this reaction.

The continuous reactor experiments took place using the same 120 mL reaction chamber with 200 mg of TiO$_2$ photocatalyst. A syringe pump provided a constant inlet stream depositing 60 mL/hr of 4 µM MB in the top of the reactor while another syringe pump withdrew 60 mL/hr of liquid at the bottom of the container. The sides of the container were covered such that light could only enter through the top surface of the reactor to simulate the irradiation conditions of a much larger surface. The reaction chamber and inlet stream were set to a pH of 9. The MB concentration and mass of nanoparticles leaving the reactor were then measured by analysing the contents of the 60 mL samples at 1 hour intervals. After centrifuging, the supernatant liquid was run through a 0.22 µm syringe filter and analysed using a spectrometer while the precipitated nanoparticles were dried before weighing. The percentage of MB degraded each hour was calculated as the difference between the inlet and outlet streams normalized by the moles of reactant in the inlet stream. The calculated degradation rate ignores the moles of MB remaining in the reaction chamber and adsorbed onto the TiO$_2$ photocatalyst but sufficiently measures the reaction trends over time. Ignoring the MB present in the reaction chamber causes the effects of dilution inside the chamber to be temporarily seen as maintained performance by the aqueous reactor, even after the photocatalytic performance has dropped. This delay is on the order of 2 hours based upon the reactor volume of 120 mL and the flow rate of 60 mL/hr. The adsorption of MB onto the surface of the TiO$_2$ was also found to be negligible relative to the measured amount of dye added and degraded each hour. In a control scenario with an initial concentration of 2.7 µM it was found that 200 mg of TiO$_2$ adsorbed a total of 0.2 mmol of MB; a total of 4.25 mmol were found to be degraded by the SNPR over the course of the entire continuous reaction while the MB concentration remained below 0.4 mM.

It is noted that the total measured mass of recovered nanoparticles in the continuous aqueous reactor was only 86% of the original 200 mg. It is expected that the remaining 27 mg was indeed extracted from the reactor chamber over time and remained in both the supernatant after centrifuging and on the dried walls of the centrifuge tubes, preventing direct measurement. The presence of nanoparticles in the supernatant was confirmed by measuring the absorbance spectrum of the unfiltered samples which showed minor absorption
peaks outside of the range of MB absorption, indicating the presence of TiO$_2$. For this reason the curve in Figure 6-8 (Supplementary Information) is normalized to the measured 173 mg as the additional 27 mg of material was expected to be equally distributed among the 20 hours of operation.

The amount of TiO$_2$ present in 1 mL of the diluted oil-in-water emulsion was measured as 40 mg and this metric was used to determine the necessary photocatalyst mass for each emulsion-based test. This was measured assuming a homogenous distribution of TiO$_2$ in a known volume of an undiluted emulsion and then subtracting the mass of TiO$_2$ which settled to the bottom of the container after dilution.

6.5 Supplementary Information

6.5.1 Fluorescent microscopy of Nile red and fluorescein

Photocatalytic degradation of Nile red and fluorescein dyes was observed fluorescently using an inverted fluorescent microscope (DMI 6000B, Leica Microsystems Inc.) while images were captured with a CCD camera (Orca AG, Hamamatsu). Ultraviolet irradiation of the photocatalyst and imaging of the dye degradation was performed using two different filter cubes. The fluorescent images were then adjusted for spatial differences in intensity due to shading using dark and reference images. As dye concentration has been shown to be proportional to the fluorescence intensity, the corrected fluorescent intensities were used to determine the exponential decay of the dyes over time (Figure 6-9a). The degradation rate was then found by taking the slope of the logarithmic normalized intensity over time as seen in Figure 6-9b.

As a control the same procedures for forming the emulsions were performed without amphiphiles. For the oil-in-water case the emulsions in the control scenario were on the order of 100 µm instead of the 10 - 20 µm in the Pickering emulsions and were seen to coalesce over time. Furthermore, large agglomerates of nanoparticles were witnessed; application of UV light showed that dye degradation occurs preferentially on the portion of the surface where the agglomerations were visible and negligibly on the other surfaces, unlike the diluted Pickering emulsions where degradation occurred uniformly.

6.5.2 Spectrometer measurements of methylene blue

Methylene blue concentration was determined by measuring the absorbance of samples at 664 nm using a spectrometer (BRC112E-USB-VIS/NIR, Edmund Optics Inc.), coupled with a light source (SLS201, Thorlabs Inc.) and deionized water as a reference. Each measurement used a reference curve taken at the same time to remove any variability in the spectrometer measurement over time. The Beer-Lambert law was then used to convert absorbance into methylene blue dye concentration using a cuvette path length of 1 cm and a molar extinction coefficient of 74028 cm$^{-1}$ M$^{-1}$ at 664 nm. Prior to measuring the absorbance spectrum the samples were centrifuged and run through a 0.22 µm filter to remove any nanoparticles present in the fluid. An example of a typical absorbance spectrum and accompanying concentration change over time is found in Figure 6-12 for the case of an aqueous suspension batch reactor with mild agitation.
Figure 6-7 | Picture of nanoparticle-stabilized photocatalytic emulsions sitting at the top of a 250 mL beaker. The amount produced is directly scalable to the quantity of materials.

Figure 6-8 | Comparison of total nanoparticle retention for the SNPR and aqueous suspension in the continuous reactor process over time.
Figure 6-9 | Fluorescent degradation of Nile red dye in individual photocatalytic nanoparticle-stabilized oil-in-water droplets of radius 34 µm and 10 µm showing the a) change in fluorescence and b) normalized intensity giving first-order degradation rates.

Figure 6-10 | Degradation rate of Nile red dye at the centre (r/R = 0) and edge (r/R = 1) of a photocatalytic nanoparticle-stabilized oil-in-water droplet.

Figure 6-11 | Spatial photocatalytic degradation of fluorescein dye inside a photocatalytic nanoparticle-stabilized water-in-oil droplet.
Figure 6-12 | The a) time dependent methylene blue absorbance spectrum and b) exponential decay curve at 664 nm for the photocatalytic degradation of methylene blue in a fixed-photocatalyst batch reactor of sedimented nanoparticles under mild agitation.
Chapter 7.

Conclusions

7.1 Summary
The reduction of CO\textsubscript{2} to useful carbon-based products is a multi-disciplinary field requiring contributions from a wide range of scientific backgrounds. Collectively the performance metrics defining technological advancements are steadily improving and approaching a pivotal point where electrochemical CO\textsubscript{2} reduction pilot plants can be justified. Both novel catalysts and system engineering have enabled these gains and new contributions to this global effort were outlined in this thesis. A central theme of the collective research body presented here was the importance of catalyst-system interactions on selective and efficient CO\textsubscript{2} reduction. Four different applications of this central theme were applied to achieve this goal and contribute to the field as a whole.

In the first such instance the impact of a catalyst’s morphology on mass transport was examined. Existing literature showed a large variation in mass transport limitations between otherwise similar experimental catalysts. Combining experimental observations with an extended electrochemical model resulted in a current density dependent diffusion thickness based upon catalyst morphology. From this foundation an enhanced understanding of how the local reaction environment varies with operating conditions helped to further create catalysts which extended the ethylene partial current density past previous barriers in an H-cell environment. More importantly, fundamental limitations of the extremely selective catalyst were identified and alternative mechanisms which circumvent this inherent flaw were proposed. The combined efforts of the first two scientific chapters in this thesis led to the design of a CO\textsubscript{2} reduction system where the local reaction environment surrounding a catalyst could be finely controlled. The thin catalyst layer allowed for the supply of excess CO\textsubscript{2} in an alkaline media which proved important for reaching both high power conversion efficiencies and selectivity for ethylene.

In a separate application of a similar theme the microenvironment surrounding a photocatalyst was controlled through the creation of nanoparticle-stabilized micro-reactors. Independently the small reactors are capable of internal and external photocatalytic reactions while being controllably dispersed within an aqueous medium. The advantages of both traditional heterogeneous and homogenous were then enabled for the purposes of continuous dye degradation.

7.2 Future Outlook
As described throughout this thesis the advancement of performance metrics is a critical focus of electrochemical CO\textsubscript{2} reduction. An economic perspective suggests that the selectivity and current density of
several reduction products are sufficient for commercialization given a cheap enough electricity source. Further reductions in reaction overpotential and large increases in catalyst stability remain necessary however for accelerated deployment and commercialization of the technology. While new and complex catalysts will be created to close this gap, parallel efforts are needed to better understand reaction kinetics and fill the existing void between reaction-diffusion modeling and Density Functional Theory. Given the large importance of reaction intermediates and the effect of surface modifications on these intermediates, the existing modeling approaches fall short as more complex catalysts and reduction products are created. The application of microkinetic models for CO$_2$ reduction can help to further elucidate the molecular catalyst-electrolyte interactions that greatly determine both reaction selectivity and efficiency while providing a better means of predicting future catalyst structures.

A separate but similarly important effort should be applied to studying gas diffusion electrodes specifically for CO$_2$ reduction. Current gas diffusion layers can be commercially purchased and show the best reduction performance to date but were not fundamentally designed for this application. Researchers have begun modifying this important system backbone but its application is not yet a fixture across the entire field. Further modifications of the gas diffusion layer’s composition, porosity and morphology may yield returns in all of the primary performance metrics. In parallel we have shown in this thesis how deposition of the catalyst can greatly influence performance. Clever means of depositing high-performing H-cell catalysts onto gas diffusion electrodes are needed as preliminary results prove that performance gains are not universally transferrable between the two platforms. An added complexity and opportunity then exists to design intricate catalysts for a gas diffusion system.

The field as a whole has reached high selectivity, current density and efficiency for different reduction products in increasing order of difficulty. From this approach carbon monoxide, formate and ethylene have seen enormous gains in a short period of time. Similar gains in methane, methanol, ethanol and propanol production are then targeted by many researchers as a next step to reach further markets. Many of the established gains, however, came primarily from outcompeting a single secondary reaction, namely hydrogen evolution for single carbon products and methane for multi-carbon products. As the number of CO$_2$ molecules, proton transfer steps and reaction intermediates increases, the number of reaction pathways, products and overall variables increase in turn. Rather than creating a highly complex surface capable of both promoting early reaction steps and targeting singular reaction intermediate late in the reaction pathway, secondary catalysts and controlling the local reaction environment will prove increasingly vital. Examples of this were shown when using hydroxide to reduce hydrogen evolution. A simple electrolyte addition to suppress higher carbon products such as ethylene, however, remain unknown. Opportunities then exist in catalyst discovery, electrolyte engineering, system modifications and the combination of all three as performance is further pushed to thermodynamic limits. Encouragingly, the field of electrochemical CO$_2$ reduction has pushed forward with periodic leaps in understanding followed by steady incremental gains. With the large avenues of research being undertaken by individuals of various scientific backgrounds, there’s reason to believe these advancements will continue.
Bibliography


