



Marshall Plan - Report

Mass Transport Effects on Product Distribution during Electrochemical CO₂ Reduction in a Custom-Designed Rotating Cylindrical Electrode Cell

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Abstract

As the global energy demand is rising continuously and the fossil fuel depletion is advancing, new technologies are needed to meet the challenges the energy industry is facing. Progress in the field of renewable energies has grown steadily. However, it is still critical to accelerate progress in the economic viability of these technologies. In the near future, no single renewable technology will be able to compete with fossil fuels. The task is to establish an infrastructure to jointly generate energy from many different areas of renewable energy in a sustainable manner.

In this work a promising field of research - the electrochemical reduction of carbon dioxide (CO_2RR) - will be discussed. This reaction can potentially produce various C_{2+} carbohydrates, oxygenates and other carbon moieties that can be used as fuels or as basic chemicals needed in the chemical industry. The input required for this reduction is simply electricity and the reactants carbon dioxide and water. Carbon dioxide (CO_2) is a major greenhouse gas that contributes to climate change and rising temperatures and exhibits an increasing concentration in the atmosphere. The local removal of CO_2 from industrial exhaust gases or the direct extraction from the air not only generates the main reactant of this reaction but also contributes in reducing its occurrence in the atmosphere to a moderate level. The second reactant, water, is abundant. The aim would be to minimize the overpotential required for this reaction and to convert excess electricity from renewable energy sources such as solar and wind into chemicals with a high energy density.

This thesis focuses on mass transfer effects during electrochemical CO_2 reduction in a successfully designed gas-tight electrochemical cell with an integrated rotating cylindrical electrode. The application of the reduction of potassium ferricyanide was used to quantify the hydrodynamics of the rotation cell. By conducting experiments on CO_2RR at different rotation speeds and electrolyte concentrations a deeper understanding of the reaction mechanism and the influence of mass transport effects on product selectivity was gained. A mathematical model was developed to rationalize that obtained data. The insights helped to further develop an advantageous experimental set-up that will add to achieve the goal of lowering overpotentials, and thus, reduce the electricity input needed. This will lead to lower costs of this technology making it more competitive in the field of energy alternatives on the road to replace fossil resources.

Kurzfassung

Mit dem kontinuierlichen Anstieg des weltweiten Energiebedarfs sowie der Verarmung fossiler Brennstoffe sind neue Technologien erforderlich, um die Herausforderungen der Energieweltwirtschaft zu bewältigen. Trotz bedeutender Weiterentwicklungen in der Forschung bezüglich erneuerbarer Energien ist es nach wie vor entscheidend die Wirtschaftlichkeit dieser Technologien voranzutreiben. Die Konkurrenzfähigkeit einer einzelnen erneuerbaren Technologie gegenüber fossilen Brennstoffen ist in naher Zukunft noch nicht denkbar. Daher liegt die Aufgabe darin, eine Infrastruktur zu schaffen, um die Energieversorgung aus verschiedenen Bereichen der nachhaltigen Energietechnologien zu vereinen.

Diese Forschungsarbeit konzentriert sich auf ein vielversprechendes Forschungsfeld der Elektrochemie zur Umwandlung von Energie aus erneuerbaren Energiequellen - der elektrochemischen CO_2 Reduktion (CO_2RR). Mittels dieser Reaktion können verschiedene C_{2+} -Kohlenhydrate und andere α -Oxygenate produziert werden, die als Brennstoffe oder als Grundchemikalien der chemischen Industrie dienen. Für diese Reaktion werden elektrischer Strom und die Reaktanten Kohlendioxid und Wasser benötigt. Der Strom kann aus der Überschusselektrizität von Solar-, Wind- und Hydroenergiequellen genommen werden, dessen Speicherung bisher als eine der größten Herausforderungen bezüglich der effizienten Nutzung erneuerbaren Energiequellen gilt. Kohlenstoffdioxid (CO_2) ist eines der Haupt-Treibhausgase, das zum Klimawandel und zu steigenden Temperaturen beiträgt und zunehmende Konzentrationen in der Atmosphäre aufweist. Die lokale Entfernung von CO_2 aus industriellen Abgasen oder die direkte Extraktion aus der Luft erzeugt nicht nur den Hauptreaktanten dieser Reaktion (CO_2), sondern trägt auch zur Reduktion dessen in der Atmosphäre auf ein moderates Niveau bei. Der zweite Reaktant, Wasser, ist im Überfluss auf der Erde vorhanden. Ziel ist es, das für diese Reaktion erforderliche Überpotential zu minimieren und Überschussstrom aus erneuerbaren Energiequellen wie z.B. Sonnen- und Windenergie in Chemikalien mit hoher Energiedichte umzuwandeln.

Der Hauptfokus dieser Arbeit liegt auf der Untersuchung von Stofftransporteffekten während der CO_2RR . Zur Evaluierung ebenjener wurde eine gasdichte elektrochemische Zelle mit intergrierter Zylinderelektrode entworfen. Die Reduktion von Kaliumhexacyanoferrat wurde angewendet um die hydrodynamischen Eigenschaften der Zelle zu quantifizieren. Zudem wurden Experimente zur elektrochemischen CO_2RR mit verschiedenen Reaktionsgeschwindigkeiten und Elektrolytkonzentrationen durchgeführt und zur Auswertung der Ergebnisse ein mathematisches Modell erstellt, welches erlaubt lokale Konzentrationen der Reaktanden und Produkte und den pH an der Elektrodenoberfläche zu berechnen. Die Ergebnisse haben dazu beigetragen den Reaktionsaufbau weiter zu verbessern um in Zukunft den Reaktionsmechanismus besser zu verstehen und dadurch geringere Überpotentiale zu erzielen, wodurch in weiterer Folge der Strombedarf reduziert wird. Dies führt zu niedrigeren Kosten dieser Technologie, was diese im Bereich der Energiealternativen, die fossile Brennstoffe ersetzen sollen, wettbewerbsfähiger macht.

Contents

1	Introduction	1
1.1	Problem Definition	1
1.2	Research Objectives	3
1.3	Thesis Overview	5
2	Theory	6
2.1	Electrochemical CO ₂ Reduction	6
2.2	State of the Art for CO ₂ RR Cell Set-ups	7
2.3	Determination of the Boundary Layer Thickness	8
3	Cell Design	9
3.1	Requirements for Gas-Tight Cell	9
3.2	Description of different Cell Parts	9
4	Experimental Section	13
4.1	Experimental Methods	13
4.2	Reduction of Ferricyanide	15
4.2.1	Cu RCE to determine the boundary layer thickness	15
4.2.2	Glassy Carbon RDE for extracting kinetic parameter	15
4.3	CO ₂ Reduction Reaction	15
4.3.1	Preparation of the Working Electrode	16
4.3.2	Experimental Measurements in Rotation Cell	17
5	Mathematical Modelling	18
5.1	General Assumptions	18
5.2	Mathematical Theory behind the Rotating Cylindrical Electrode	19
5.3	Main Structure	19
5.4	Modification for Ferricyanide Reduction	22
5.5	Modification for CO ₂ RR	23
6	Results and Discussion	26
6.1	Determination of the Boundary Layer Thickness	26
6.1.1	Cu RCE to determine the boundary layer thickness for the CO ₂ RR	26
6.1.2	Glassy carbon RDE as an example for extracting kinetic parameters	29
6.2	Electrochemical CO ₂ RR	30
6.2.1	Influence of the Electrode Rotation Speed at fixed Potential	32
6.2.2	Influence of Electrode Rotation Speed over Potential Range	33
6.2.3	Influence of the Electrolyte Concentration	45
6.2.4	Influence of Surface Modifications of the Working Electrode	47
6.3	Mechanistic Considerations	49

6.3.1	HER, CO and Formate - $2e^-$ transfer reactions	50
6.3.2	Methane CH_4 and Ethylene C_2H_4 - pH and C-C coupling	51
6.3.3	Beyond CO - pathway to multicarbon products	53
7	Conclusion and Outlook	55
7.1	Thesis Summary	55
7.2	Future Directions	55
7.2.1	Cell Design	56
7.2.2	Experimental	57
7.2.3	Modelling	57
7.3	Final Remarks	58

List of Figures

1.1	Cycle for CO ₂ RR as technology for energy transformation and storage . . .	1
1.2	Reaction pathways from different experimental and theoretical studies[7] .	4
3.1	Rotation cell	10
3.2	Radial ring bearing	10
3.3	Working electrode compartment	11
3.4	Counter electrode compartment	12
4.1	CV for the preparation of Cu Cubes	16
4.2	Polycrystalline copper vs. CuCubes	16
5.1	Mass transfer boundary layer[11]	19
6.1	Lab set-up of the rotation cell	26
6.2	Limiting current - reduction of potassium ferricyanide on copper	27
6.3	Boundary layer thickness as a function of the electrode rotation speed . . .	28
6.4	CV blank sweeps compared to CV sweeps with 10 mM ferricyanide	28
6.5	Levich-Koutecky plot - measured vs. estimated values	29
6.6	Experimental vs. simulated CV data ([Fe(CN) ₆] ³⁻ /[Fe(CN) ₆] ⁴⁻ redox-couple)	30
6.7	Concentration gradient of potassium ferricyanide over time and distance at 0 and 800 rpm	30
6.8	Potential and current densities over time of all experiments	31
6.9	Changes in product selectivity due to changes of the electrode rotation speed in 0.1M and 0.2M KHCO ₃	33
6.10	Total current densities in 0.1 M and 0.2 M KHCO ₃ at 100 and 800 rpm . .	33
6.11	Limiting current depending on the electrolyte concentration and Linear sweep to examine current between Pt- and Ag/AgCl-electrode	34
6.12	Faradaic efficiency and logarithmic partial current density at different electrode speeds paired with different electrolyte concentrations	35
6.13	Concentration gradients of buffer species and the pH in the boundary layer at a steady state condition	36
6.14	Concentration of CO ₃ ²⁻ and HCO ₃ ⁻ at the outer Helmholtz plane	37
6.15	A) pH ($\hat{=}$ $- \log[H^+]$) at the outer Helmholtz plane B) Concentration of buffer species in CO ₂ saturated bicarbonate electrolyte at 298,5 K and 1 atm[25]	38
6.16	3D plots of the concentration gradient of species and the pH gradient in the boundary layer over time	38
6.17	Concentration gradient of product species in the mass transfer boundary layer	39

6.18	Partial current density of hydrogen, formate, CO and further than CO reduced	40
6.19	Partial current density of hydrogen normalized by the proton concentration at the OHP	40
6.20	Reduction peak in CV sweeps attributed to the direct formation of bicarbonate to formate	41
6.21	Local concentration of CO at OHP	41
6.22	Partial current density of methane and ethylene	42
6.23	Partial current density of beyond CO products	43
6.24	Partial current density of beyond CO products in 0.1 M and 0.2 M KHCO_3	43
6.25	Ratio of $>2e^-$ oxygenates to hydrocarbons over potential range at different reaction conditions compared to the results of Wang et al.[28]	44
6.26	Comparison of C1, C2 and C3 products over potential range at different reaction conditions	45
6.27	Surface facets of copper	48
6.28	Comparison between polycrystalline copper and CuCubes	48
6.29	Reaction mechanism for $2e^-$ products of CO_2RR [31]	50
6.30	Partial current density of methane and ethylene	52
7.1	Further developed cell design	56

List of Tables

6.1	Comparison of measured with estimated values of boundary layer thickness	27
6.2	Average potential of experiments under different reaction conditions	45
6.3	Faradaic efficiency and normalized activity in different electrolyte concentrations (0.1 M, 0.2 M, 0.5 M KHCO_3)	46
6.4	Ethylene to Methane ratio for polycrystalline copper and CuCubes in 0.2 M KHCO_3	47

List of Abbreviations

Greek Letters

α	symmetry constant
β	factor
δ	thickness [m]
ϵ	permittivity [As/(V m)]
μ	kinematic viscosity [m ² /s]
∇	Nabla operator
ν	stoichiometric coefficient
ω	angular rotation speed [rpm]
ϕ	electric potential [V]
ρ	density [kg/m ³]

Physics Constants

F	Faradaic Constant [C/mol]
k_B	Boltzmann Constant [J/K]
R	universal gas constant [J/(mol K)]

Other Symbols

c	concentration [mol]
CO_2RR	carbon dioxide reduction reaction

D	diffusion coefficient [m/s ²]
d	rotor diameter of RCE
E	potential [V]
E^0	standard potential [V]
FE	faradaic efficiency [%]
GC	gas chromatography
HER	hydrogen evolution reaction
I	current [A]
J	flux term
j	current density [A/m ²]
k	reaction constant, 1st order:[s ⁻¹], 2d order:[s ⁻¹ M ⁻¹]
m	space constant
NMR	nuclear magnetic resonance spectroscopy
r	rate term
RCE	rotating cylindrical electrode
RDE	rotating disc electrode
$sccm$	standard cubic centimeter per minute
T	temperature [K]
t	time [s]
u	function u
v	scan rate [V/s ²]
x	distance [m]
z	charge number

Chapter 1

Introduction

The goal of this thesis is to investigate the electrochemical CO_2 reduction reaction (CO_2RR) for transformation and storage of excess electricity deriving from renewable and sustainable energy sources with a specific application - a gas-tight rotating cylindrical electrode cell - to study mass transport effects. The research field of electrochemical CO_2 reduction is loaded with inconsistency as most different reaction set-ups and conditions were used, some leading mass transport limitations that are strongly influencing the reaction outcome. It is pivotal to break the process down to the most elementary experiments with a set-up that is capable of eliminating mass transport limitations to gain more knowledge about the fundamental laws of the system and to decouple intrinsic phenomena from mass transport effects. With the findings gathered in this study further steps can be set for the ongoing development of an efficient catalyst for the CO_2RR .

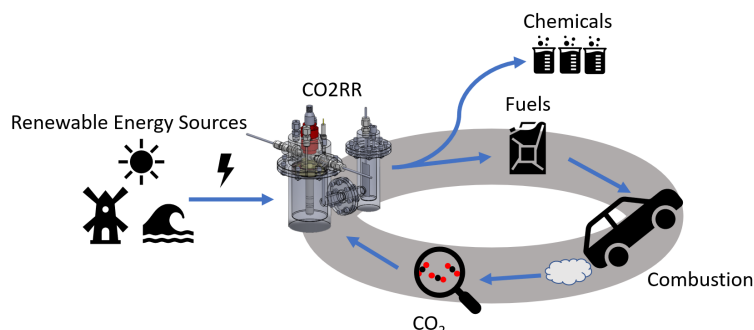


Figure 1.1: Cycle for CO_2RR as technology for energy transformation and storage

1.1 Problem Definition

The constantly growing energy demand is posing considerable challenges in the near future to maintain the standards of the modern society as this gigantic energy demand has to be covered somehow. For many years, the main energy source to generate electricity and fuels has been deriving from fossil resources which accounted for 82% of the worlds total energy supply.[1] Yet, it has been distinct for long that the oil, natural gas and coal reservoirs won't be filled indefinitely. Due to the energy crisis in the 1970s research in alternatives to fossil fuels was given more interest. Efforts were made in different fields such as the field of electrochemistry. In the 80s Hori et al. made the discovery that out of all transition metals copper has the unique ability to electrochemically reduce CO_2 to further reduced products such as methane (CH_4) and later on he also discovered multi- carbons products

such as ethylene.[2][3] The products of this reaction are useful as fuels or basic chemicals in the chemical industry. Although this discovery was a major breakthrough in this field, lots of effort still had to be put into making this technology more efficient. As the crisis was overcome, less attention was given to this field of research. In the last couple of years, a shift in the awareness of society on the energy problem was observable due to the climate change and the resulting challenges such as global warming, pollution of air, acidification of oceans and soil, and so forth. This revived the effort in finding sustainable technologies from renewable energy sources that contribute to the global energy demand and turn away the global focus from the dominating fossil resources. Various sustainable technologies were developed and are being operated industrially today to generate and store renewable energies. Only in the last year the growth of renewable energies was 41%.[4] Though, there is still no technology as efficient or promising to replace fossil resources as sole energy supplier in the near future. A broad network of alternative energy sources has to be established that can integrate a variety of sustainable technologies into a collective energy grid. To be considered as a sustainable technology capable of competing with fossil resources some key points have to be complied as there does not exist an ideal technology yet. Most importantly, a high efficiency has to be achieved that meets economical feasibility requirements such as low capital and maintenance costs. For the matter of sustainability, the negative environmental impacts such as emissions of greenhouse gases and other pollutants have to be kept low. Monocultures should be avoided, diversity of plants and animals kept high, and dangerous work places (e.g. mining) made safer or eliminated. Further, the availability of energy has to be ensured at all times, which for some energy sources requires transformation of primary energy carrier for proper storage. Life cycle assessments should be looked at and considered when choosing or working on new, or improving established technologies. When considering those factors, fossil resources provide high efficiency factors leading to low prices, which is the reason for its dominance in the field of energy generation. Still, those sources cause vast damage to the environment and human health. A sustainable and efficient alternative is provided by biomass conversion. Biomass can be turned into value-added products through refineries. Additionally, the combustion of biomass has the ability of providing electricity. Although this technology is already well established, the cultivation of biomass takes up enormous areas because of low power density and can result in monocultures leading to extinction of species. Demand for renewable energy sources derived from solar-, wind-, and hydro-power is rising yearly and the huge progress made in those technologies in the last years makes those technologies promising competitors. The abundance of solar radiation, water and wind leads to increasing investment in installation of solar panels, wind wheels, etc. Still, to be at a competing level with fossil resources they pose some more difficulties that have to be overcome. The investment costs are high. There are hourly, diurnal, and annual fluctuations and for some applications there is only regional availability which leads to long transport routes that can result in high losses of efficiency. To guarantee constant energy supply and efficient transportation over long distances, the excess electricity needs to be transformed and stored in a more stable form of energy. This would also help to cover peak energy demands. Several technologies in the field of electrochemistry to transform and store this excess of electricity were already investigated thoroughly. Examples are batteries and the electrochemical process of water splitting to produce H_2 . Batteries are widely used in the industry as well as for personal use. The most established battery is the lithium ion battery. The challenges this technology is still facing are high production costs and performance which is quantified by usable energy density, power density, cycle lifetime and robustness.[5]

Another option for energy conversion is seen in the generation of hydrogen. It can be done electrochemically through water splitting. Hydrogen has the possibility of being used as fuel for fuel cell cars but can also be converted back to electricity. However, most hydrogen generated today still derives from fossil fuels or biomass gasification and the efficiency of the electrochemical process has to be improved still. Moreover, even though this technology seems to be a very promising and potent candidate, the infrastructure and distribution grid for hydrogen is not developed enough to contribute at a reasonable level in the near future. Hori’s efforts to electrochemically convert CO_2 to value-added products such as fuels or basic chemicals for the chemical industry were reconsidered in the last few years and increasing research interest in the area of sustainable energy storage led to further enhancement of this technology in the last decade. Although there are only a few industrial application so far, great efforts have been made in this area that combines chemistry and electronics for energy conversion and storage with electricity deriving from solar, wind and water based renewable energies. The main advantage of this approach is that both main reactants - CO_2 and water - are abundant. Moreover, CO_2 is a greenhouse gas with rising concentration level in the atmosphere due to exhaust gases from industrial sources and the transportation sector. Punctual capturing of CO_2 at industrial facilities or extracting it from the air directly would lower the unfavorable CO_2 concentration in the atmosphere while providing the key reactant of this reaction. This would put this application into the category of net zero CO_2 emission technology. Typically, the reaction is performed at room temperature and atmospheric pressure which helps lowering the complexity of reaction devices. Further, the scalability of the set-up is flexible. Those two facts are the key for the decentralisation of this application and give the possibility to bring this technology to isolated areas providing them with energy and the supply of basic chemicals. The products of the electrochemical CO_2 reduction reaction, that are basically the same substances that usually derive from fossil resources, offer high energy density. Product species like ethanol can be directly used as drop-in fuel as the infrastructure already exists. Other products like ethylene are used in the chemical industry as base chemicals needed, for instance, to produce medicine or daily tools. Even though there are many advantages for this application, it still faces some difficulties when it comes to the technical performance. A main issue, presently, are the high overpotentials needed to generate the desired products. The high energy input decreases the efficiency of the device. Further, the selectivity is still very poor as the charge transfer coefficients of different products with the same amount of electron transfers during the reaction, are similar. This leads to laborious and costly purification steps and decreases the economical feasibility of the whole process.

1.2 Research Objectives

To reach the objective of lower overpotentials for the CO_2RR , this work will focus on shedding more light on the reaction mechanism by eliminating mass transport effects. Mass transport limitations are appearing during reactions where the diffusion of reactants to the electrode surface is slower than the reaction rate. This lowers the efficiency of this reaction and has led to distortion of many results in this field as they were not normalized to mass transport limiting effects. Consequently, there are many converse studies and theories about the reaction pathways that are supposedly leading to the main intermediates and products. One of the problems for the incoherence of results in this field is caused by the use of different reaction set-ups with variations of the cell design resulting in different hydrodynamics. Further, huge variations are seen in the choice of the

catalyst, the electrode material and the reaction conditions such as the electrolyte (ions, concentration and pH), temperature, and pressure. Figure 1.2 represents an overview on different groups of schools combining mechanistic results of several computational and experimental studies. The graph reveals quite figuratively why a deeper knowledge about the reaction mechanism has to be acquired as well as a conformity introduced on how to execute experiments and the data analysis universally. Clark et al. worked out a guideline to enhance the interinstitutional reproducibility of data when it comes to CO₂RR. [6] The key variables that are mentioned to achieve a uniform way of generating data and how some of those points will be addressed in this thesis are being discussed in the following paragraph.

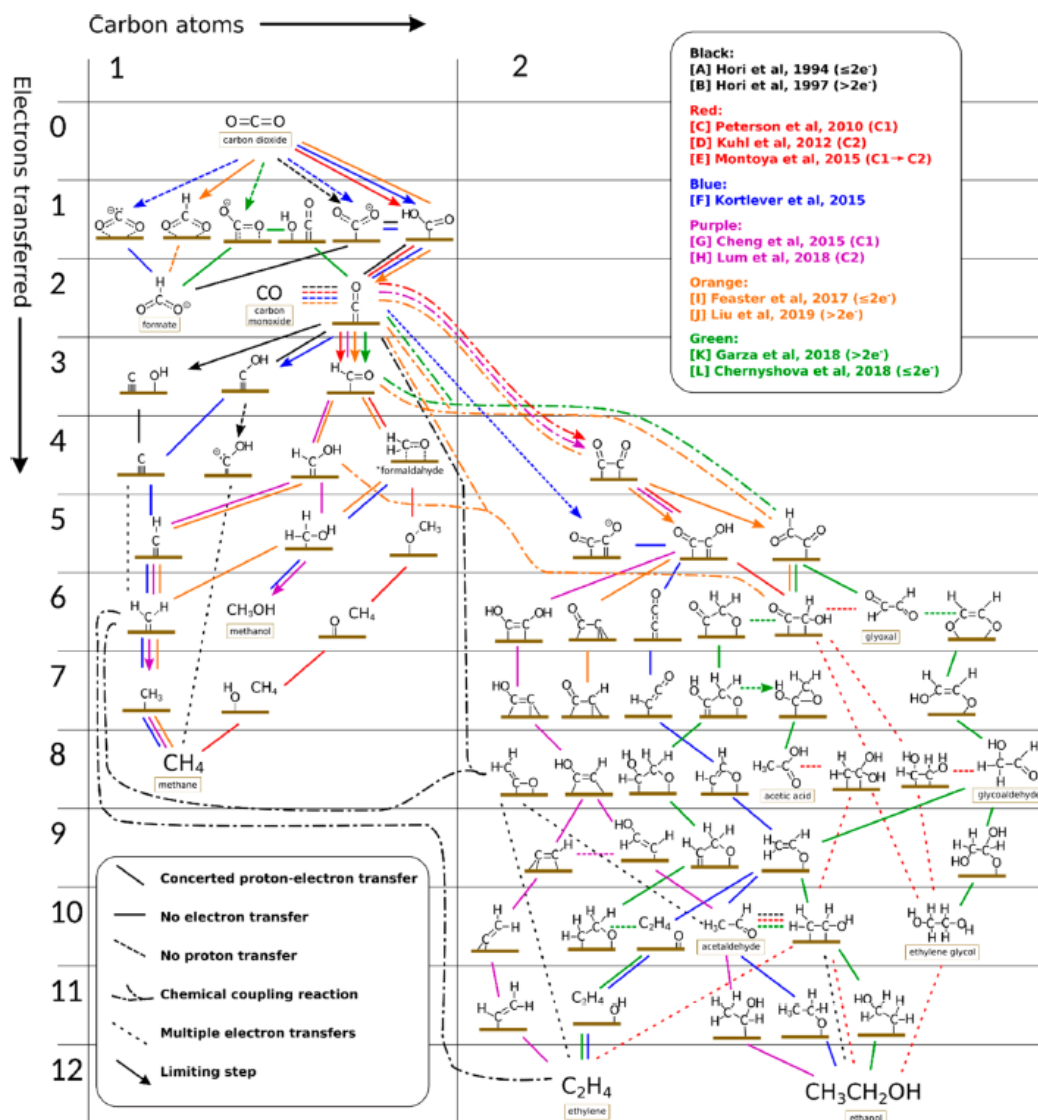


Figure 1.2: Reaction pathways from different experimental and theoretical studies[7]

Data from other studies that did basic experiments on CO₂RR with standard catalysts and reaction conditions should be reproduced by the research group prior to using a new catalysts or reaction conditions that haven't been used before. If the reproduction was successful, the next steps can be approached. Reporting data still remains a challenge as mass transfer effects overlap with intrinsic reaction kinetics. To eliminate mass transfer limitations and investigate diffusion-independent reaction conditions, a rotating

cylindrical electrode set-up will be designed in a way to ensure a gas-tight environment for avoiding impurities and detecting gaseous products while still being able to rotate. Further, the hydrodynamic properties of the system can be evaluated by conducting the reduction of potassium ferricyanide in the same device as the CO₂ reduction experiments. This well studied and simple reaction helps to quantify the mass transfer boundary layer thickness. In this thesis the profit of deploying this simple reaction previous to operate the more complicated CO₂ will be discussed and modeled. Simulations and their comparison to experimental cyclic voltammetry (CV) data that can help to identify system parameters will be presented. This method can be used to predict parameters of systems investigated in the future. The electrochemical CO₂ reduction will then be studied at different reaction conditions such as various rotation speeds and electrolyte concentrations over a specific potential range. Great attention will be directed on the proper analysis of the results. As many studies only report the faradaic efficiency of the generated products, this might distort the discussion as those values are relative values. The faradaic efficiency of product species shows changes in selectivity. To see changes in activity, it is more of interest to look at the partial current densities of products that reveal the absolute value of the produced species. The aim is to re-evaluate the CO₂RR in an environment where mass transfer effects are eliminated and to analyze and report the results with the utmost care regarding parameters used for comparing data. This will add one building block to a stronger foundation on which future studies can be built upon.

1.3 Thesis Overview

The state of the art regarding the cell design, the theory behind the reduction of potassium ferricyanide and, most importantly, the theory of the CO₂ reduction reaction will be discussed in **Chapter 2**.

The design of the RCE cell is based on the design of a hermetically sealed gas-tight rotating disc electrode (RDE) unit that was presented in a paper from Jung in 2016. [8] This design was further developed by using the 3D-CAD program SolidWorks and is described in **Chapter 3**.

The experimental methods used in this thesis and all experiments that were carried out, are described in **Chapter 4**. This includes the preparation of the working electrode, the reduction of potassium ferricyanide, the CO₂ reduction as well as the analysis of the generated products via gas chromatography and nuclear magnetic resonance spectrometry.

To support the analysis of the experimental results two codes were developed using the numerical computing program MatLab by MathWorks. In **Chapter 5**, the main structure of the code was described first, and after that, the variations of the code that had to be done to fit each application, were discussed after.

The results of each experiment combined with the results of the mathematical modelling will be presented in **Chapter 6**.

The summary of the results and the conclusion of this thesis will be discussed in **Chapter 7**. Additionally, an outlook for further directions in gaining more insight into the reaction mechanisms in order to further develop the reaction set-up and to make this technology economically feasible, will be given in that chapter.

Chapter 2

Theory

In this chapter a short overview will be given on the state of the art regarding the cell set-ups that were used so far in the scope of the electrochemical CO₂ reduction. Further, the theory behind the two reactions conducted in this thesis will be discussed. To determine the boundary layer thickness, the reaction to reach this goal - the reduction of potassium ferricyanide - and its advantages for this application will be examined. Ultimately, the emphasis will be placed on the basics of the electrochemical CO₂ reduction and the most important factors influencing this reaction.

2.1 Electrochemical CO₂ Reduction

As simple as it is to generate data with electrochemical tools, the data analysis is often challenging. This especially applies for the reaction focused on during this work - the electrochemical reduction of carbon dioxide. CO₂ serves as the main reactant and as a buffer at the same time, which makes the understanding of this system even more demanding. The products detected so far are reactions from 2e⁻ up to 18e⁻ transfers. Further, the CO₂RR is sensitive to many factors from atomic scale to reactor scale regarding its product selectivity. Highly favored is the production of high energy dense multi-carbon products. Some factors, that will be investigated in this work to change the reaction outcome, are discussed in the following.

Firstly, various cell designs, that have been tested, are producing different hydrodynamics affecting the outcome of the reaction. Mass transport limitations occur faster than in other reactions because of the low solubility of CO₂ in aqueous solutions. A cell design to overcome those challenges is presented and used in this thesis and will be discussed in detail. Further, the performance of the electrode depends on its composition, surface structure and morphology. To date only copper has the ability to further reduce CO among all transition metals and accordingly was used as the working electrode in this thesis with the goal to achieve high faradaic efficiencies for C₂+ products. Another main factor having a crucial impact on product selectivity, is the local pH. Assessing pH changes near the electrode surface that are related to buffer effects and proton (H⁺) consumption as well as hydroxide (OH⁻) formation during the CO₂RR helps in explaining the mechanism of reaction. The first discovery of the influence that the pH has on selectivity during CO₂RR was done by Hori et al. providing important insight into the reaction mechanism.[9][10] It also has been shown that a high pH might shift acid-base concentration toward (bi)carbonates decreasing the concentration of CO₂ near the electrode surface which favor the hydrogen evolution reaction.[7] In general, the efficiency of the CO₂RR has a volcano-type depen-

dence on the pH.[7] Thus, it is important to find the right pH range for the CO₂RR at the electrode surface. With the mathematical code described later, it is possible to evaluate the pH gradient as the formation of OH⁻ is taken into consideration. Due to the production of OH⁻ at the electrode surface the surface pH differs from the bulk pH which is another important factor in this reaction. Several studies were conducted in recent years to understand the role the electrolyte investigating different ion identities and quantities as well as its buffer ability. The strong influence of the electrolyte on the reaction outcome is adding to the complexity of the reaction system regarding the CO₂RR. Due to the importance of surface pH, different systems of buffered, somewhat buffered and unbuffered electrolytes (KCl, KClO₄, K₂SO₄) were investigated in past studies. In unbuffered systems the local pH near the electrode surface can vary widely from the bulk pH. Highly buffered systems lead to smaller pH gradient and therefore a lower pH at the electrode surface, however, it was shown that alkaline conditions are favored for the production of further reduced products. It was shown that a weakly buffered system using KHCO₃ was exhibiting the highest current efficiencies by stabilizing the concentration of CO₂ at the electrode surface.[11] Even though, KHCO₃ is favorable over KOH for the CO₂RR an increase of catalytic overpotential can be seen in this electrolyte due to formation of CO₃²⁻ as it causes a lower ionic conductivity in KHCO₃ systems than in KOH.[12] Even though the experiments usually are conducted at ambient temperature and pressure, it is important regardless, to investigate different reaction conditions for further mechanistic understanding. Those aspects were not focused on in the experimental section, however were considered regarding the cell design for future experiments.

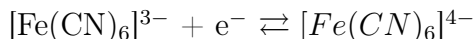
2.2 State of the Art for CO₂RR Cell Set-ups

To date the most common cell design used in the field of research on electrochemical CO₂ reduction for gaining more basic knowledge about the mechanism behind this reaction are conventional H-type cells. Although, for the gas analysis those cells are suitable, for liquid products the detection limits should be considered and are restricted to a certain extent in commercial H-type cells due to usually high electrolyte volumes. A modified H-type flow cell with limited electrolyte volume was the first application where 16 products in total were identified during CO₂RR.[13] Five of those products were detected for the first time in the field of electrochemical CO₂ reduction. The advantage of this sandwich-type cell is a high ratio of electrode surface area to electrolyte volume resulting in a high concentration of products above detection limits. Nevertheless, mass transfer effects due to depletion of aqueous CO₂ at the electrode surface at higher over potentials were leading to lower partial current density. To tackle those constraints some researcher introduced mixing into their electrochemical cells. Some applied mixing through increasing the flow rate of the CO₂ bubbles which is not efficient as you lose a higher amount of CO₂ compared to the gain in activity. Others have tried to recirculate CO₂ saturated electrolyte turning the electrochemical set-ups into more sophisticated devices that further need higher energy inputs. A method that is commonly in use for other application is a rotating working electrode to control the mass transport effects. The first research group to design a cell with an integrated rotating disc electrode in a gas-tight environment was Jung et al. in 2016.[8] The rotation of the working electrode at different speeds allows to control the boundary layer thickness, and therefore, minimizes concentration polarization and enables a higher supply of reactants to the electrode surface. The proposed concept of using a rotor that is magnetically coupled with the rotating working electrode tip was used in

this thesis and further developed. The design and advancement of this concept will be described in detail in the following part.

2.3 Determination of the Boundary Layer Thickness

As already outlined before, it is of paramount importance to differentiate between kinetic activity and mass transport effects that are affecting the faradaic efficiency of each product. If not sufficient reactant is reaching the electrode surface during the reaction, there will be a decrease in the product concentration and a distortion of the electrode activity. This would lead to the fact that results of different studies, that were conducted in different cell set-ups, cannot be compared due to unequal hydrodynamics. Many studies in this field might have experienced limited mass transport but were not labeled as such. For future studies, it is important to evaluate the hydrodynamics in an uniform way. As already described before, the rotating working electrode allows to control the boundary layer thickness, however to determine the size of this layer, the reduction of potassium ferricyanide and oxidation of potassium ferrocyanide was performed for this thesis. This quasi reversible redox reaction is a well established reaction that serves for many applications and is suitable to study mass transport phenomena and determine the boundary layer thickness in newly introduced systems.



The observed reaction rate is independent of the applied voltage which means that it is only limited by mass transfer regardless of the applied overpotential.[6] Moreover, the two species have favorable properties such as their stability or the fact that they usually do not tend to adsorb on an electrode surface and do not hydrolyze significantly. As they only have two valence states available, the reaction is a one-electron reaction.[14] One challenge that remains, is that ferricyanide is an oxidizing agent and can lead to corrosion of some metals used as electrodes. In some studies a film, identified as a ferricyanide complex that formed on the electrode surface, was observed after some time, altering the outcome of the experiment.[15] Therefore, inert metals, preferably gold, nickel or platinum are usually used for this sort of reactions. As those metals were not available as a cylindrical electrode for this thesis, copper was used as the working electrode. Even though copper is not the first choice for this reaction, it can be used either way although a different procedure had to be chosen to make sure, that the copper electrode does not get oxidized. The oxidation of copper occurs at positive potentials. Therefore, only a small potential range at more negative overpotentials were scanned, which only detects the limiting current occurring for reduction of potassium ferricyanide. The values of the measured limiting current can be used to calculate the boundary layer thickness.

Chapter 3

Cell Design

3.1 Requirements for Gas-Tight Cell

The main requirement for the cell is to introduce rotation to the working electrode for reducing the boundary layer thickness and, consequently, eliminating mass transport limitations. At the same time the cell has to be gas-tight for the purpose of quantifying gaseous products and to avoid unwanted side reactions. As there are two independent half-reactions happening at the WE and the CE, that could interfere with each other, the design has to include two compartment cells with an ion-exchange membrane in between to separate the liquid and gaseous species of each compartment. The compartment cells has to be designed in a way to maximize the surface area of the electrode to electrolyte volume ratio. The detection of products becomes easier, if fewer electrolyte is used, as the concentration increases accordingly. Gas in- and outlets serve for the continuous supply of CO_2 during the reaction as well as leading exhaust gas to the analyzer. To achieve high faradaic efficiencies, a selective catalyst has to be developed. This thesis won't focus on the development of a suitable catalyst, however it will pave the way for this task by designing and testing a system that will help in understanding fundamental processes happening at the electrode surface. The cell design will be closer described in the following section. For the parts that were commercially available the vendors are mentioned, all other parts were CNC-machined by 3D Hubs. The main difference between the described cell design and the configuration reported by Jung et al. [8] was the use of a rotating cylindrical electrode instead of a rotating disc electrode. The main reason for this was that the formation of gaseous products during the reaction was causing bubbles which were sticking to the horizontal surface of the rotating disc electrode. With a RCE tip, this was prevented as the bubbles ascend from the electrode tip to the headspace and do not alter the electrode surface area during the reaction. Further, the RCE provides a higher surface area compared to the RDE (3 cm^2 vs 0.196 cm^2) leading to a higher current flow.

3.2 Description of different Cell Parts

The decoupled rotating cylindrical electrode (RCE) shaft containing magnets for the rotation is the centerpiece of the gas-tight electrochemical cell. The customized shaft had to be split into two parts. One part is placed outside of the electrochemical cell and consists of an adaptor that is screwed to the rotor (Pine Research Instrumentation) and has the driver magnet attached. The driver magnet is fixed at minimum distance above the Teflon shell which encapsulates the follower magnet.

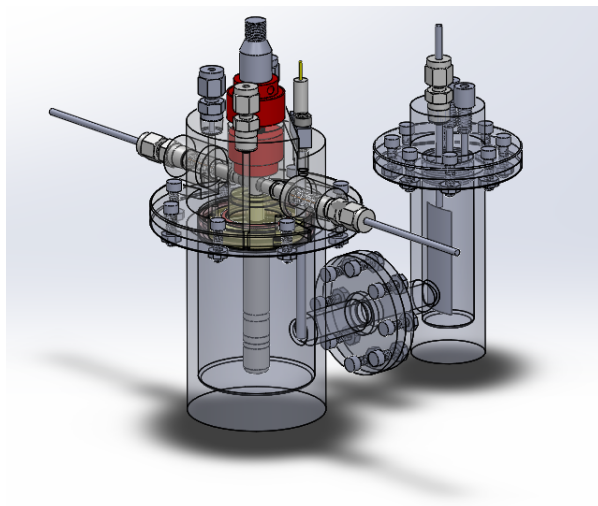


Figure 3.1: Rotation cell

The second half of the shaft is topped by the follower magnet and screwed into the RCE tip (Pine Research Instrumentation) that reaches into the reaction chamber. The magnets (Magnetic Technology LDT.) are planar discs and their magnetization consists of 6 poles that are alternating N-S axially. This way it is ensured that the magnet is locked in while rotating, providing good accuracy of the responding rotating speed which was tested with a tachometer (Pine Research Instrumentation). An axial thrust bearing with the right size was tested first as a contact between the follower magnet and the Teflon shell to prevent friction. It was consisting of three parts all of which were made of steel, hence, magnetic. This was causing the parts to be repelled by the magnet and not suitable for this application. All commercially available axial thrust bearings made out of plastic were either too thick, which would increase the gap between the two magnets considering the fact that the magnetic force is decreasing exponentially with distance. Therefore, this issue was solved by using a radial ball (igus,inc.) bearing, where the shell with a bigger diameter was shortened with sandpaper on one side and the inner part was shortened on the other side. This way rotation was possible around a vertical axis while at the same time applying pressure to the Teflon shell along this axis.

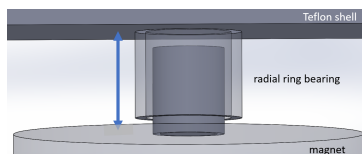


Figure 3.2: Radial ring bearing

The electric contact is introduced from two opposite sides of the Teflon shell and was made by using two stainless steel rods (Uxcell) that were glued with a conductive silver adhesive (Electron Microscopy Sciences) to brush-plungers (Pine Research Instrumentation) at its ends. The brush-plungers compensate for any vibration of the RCE shaft and ensure an electric connection. To seal the inlets on each side Swagelok connections (Part No. T-200-1-2) were used.

The custom-made Ag/AgCl reference electrode (RE) from CH Instruments can be inserted with a pressure plate through a hole in the Teflon shell into the reaction chamber.

The pressure plate is screwed into the Teflon shell, with an O-ring pressed in between, to provide a sealed inlet for the RE.

The bottom part of the Teflon shell is sealed with a CNC-machined bearing assembly that is made out of polyether ether ketone (PEEK). PEEK is a polymer with a high chemical resistance and high hardness. It shields the follower magnet and electric connection from splashes coming from the liquid electrolyte when rotating. Additionally, the PEEK part has a flanged sleeve bearing (McMaster-Carr) embedded to its center to avoid friction with the RCE shaft and provide better alignment to stabilize the rotation.

Plastic tubing (Cole Parmer, IDEX) is used for the gas in- and outlet and is directly inserted into the electrolyte on the WE side for the bubbling of CO_2 . The gas flow has to be introduced to both compartment cells at the same rate for pressure equalization of the ion-exchange membrane. Swagelok connections and male nuts (Cole Parmer, IDEX) are used for gas-tight sealing.

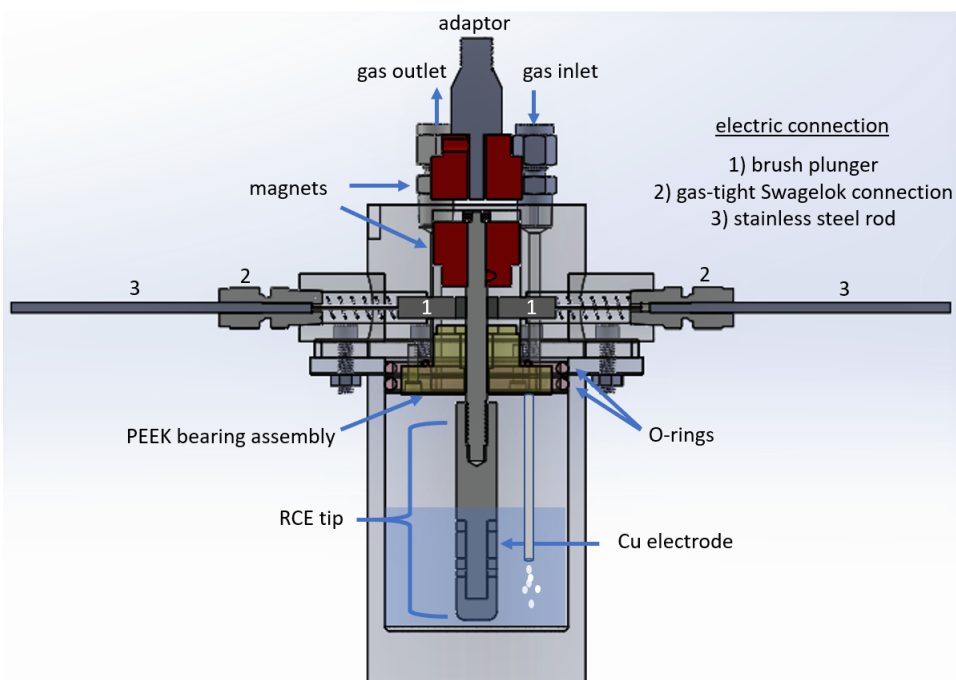


Figure 3.3: Working electrode compartment

For the counter electrode (CE) a platinum plate was glued to a stainless steel rod (Uxcell) with an electrically conducting silver glue. (Electron Microscopy Sciences) The requirements for the CE are a big surface area to ensure that no current limitations arise.

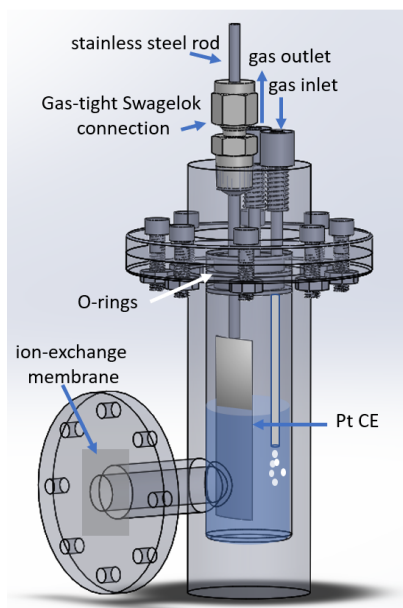


Figure 3.4: Counter electrode compartment

The bodies of each compartment cell are made out of polycarbonate (PC). PC is a material that has good properties regarding its chemical and heat resistance. Furthermore, its transparency enables to visually observe the reaction progress that is happening inside the compartment cells. The connection between the two compartment cells is made through a bridge. In the center of this bridge an anion-conducting membrane (Selecion AMV AGC Inc.) is placed and is sealed with an O-ring.

All O-rings, screws, and hex nuts used in this prototype were purchased from McMaster-Carr. For the O-rings that sealed the bridge between the WE compartment cell and the CE compartment cell an FEP-encapsulated Silicon Ring were used to prevent decay caused by the contact of the O-ring with the electrolyte.

Chapter 4

Experimental Section

4.1 Experimental Methods

In this section various experimental techniques used for the generation of data will be introduced. As some experimental parameters were varying for the two different experimental set-ups (reduction of potassium ferricyanide / CO_2 reduction), the parameters are listed in the corresponding section.

Electrical Measurements

For all of the electrical measurements a potentiostat from *Metrohm Autolab B.V.* was used for the regulation of potential and current. (Type - PGSTAT302N, Serial no - AUT87747) For the measurement control and data analysis the program NOVA (*Metrohm Autolab B.V.*) was used.

Mass Flow Control MFC

The mass flow controller is deployed to regulate the gas flow during the reactions. During the CO_2 reduction a known feed of CO_2 is needed to determine the concentration of aqueous CO_2 in the system. The instrument was purchase from MKS Instruments. (Model No. GM50A)

Mechanical Polishing

To get rid of contamination and surface roughness the electrodes have to be mechanically polished with a material that is harder than the metal. In this work 600 grit sandpaper was used for pre-treatment on which the electrode was polished for 3 minutes. After rinsing the electrode, an alumina slurry ($0.05\ \mu\text{m}$, Allied High Tech Products Inc.) on micro-cloth was used to achieve a smooth surface. The polishing was done for 5 minutes. Then the electrode was rinsed with Millipore water and sonicated for 10 minutes. After the Millipore water was exchange this step was repeated. To finish this step, the electrode was washed and blow dried.

Electropolishing

Electropolishing helps to get rid of persistent contamination and small irregularities of the electrode surface. It is performed after mechanical polishing. The cylindrical electrode is connected as the working electrode. A hollow copper cylinder surrounding the cylindrical electrode was used as the counter electrode. By applying a potential a small layer of the WE surface is stripped and dissolved, forming an oxide. Its precipitation can be observed as a blue slurry. On the CE side the formation of H_2 can be observed.

Impedance FRA/PEIS

The PEIS (potentiostatic electrochemical impedance spectroscopy) measures the resistance given by the inner system of the reaction cell including electrolyte resistance and surface processes. As impedance is the resistance resulting from alternating-current different frequencies are scanned at a fixed potential. In this thesis, an impedance measurement was conducted before each experiment to extract the value of ohmic resistance. The iR compensation was done manually after each experiments with the extracted ohmic resistance value.

Cyclic Voltammetry CV

When conducting a cyclic voltammetry experiment, a potential is scanned up and down a fixed potential range. The resulting current contains information about processes that are happening in the system. As simple as this method is, the interpretation can be challenging. In this thesis, this method was used for the reduction of ferricyanide. It was further used, in the scope of the electrochemical CO₂ reduction, to remove potential residual contamination, such as oxides, from the surface of the electrodes before each experiment as well as to determine the potential at which the subsequent experiment will be performed.

Chronoamperometry

During chronoamperometry the electric potential is held at a constant value resulting in a current that follows the applied potential. For the actual experiment, the reduction of carbon dioxide the method chronoamperometry was chosen. The determined potential was held at the same value for about 1.5 hours. For the analysis of the gaseous products that were generated during this time a gas sample was injected into the gaschromatograph 15 minutes into the experiment and after that periodically approximately every 20 minutes for three more times.

Gas Chromatography GC

Gas chromatography is widely used for identifying and quantifying gaseous products. Different detectors coupled with the GC help to specifically target particular products. For the quantification of gaseous products of the CO₂RR a gas chromatograph from SRI Instruments (Model Number 8610C) was used. It contained three columns: a 5 meter Haysep-D precolumn, a 2 meter MoleSieve 5A column and a 2 meter Haysep-D column. The detectors that were attached to the GC, were a thermal conductivity detector (TCD) for the detection of hydrogen (200 ppm to 100%) and a flame ionization detector including a methanizer (FIDmeth) to detect hydrocarbons. (1 ppm to 50.000 ppm)

Nuclear Magnet Resonance Spectroscopy NMR

For the analysis of liquid products the nuclear magnet resonance spectroscopy uses an oscillating electromagnetic field to stimulate the atomic nuclei, matching its intrinsic frequency. The nuclei successively emits a characteristic electromagnetic signal and helps identifying different species. In this work a DRX500 spectrometer (Bruker Biospin GmbH) was used. Even though this technique is not commonly used for the quantification of products, internal and external standards were used to evaluate the amount of liquid products yielded during the CO₂R. A standard curve of commercially purchased standards of each product was generated. Phenol and dimethyl sulfoxide were used as internal standards to compare the signal intensity to. Those two substances carry the advantage of being

chemically stable, inert and non-volatile. Due to the aqueous electrolyte used in the experiment, water suppression had to be implemented into the procedure, otherwise the enormous water signal would obscure most of the product peaks.

4.2 Reduction of Ferricyanide

4.2.1 Cu RCE to determine the boundary layer thickness

As the custom designed rotation cell was already in use for CO₂RR experiments and contamination with Fe-ions (an active CO₂R material) had to be prevented, the reduction of potassium ferricyanide was done in a glass cell, that had comparable dimensions to the rotation cell. Before each experiment the cylindrical electrode was mechanically polished as described in the procedure before. After the mechanical polishing, the electrode was electropolished in 85% phosphoric acid at 1.6V vs. Cu for 300 seconds and rinsed with Millipore water. For the experiment, a 0.1 M KClO₄ solution was used as the electrolyte. The reference electrode in use was a commercially available Ag/AgCl RE. During the whole experiment nitrogen was purged to achieve an inert atmosphere. After the atmosphere was saturated, the impedance was measured to determine the resistance of the solution. Then a cyclic voltammetry sweep between -0.5V and -1.6V vs. Ag/AgCl was taken as a blank. After adding 10 mM potassium ferricyanide to the solution, the same potential range was scanned again. The rotation speeds that were examined were 25 rpm and then doubling this value until 1600 rpm was reached.

4.2.2 Glassy Carbon RDE for extracting kinetic parameter

This experiment was done prior to CO₂RR experiments and was therefore done in the custom designed cell. The cell was cleaned thoroughly afterwards. To prepare the electrode, the glassy carbon was mechanically polished with alumina slurry on microcloth, sonicated and rinsed with Millipore water. Before the experiment the impedance was measured. Afterwards, a cyclic voltammetry sweep was conducted in a potential range between 0.9V and -0.5V vs. Ag/AgCl. The rotation speeds of the rotating disc electrode were 100, 200, 400 and 800 rpm.

4.3 CO₂ Reduction Reaction

For the generation of data the electrochemical set-up described in chapter ?? was used. To assess the influence of the electrode rotation speed on the product distribution, several rotation speeds were tested at a fixed potential. Subsequently, two rotation speeds with a significant difference were chosen and fixed and experiments over a range of potential were done. This procedure was repeated for two different electrolyte concentrations, 0.1 M and 0.2 M KHCO₃, to study the influence of the electrolyte. To achieve an outlook and predict the behaviour of higher electrolyte concentrations, two measurements were conducted at 0.5 M KHCO₃. This leads to a better understanding of the influence of the boundary layer thickness on the product selectivity as well as the role of the electrolyte in this matter. Further, the influence of the electrode morphology is of high interest. Therefore, two experiments with copper cubes were conducted and a mechanistic hypothesis based on the results will be proposed in the discussion section.

4.3.1 Preparation of the Working Electrode

Polycrystalline copper was used as the standard material for the RCE. The cylindrical electrode was mechanically polished following the procedure as described before. After rinsing and blow drying, the working electrode was placed on a copper hook and emerged in 85% phosphoric acid. The counter electrode - made out of a copper foil - was bent into a hollow cylinder surrounding the cylindrical electrode. A fixed potential of 1.6V vs. Cu was applied for 300 seconds for electropolishing.

For two measurements, that are described later, copper cubes were produced. Those copper cubes were formed in situ after the electropolishing of the polycrystalline copper electrode. After that, the electrode was cleaned, dried and placed into 0.1M KHCO_3 . Then, 4 mM of KCl were added and the potential was cycled between -1.75V and 0.30V at 5 mVs^{-1} for 4 cycles until a stable CV was achieved. The stop potential was at the lower vertex potential.[16]

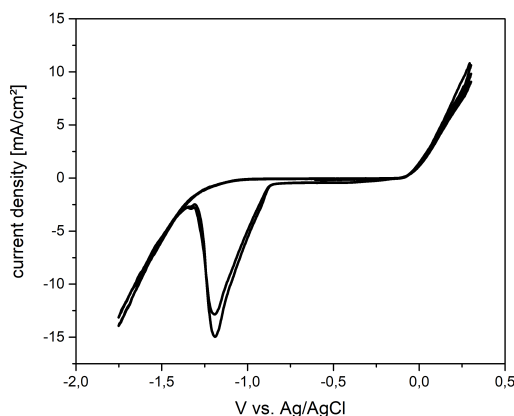


Figure 4.1: CV for the preparation of Cu Cubes

The mechanism happening during the cycling is based on the formation of CuCl in the solution during the reduction under oxidizing conditions. CuCl precipitates in solutions above pH 4 and is shifted via equilibrium reaction in the presence of water to Cu_2O in near neutral and basic solutions with low chloride concentrations. With each cycle a more structured surface is formed. The peak that can be found at a potential of -1.2V vs. Ag/AgCl in figure 4.1 is based on the reduction of Cu_2O to metallic copper.[16]

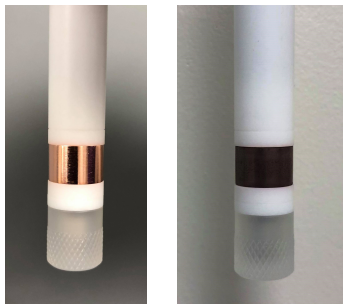


Figure 4.2: Polycrystalline copper vs. CuCubes

4.3.2 Experimental Measurements in Rotation Cell

To set up the cell, the compartment cells and every part reaching into the reaction chamber were rinsed with Millipore water several times and blow dried. Next, an O-ring was placed inside the groove of the ion bridge, the ion-exchange membrane was placed on top, and the two compartment cells were screwed together tightly to avoid leaks. The compartment cells were then filled with electrolyte - 82 mL on the WE compartment side and 22 mL on the CE compartment side. After that, the WE and CE cap were assembled and put on top of each compartment cell. A continuous gas flow of 20 sccm CO_2 was set and all gas lines attached to the cell and connected to the gas chromatograph. The reference electrode including the pressure plate was inserted last to avoid fractures. CO_2 was bubbled for 15 minutes until an inert atmosphere was reached. In the mean time a stable rotation of the working electrode was established and the cell fixed with clamps.

Then, the electrochemical measurements were started. At first an impedance measurement was conducted to extract the value of resistance. This value was used for the manually applied iR correction after the experiment. Subsequent cyclic voltammetry was done to reduce eventual remains of oxidation on the WE electrode. The resulting voltammogram was used to estimate the potential that was applied during the following chronoamperometry, where the actual CO_2 reduction was taking place. During the chronoamperometry, the potential was held at the same value for 4679 seconds. For the analysis of the gaseous products, that were generated during this time, a gas sample from the headspace was injected into the GC 15 minutes into the experiment and after that periodically every 20 minutes for three more times.

The liquid samples were measured with an NMR spectrometer after the experiment. Internal standards were used as a reference. 50 mM phenol was used to quantify formate which was found on the left of the suppressed water peak whereas every other product was referenced to 2.8 mM dimethyl sulfoxide on the right hand of the water peak. 700 μl of the reaction solution including products and electrolyte were mixed with 35 μl of internal standard. The ratio of the area of the product species to the area of the internal standards were compared to the ration of the area of external standards to the area of internal standards. The external standards were made from stock solutions and measured prior to running CO_2R experiments.

The electrolyte potassium bicarbonate KHCO_3 with a concentration of 0.1 M, 0.2 M and 0.5 M was used. The bulk pH of those solutions with CO_2 saturation is lying between 6.8 and 7.5. An Ag/AgCl reference electrode is used, that is suitable because of its simplicity, commercial availability and it can be used in near-neutral pH conditions.

The first experiments were done at a fixed potential while scanning different rotation speeds. Two rotation speeds were selected that were showing significant differences in the faradaic efficiency of products. Those two rotation speeds - 100 rpm and 800 rpm - where tested over a potential range where an area of kinetic control as well as a mass transport limited regime was falling into. All of the experiments above where conducted at two different electrolyte concentrations (0.1 M and 0.2 M) to evaluate the influence of the electrolyte on the product selectivity. For a further outlook, two experiments where conducted with 0.5 M KHCO_3 . Additionally, to show a preview of the effects that changes in the rotation speed have on a different surface morphology of the working electrode two data points were collected with a nanostructured copper electrode.

Chapter 5

Mathematical Modelling

This section will cover the framework of a mathematical model describing electrochemical systems. The code will be modified for two different applications in this thesis. With this code different kinetic parameters can be extracted for the reduction of potassium ferricyanide. It can further be used to calculate pH gradients and near surface concentration gradients of reactants and products during the CO₂ reduction reaction. Those two codes will vary regarding different reaction conditions and input values, however, the main structure will remain the same and will be described in this chapter. The modifications of each code will be discussed in the corresponding section.

5.1 General Assumptions

The Poisson-Nernst-Planck (PNP) equation is commonly used to describe an electrochemical system close to the working electrode surface area - the electrochemical double layer including the diffusive layer.[11][17][18] To set the framework of the system the following assumptions can be made:

- The electrolyte is an ideal solution and, therefore, concentrations can be used instead of activities.
- The cylindrical surface is uniformly accessible.
- A steady-state condition exists. ($\partial c_i / \partial t = 0$)
- An isothermal condition exists.
- The electrolyte is Newtonian and the physical and transport properties are constant.
- Diffusivities of all reactants are constant.
- Limiting current condition exists.
- Convection can be neglected.
- The electrode is rotating about its axis in the center of a stationary, circular, cylindrical electrode.[19]

The code is valid for a one-dimensional finite geometry in direction normal to the electrode (figure 5.1).

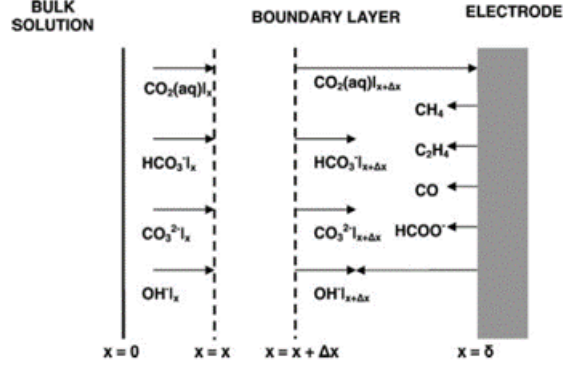


Figure 5.1: Mass transfer boundary layer[11]

5.2 Mathematical Theory behind the Rotating Cylindrical Electrode

The principle behind the rotating cylindrical electrode is based on the Nernst-Planck equation 5.1 consisting of three terms that describe the mass transport.[20] The first term describes the diffusion which is caused by a concentration gradient. This gradient appears because of the consumption or production of reaction species during faradaic reactions. The second term is based on the ion migration that derives from a potential gradient after applying an external electric field. The last term is representing the convection due to the rotation of the electrode.

$$-J = D_i \nabla c_i + \frac{z_i F}{RT} D_i \nabla (c_i \nabla \phi) - R_i v \quad (5.1)$$

In systems where no mixing is applied, a non-uniform boundary layer is formed. The thickness of this layer can reach up to several hundred micrometers. Therefore, if no rotation is applied the following equation (5.2) can be used for describing the diffusion boundary layer thickness .

$$\delta_N = 6 * (D_i * t_\infty)^{1/2} \quad (5.2)$$

By introducing a rotation to the system, the boundary layer thickness is evenly reduced to only a few micrometers. A well established equation developed by Levich 5.3 links the diffusion boundary layer thickness to the angular frequency for rotating disc electrodes.[20]

$$\delta_N(RDE) = 1.6 * \omega^{-1/2} * \nu^{1/6} * D_i^{1/3} \quad (5.3)$$

Einstein et al. modified the equation to fit applications with rotating cylindrical electrodes.[19]

$$\delta_N(RCE) = 0.9962 * d_i^{-0.4} * \nu^{0.344} * D_i^{0.356} * \omega^{-0.7} \quad (5.4)$$

5.3 Main Structure

For evaluating mass transport effects, a built-in PDEPE solver of MatLab can be used. The 1D parabolic and elliptic partial differential equation calculates a function u , representing the concentration of species over time and distance. As the concentration of

species varies in an electrochemical cell due to homo- and heterogeneous reactions and mass transfer effects, this solver fits well for this problem.

MatLab is using the finite element method to solve the problem. The concept of the finite element method is to divide the continuous domain of the original problem into elements of finite size. Those subdomains are, in the case of a time-dependent problem, solved by several ordinary differential equations and then assembled into a global system to solve the entity of the problem. The backward Euler scheme is used for time discretization. As one of the most simple techniques to analyze differential equations it uses linear approximation over a small distance to solve an initial-value problem. It is an implicit method where the function uses other unknown variables at the same point in time to be solved.

For the construct of the main function, the mathematical description of mass transport effects has to be put in the form of the PDEPE solver (equation 5.5).

$$c(x, t, u, \frac{\partial u}{\partial x}) \frac{\partial u}{\partial t} = x^{-m} \frac{\partial}{\partial x} (x^m f(x, t, u, \frac{\partial u}{\partial x})) + s(x, t, u, \partial u / \partial x) \quad (5.5)$$

To achieve the form depicted in equation 5.5 the differential conservation law (equation 5.6) can be used, which describes the material balance for a small volume element. In equation 5.6 c is representing the concentration of species i . Adding the Nernst-Plank equation as the mass transport term to the equation results in the final form that can be used to solve the system. As mentioned before, the convection term of the Nernst-Plank equation can be neglected in the diffusive layer, whereas an extra term r_i that is representing the homogeneous reactions in the electrolyte is included.

$$\begin{aligned} \frac{\partial c_i}{\partial t} &= -\nabla J_i + r_i \\ &= D_i \nabla^2 c_i + \frac{z_i F}{RT} D_i \nabla (c_i \nabla \phi) + r_i \end{aligned} \quad (5.6)$$

In the following paragraph, each term of the PDEPE solver will be described closer and expressed through the mass transfer equation.

m is a geometrical factor determining the coordinate system in which the problem is located (cartesian: $m = 0$, cylindrical: $m = 1$, spherical: $m = 2$). x is the spatial domain and t is a finite time range. The time maximum has to be chosen regarding the point at which an equilibrium state has been reached and no change in the reaction rate is observed. This differs depending on the applied potential and rotation speed. In the PDEPE solver u is the function representing the concentration and c is the pre-factor for the derivation of the concentration over time. The pre-factor $c(x, t, u, \partial u / \partial x)$ of $\partial u / \partial t$ is 1 in both of the two applications described later.

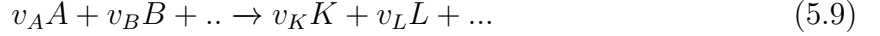
$$c = 1 \quad (5.7)$$

f is described as the flux term which consists of one part for diffusion and another part for ion migration. Same as the convection, ion migration could be neglected too, if a highly concentrated electrolyte was in use. If the ion migration is included, it is expressed by the term $\frac{z_i F}{RT}$ as part of the flux term. Including this term into the code slows the code down

significantly. To get a rough overview over general trends in concentration gradients it can be omitted. However, to get a more accurate solution as well as a gradient for the potential over time and distance it has to be included.

$$f(x, t, u, \frac{\partial u}{\partial x}) = D(\frac{\partial u}{\partial x} + \frac{z_i F}{RT}) \frac{\partial u}{\partial x} \quad (5.8)$$

s represents the source term $s(x, t, u, \partial u / \partial x)$. The homogeneous equilibrium reactions, that are taking place in the electrolyte, are described by this term.



The equation contains the chemical formulas for reactants and products and the stoichiometric coefficient ν_i . k_f is the reaction constant for the forward reaction and k_b is the reaction constant for the backward reaction.

$$\begin{aligned} s &= \frac{\partial u_i}{\partial t} \\ &= k_f [A]^{\nu_A} [B]^{\nu_B} .. + k_b [K]^{\nu_K} [L]^{\nu_L} .. \end{aligned} \quad (5.10)$$

Further, if the ion migration is included in the flux term, the potential gradient caused by an externally applied electric field, has to be added to the source term. In general, for the macrosystem, electroneutrality can be assumed. Nevertheless, a potential gradient exists in the microsystem close to the electrode and can be defined by using the Poisson equation (5.11).

$$\nabla^2 \phi = \rho / \epsilon \quad (5.11)$$

The permittivity ϵ can be expressed through the product of ϵ_0 , the permittivity of vacuum, and ϵ_r , the relative permittivity of water. ρ is the charge density and describes the sum of the concentration multiplied by the valency of all species. (equation 5.12)

$$\rho = F \sum_{i=1}^n z_i c_i \quad (5.12)$$

To fully define the system the initial and boundary conditions have to be set. The initial conditions are set at $t = 0$. It is assumed that the system resides in an equilibrium state, which results in the equal distribution of the concentration of each species in the diffusion layer as well as the bulk electrolyte. Therefore, the initial function equals the bulk concentration u_{bulk} .

$$u(x, 0) = u_{bulk} \quad (5.13)$$

Second-order differential transport equations require two boundary conditions. Those have to be put in the form of equation 5.41.

$$p(x, t, u) + q(x, t, u) * f(x, t, u, \partial u / \partial x) = 0 \quad (5.14)$$

The system looked at - the mass transport limited layer - is confined by the bulk electrolyte on one side, considered as the left side (pL, qL), and the electrode on the other,

considered as the right side (pR, qR). The electrolyte border of the boundary layer is defined by the constant bulk concentration. As there is no flux (change of concentration) on the bulk electrolyte side, $q(x,t,u)$ equals zero which means $p(x,t,u)$ also has to be set zero. To express this mathematically, the estimated value for the function uL has to be subtracted by the bulk concentration $ubulk$.

$$\begin{aligned} pL &= uL - ubulk \\ qL &= 0 \end{aligned} \quad (5.15)$$

Due to the reactions at the electrode/solution interface, the concentration of reactants and products changes, which causes a flux of electrochemically active species. As mentioned already, the flux is defined by the main function, whereby $q(x,t,u)$ has to be set as 1. $p(x,t,u)$ is defined by the current flow of the system and can be calculated with the current efficiency of product species cef_i and the electrons exchanged during the reaction zef_i . As only the current efficiencies of detected product species are evaluated, $p(x,t,u)$ of all other reacting species can be expressed through the sum of the terms of each produced species, which are multiplied by the stoichiometric coefficients ν_r of reactants. If the species gets consumed then pR is negative. In the case of product formation, it becomes positive.

$$pR_{detected} = \frac{j}{F} * \frac{cef_{pr}}{zef_{pr}} \quad (5.16)$$

$$pR_{undetected} = \pm \frac{j}{F} * \sum \nu_i \frac{cef_i}{zef_i} \quad (5.17)$$

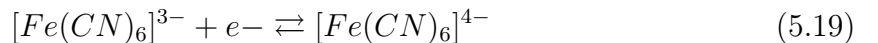
$$qR = 1 \quad (5.18)$$

The surface flux of non-electrochemically active species is 0.

The framework of this mathematical model includes most essential parts of the code. The modifications of the two different applications of the model will be described closer in the next two sections. The two finished codes can be found in the appendix.

5.4 Modification for Ferricyanide Reduction

This modification of the main code will help to identify system parameters and predict the behaviour of the system and its hydrodynamic properties with different reaction conditions. (equation 5.19)



The simulation of the experiment can be compared to experimental data at different rotation speeds. Beside identifying mass transfer parameters, this procedure can help pointing out eventual deviations of electrochemical systems from ideal behaviour.

The code was analyzed for 4 different species. $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and the electrolyte ions, K^+ and ClO_4^- . For the modelling of the cyclic voltammetry experiment the structure of the main function stays the same. ($m=0$, $c=1$, $f= D^*du + D^*zF/RT$) As there are no homogeneous reactions happening in the electrolyte, the source term only

becomes relevant for the potential gradient.

The initial condition equals the weigh-in amount of potassium ferricyanide. The initial amount of potassium ferrocyanide should equal zero. It is not compatible with the code to do so, therefore, a value has to be set which is close to zero. On the electrolyte side, which borders with the electrolyte-bulk, the concentration stays the same as the initial concentration during the course of the reaction and can be set as explained in section ???. For the boundary condition on the electrode side the Neumann condition can be used. The focus is laid on the values that have to be used for the current density j .

$$-j/F + \frac{df}{dt} = 0 \quad (5.20)$$

$$pR = -j/F \quad (5.21)$$

The Butler Volmer equation 5.22 represents one of the most basic equations of electrochemical theory. It expresses the driving force of a electrochemical/faradaic reaction and is used to evaluate the current profile. This equation can help to identify important system parameters such as the forward and backward reaction constants k_f and k_b , the symmetry factor α and the standard potential E_0 for the redox couple. For a ideal reversible reaction α is 0.5. As this reaction is seen as quasi reversible, α should take a value close to 0.5.

$$I = k_f * c_1^0 * e^{\alpha * \frac{F}{R*T} * (E-E_0)} - k_b * c_2^0 * e^{-(1-\alpha) * \frac{F}{R*T} * (E-E_0)} \quad (5.22)$$

The potential E is scanned over a specific potential range during the CV measurement. It has to be noted, that the code does not follow the time line in a straight manner. The way MatLab works for solving this problem is that the solver does not calculate the values at the exact time points determined in the mesh but approximates a solution close to those values. This is why the potential E cannot solely be multiplied by the time inside the function whereby equation 5.23 was used to correlate time and potential. For the scan from upper vertex to lower vertex equation 5.23 subtracts the time term from the upper vertex potential and vice versa.

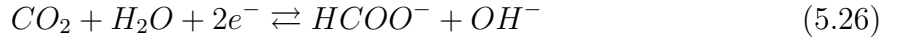
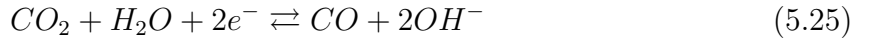
$$E = E(uv) \pm \nu t \quad (5.23)$$

5.5 Modification for CO₂RR

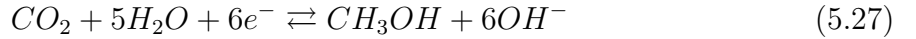
In this section the basic structure of the code will be further developed to extract the local concentration of species from experimental data. The code allows to map changes in the local activity by plotting the product distribution as a function of time and distance with a 1D PDEPE solver. This work is leaned on an earlier work done by Gupta et al. describing a steady-state system.[11] The code was further developed to meet the requirements of the system in operation including the rotating cylindrical electrode. Gupta et al. only included diffusion and neglected ion migration which is included in this model. Compared to the modification for the reduction of potassium ferricyanide, many more factors have to be taken into consideration for the CO₂RR. For the electrochemical reduction of potassium ferricyanide only a one electron reaction is taking place, whereas during the CO₂ reduction several reactions with proton-coupled electron transfer with 2 electrons up to 18 electrons at the electrode surface as well as homogeneous buffer reactions in the electrolyte are involved are happening.

The center piece of the code for the CO₂ reduction are the heterogeneous catalyzed reactions on the catalyst surface. The products that were taken into consideration are hydrogen H₂, carbon monoxide CO, formate HCOO⁻, methane CH₄, ethylene C₂H₄, ethanol C₂H₅OH, n-propanol C₃H₇OH, allyl alcohol C₃H₅OH, methanol CH₃OH, acetate CH₃COO⁻, ethylene glycole (CH₂OH)₂, glycolaldehyde HOCH₂CHO, acetone C₃H₆O, hydroxyacetone CH₃C(O)CH₂OH, acetaldehyde CH₃CHO, propionaldehyde C₃H₅CHO and ethane C₂H₆. The chemical equations of each product are shown in equations 5.24 - 5.30 and include the number of electrons needed for the charge transfer as well as the number of hydroxide ions OH⁻ formed.

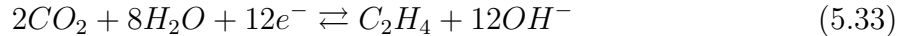
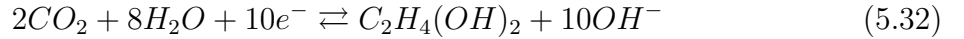
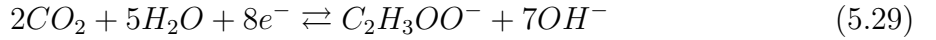
2e⁻ products



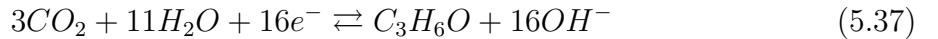
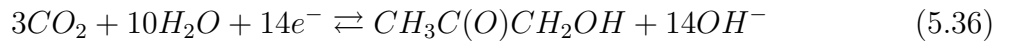
C1 products



C2 products



C3 products



The boundary condition on the electrode surface, and thereby the heterogeneous reactions, is defined by the Neumann boundary condition. The concentration values are expressed through the function 5.41.

$$p(x, t, u) + q(x, t, u) * f(x, t, u, \partial u / \partial x) = 0 \quad (5.41)$$

Because of the formation and consumption of species, a flux of species is present at the electrode surface over time and therefore the value for q_R equals one as $f(x,t,u,\partial u/\partial x)$ is already defined in the main equation. The variable p_R represents the current density and is determined by experimental data of the current efficiency of each product species. The CO_2 and OH^- consumption, respectively the formation of product species can be expressed through those values as well.

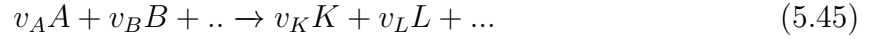
$$p_R = -FE_i/A \quad (5.42)$$

$$q_R = 1 \quad (5.43)$$

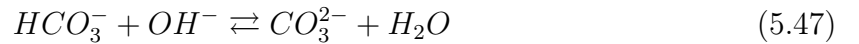
The faradaic efficiency of each species FE_i is calculated through equation 5.44 using the measured values of the current density.

$$FE_i = \frac{z * k * F * 1000}{-j} \quad (5.44)$$

The boundary condition at the bulk electrolyte is set through the initial concentration of species as explained before in the main structure of the code.



One aspect, that is different for this system than for the simulation of potassium ferri-cyanide, is the existence of a source term $s(x,t,u,\partial u/\partial x)$. The homogeneous equilibrium reactions, that are taking place in the electrolyte, are represented by this term. By using the weakly buffered electrolyte KHCO_3 , CO_2 reacts with OH^- to bicarbonate due to an equilibrium reaction. To correctly estimate the surface pH and the actual concentration of CO_2 at the electrode surface those reaction have to be taken into account.



The equation in the code contains the chemical formula for reactants and products and the stoichiometric coefficient ν_i . k_f is the reaction constant for the forward reaction and k_b is the reaction constant for the backward reaction.

$$\begin{aligned} s &= \frac{\partial u_i}{\partial t} \\ &= k_f [A]^{\nu_A} [B]^{\nu_B} .. + k_b [K]^{\nu_K} [L]^{\nu_L} .. \end{aligned} \quad (5.49)$$

With all this included, the concentration gradients of reactants and pH gradients can be calculated and plotted. Those plots will be discussed in the next section together with the results of the experimental part.

Chapter 6

Results and Discussion

The final set-up that was used for the generation of all experimental results in this thesis is depicted in figure 6.1. During the reaction the cell was fixed with clamps to avoid vibrations at higher rotation speeds. The blue spots that can be seen at the end of each side of the ion bridge are glued parts. Due to the complicated cell structure it was not possible to manufacture the compartment cell units as one part. Therefore, plastic welding was applied. The adhesive that was used for the welding had to carry the following properties: chemically resistant, especially non-soluble in aqueous electrolyte (acidic or alkaline), non-conductive and high adhesive strength. In the electronics epoxy adhesives are widely used that provide those features mentioned. The adhesive that was used is called 'Loctite 2151' (Henkel).

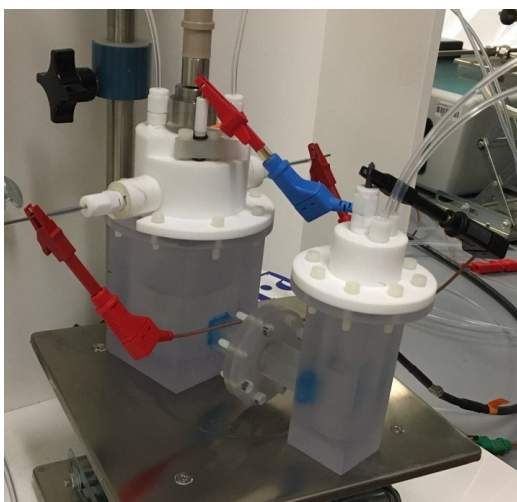


Figure 6.1: Lab set-up of the rotation cell

6.1 Determination of the Boundary Layer Thickness

6.1.1 Cu RCE to determine the boundary layer thickness for the CO_2RR

A potential range between -0.7V and -1.2V vs. Ag/AgCl was chosen for the data analysis at which a current plateau was occurring (figure 6.2). Below this range at a potential of around -1.40V vs. Ag/AgCl hydrogen formation starts. At more potentials copper

would be oxidized. The resulting current plateau represents the limiting current for the reduction of ferricyanide.

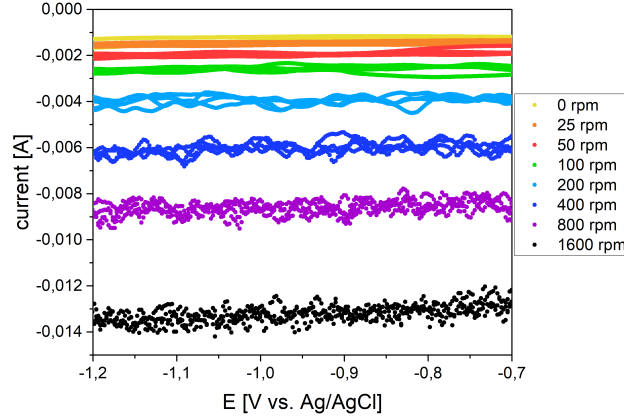


Figure 6.2: Limiting current - reduction of potassium ferricyanide on copper

The measured values of the limiting current can be used to calculate the boundary layer thickness. Some equations have to be introduced for this matter. First of all, the peripheral velocity U_{cyl} , which is depending on the angular rotation rate ω and the radius of the outer cylinder surface d_{cyl} , has to be calculated with equation 6.1.

$$U_{cyl} = r_{cyl}\omega = \frac{\pi d_{cyl}F}{60} \quad (6.1)$$

Using the U_{cyl} , the Reynolds number R_E can be calculated with equation 6.2 which describes the flow in the cell. Eisenberg et al. stated that up to a Reynolds number of 11,000 the ferro-/ferricyanide electrode reaction can be considered as predominately mass transfer controlled which equals a rotation speed of approximately 1464 rpm ($\hat{=}$ 153 rad/s) before chemical polarization becomes significant.[19]

$$R_E = U_{cyl}d_{cyl}\frac{\rho}{\mu} \quad (6.2)$$

The limiting current can be calculated with the modified Levich equation (6.3). It is important to put attention on the prefactor and adjust it regarding the unit of the angular rotation rate ω . If ω is given in rad/s a prefactor of 0.791 is used. When using rotations per minute (rpm) as prefactor 0.996 has to be used. In this case the calculations will be done with rpm.

$$i_{lim} = 0.9962zFc^0d_{cyl}^{-0.3}\left(\frac{\mu}{\rho}\right)^{-0.344}D^{0.644}U_{cyl}^{0.7} \quad (6.3)$$

Ultimately, to calculate the boundary layer thickness δ , equation 6.4 was used.

$$\delta = \frac{Dc^0AF}{i_{lim}} \quad (6.4)$$

The measured values are compared to estimated values in table 6.1.1.

electrode rotation speed [rpm]	25	50	100	200	400	800	1600
$BLT_{meas}[\mu m]$	143	108	81	53	35	24	15
$BLT_{est}[\mu m]$	296	182	112	69	43	26	16

Table 6.1: Comparison of measured with estimated values of boundary layer thickness

Figure 6.3 shows experimental and calculated values of the boundary layer thickness as a function of the electrode rotation speed.

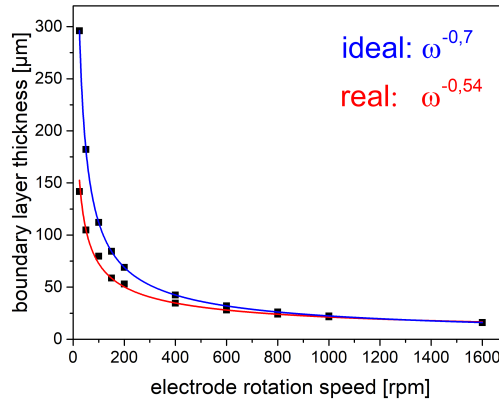


Figure 6.3: Boundary layer thickness as a function of the electrode rotation speed

In an ideal system i_{lim} is proportional to $\omega^{-0.7}$. A deviation from this might be caused by a contamination of iron ions from former experiments that increases the base current. It also might derive from an interaction between KClO_4 , which is a common electrolyte for this reaction, with the copper surface. Therefore, a blank was measured before adding potassium ferricyanide to the solution. The resulting current-voltage graph can be found in figure 6.4. The area between the dashed lines corresponds to the potential range of which the values were used for the analysis and calculation of the boundary layer thickness δ . The blank scans (strong color) are put into comparison with the CV scans where 10 mM potassium ferricyanide was added (faded color). While a rather flat plateau is reached for the ferricyanide reduction, the blanks show a distinct slope.

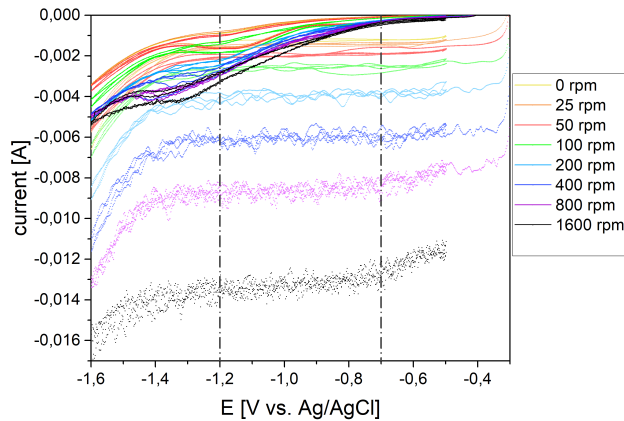


Figure 6.4: CV blank sweeps compared to CV sweeps with 10 mM ferricyanide

The averaged currents of the blank were subtracted from the main measurements in this region, however, no conclusive solution was found. For the following analysis of concentration gradients and surface concentrations during the electrochemical CO_2 reduction the calculated values received from the measured limiting current density with a correlation to the power of -0.54 were used. To extract the values of the kinetic current which is the current that is independent of mass transport, the Koutecky-Levich plot (figure 6.5) can be used. The inverse value of the limiting current is plotted against $\omega^{-0.54}$ and the

trend line can be extrapolated. The point where the extrapolated line crosses the ordinate equals an infinite rotation speed where mass transfer effects are eliminated, and thereby, reveals the kinetic current value. For comparison, the estimated values of the inverse limiting current were plotted against $\omega^{-0.7}$.

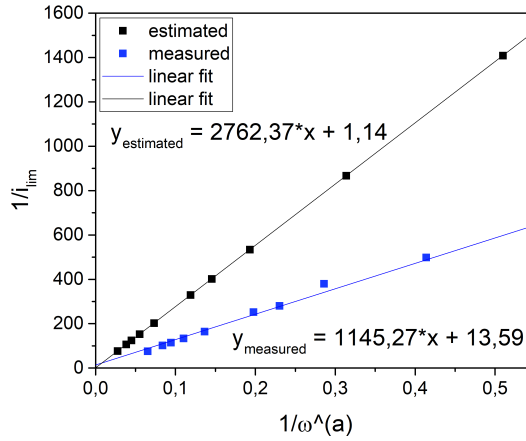


Figure 6.5: Levich-Koutecky plot - measured vs. estimated values

For the measured values a kinetic current of 0.877 A could be extracted whereas the estimated values lead to a kinetic current of 0.074 A.

In general, it is recommended to use conditions as similar as possible to the reaction conditions that are later applied during the CO_2RR . This would include the electrochemical cell set-up, the electrolyte and the gas atmosphere. The glassy carbon cell that was used had very similar dimensions compared to the actual prototype used for the CO_2 reaction. A similar electrolyte was used when introducing KClO_4 instead of KHCO_3 . Instead of CO_2 , an inert gas was used.

6.1.2 Glassy carbon RDE as an example for extracting kinetic parameters

A catalyst that was less easy to oxidize such as a glassy carbon electrode was not available for the cylindrical version of the rotating electrode. However, to demonstrate how to simulate the reduction of ferricyanide and oxidation of ferrocyanide with the MatLab code to extract kinetic parameters, experiments were performed with a glassy carbon disc electrode. The glassy carbon allows to perform cyclic voltammerty experiments at more positive potentials without oxidizing the electrode material. The characteristic duck shape of voltammograms of redox reactions (figure 6.6) was obtained. Four different electrode rotation speeds were tested. In figure 6.6 a comparison of the experimental and simulated data is shown. Looking again at equation 6.3, the limiting current largely depends on the initial concentration of the reactant. Hence, deviations of the simulated current values from the experimental current values might derive from contamination of earlier experiments. Another reason for the higher currents from the measurements could be the choice of the scan rate. A higher scan rate might lead to an increase of the current.[radhi] In the experiments conducted in the scope of this thesis as scanrate of 50 mV/s was used.

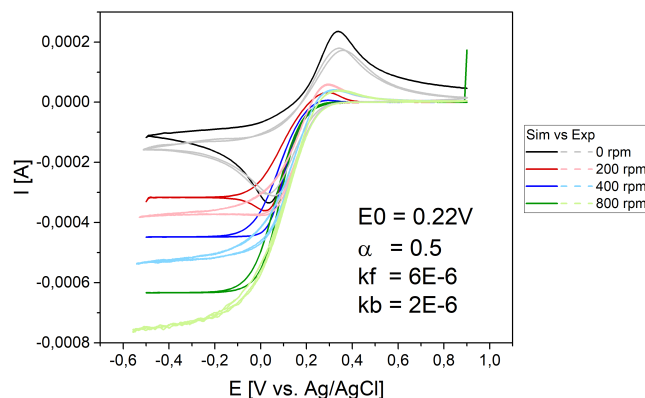


Figure 6.6: Experimental vs. simulated CV data ($[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox-couple)

The extracted kinetic values are depicted on the bottom right of figure 6.6. α is the symmetry value which is supposed to be close to 0.5 as the reaction is quasi reversible which was also obtained from the simulations. k_f represents the forward reaction constant and k_b the backward reaction constant. A sign for slow electron transfer kinetics are the separation of the peaks potentials. The further those values are apart, the slower the kinetics. A value of $6\text{E-}6$ was obtained for k_f and $2\text{E-}6$ for k_b . The standard potential E^0 was determined to be 0.22V vs Ag/AgCl with the simulations.

Additionally, a 3D plot of the concentration gradient in the boundary layer over the course of the reaction can be configured with MatLab. In figure 6.7 the concentration gradient of ferricyanide over time and distance is depicted. Figure A) shows the trends at 0 rpm while figure B) derives from the experiments at 800 rpm. It has to be noted that the distance axis are different regarding each resulting diffusion layer thickness. Nevertheless, it can be seen that at 800 rpm processes are fast while at 100 rpm the concentration gradient seems distorted and an equilibrium is reached slower.

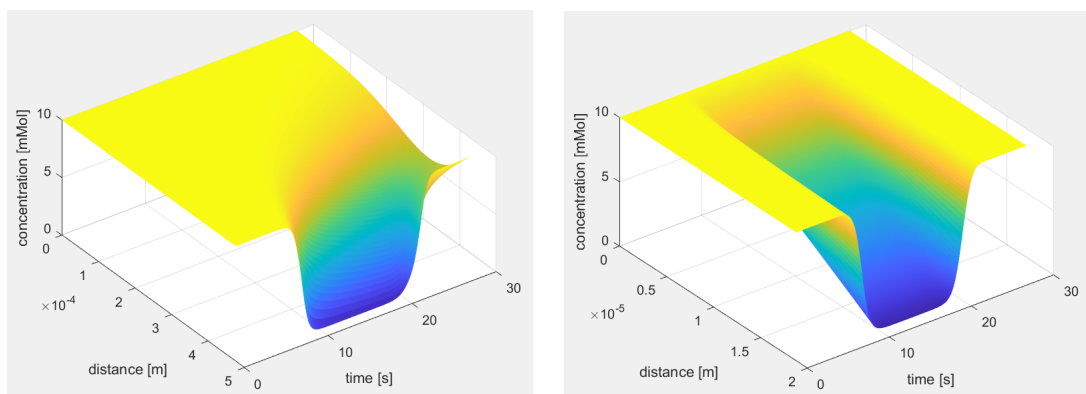


Figure 6.7: Concentration gradient of potassium ferricyanide over time and distance at 0 and 800 rpm

6.2 Electrochemical CO_2RR

In the following presentation of results each data point represents the average partial current density or faradaic efficiency of a generated product in the course of one experiment of approximately 1.5 hours. The values for gaseous products were averaged from three

GC measurements during the experiment, while the liquid products were sampled at the end of each experiment with NMR spectroscopy. All liquid products were detected in the working electrode compartment cell. Only formate and acetate, that are present in their negatively charged form, diffuse to a certain extent through the anion exchanging membrane into the CE compartment cell. Thereby, samples from both compartment cells have to be analyzed with NMR spectroscopy. The measured values were recorded as potential E with the unit V vs. Ag/AgCl. For comparability with other studies, equation 6.5 was used to convert those values into V vs. SHE. The current I is the averaged current over time. R represents the ohmic resistance value that was determined with impedance spectroscopy before each experiment.

$$E[V_{vs.SHE}] = E[V_{vs.Ag/AgCl}] + 0.197 - IR \quad (6.5)$$

In figure 6.8 the potential and current of all experiments that were conducted in the scope of the analysis of the CO₂RR were plotted over time.

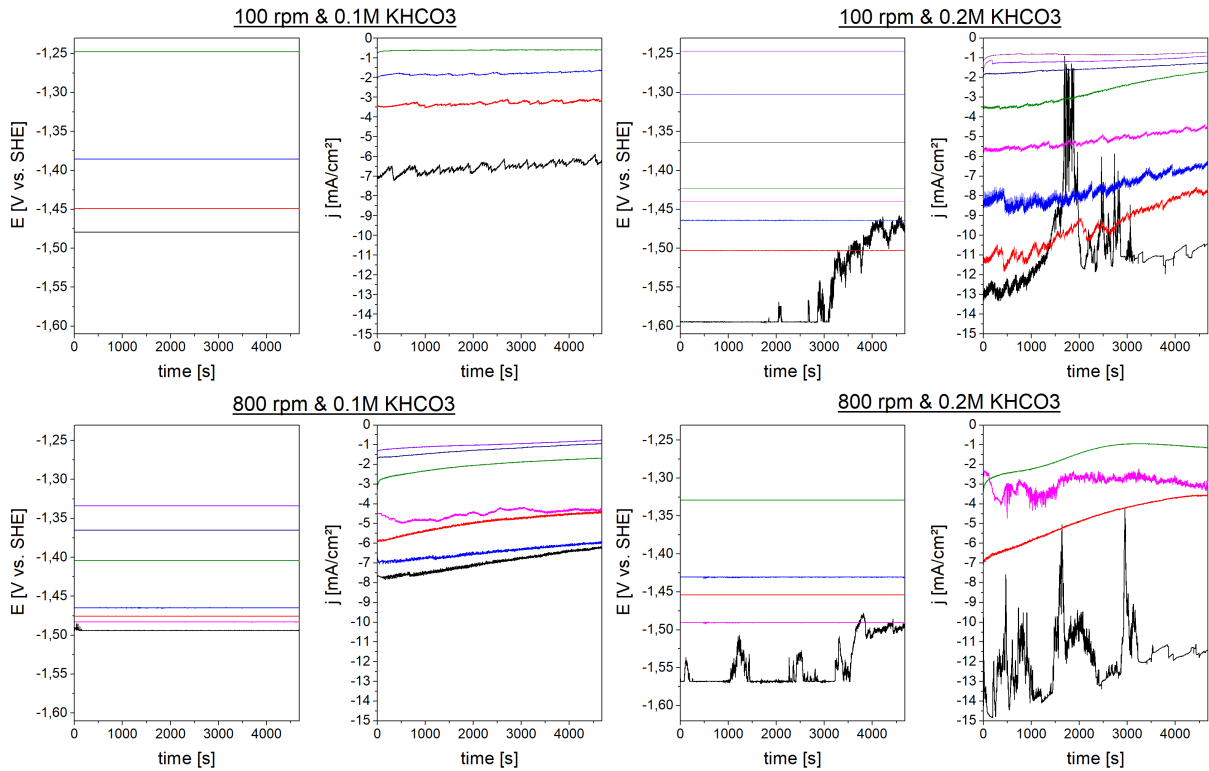


Figure 6.8: Potential and current densities over time of all experiments

For most experiments a stable trend was achieved. However, two experiments at higher negative overpotentials faced some instability due to a high resistance deriving from poor electric connection or partial surface oxidation. The extension of the rotor adaptor and RCE shaft where the magnets were screwed to, were designed as a double D cut and had a slightly smaller diameter than the inner diameter of the magnets. Therefore, when screwed tightly, the extension was pressed to one side causing an imbalanced magnet. This was leading to a slight 'wobbling' of the magnet when it was rotating at higher speeds. Consequently, it was more challenging to achieve a stable electric connection at higher rotation speeds as the brush plungers were pushed sideways by the rotation of the RCE shaft. Regardless, those measurements were included into the evaluation of results as for each experiment the averaged potential and averaged current over time was taken into

account. In general though, the electric connection was found to be stable throughout experiments of 1.5 hours. It can be noted that the current slightly decreases over time. This trend is becoming more significant at higher electrolyte concentrations and higher electrode rotation speeds. Several factors can be the cause for this phenomenon. Firstly, gas bubbles that are formed during the reaction get trapped in the ion bridge, which reduces the cross section of the membrane and consequently decreases the current flow. Another reason for this trend might be the fact that IR correction was only done manually after the experiment without considering any changes in resistance during the reaction. However, the impedance measurement was done before and after the measurement and the values of the ohmic resistance remained approximately the same. In earlier studies, a decrease of the current density has also been noted and has been attributed to changes in temperature[13] or contamination with traces of heavy metals, intermediates or persisting organic residuals in highly pure water.[21] Schouten et al. note that the deactivation of the copper electrode is strongly potential dependent and suggest that this might be caused by restructuring of the copper surface that has been observed under alkaline conditions as used in this thesis.[22][23] Yet, high faradaic efficiencies were achieved for most of the experiments with values above 90%. Only for measurements at a lower rotation speed of 100 rpm combined with a lower potassium bicarbonate concentration of 0.1M the faradaic efficiency values were slightly lower, lying between 78% and 87%. Those high efficiencies agree with the findings of earlier studies, and are fortifying the rising interest of research in this promising field. Nevertheless, the lack of selectivity still poses a challenge. Therefore, the first aspect tested experimentally was the influence of the electrode rotation speed on the product distribution.

6.2.1 Influence of the Electrode Rotation Speed at fixed Potential

With an increase of the rotation speed the size of the boundary layer thickness decreases which is an important factor regarding the supply of reactants at the electrode surface. The experiments were done at rotation speeds between 25 and 1000 rpm which equals boundary layer thicknesses between 143 - 24 μm considering the results obtain from the reduction of potassium ferricyanide. Figure 6.9 shows the results of the experiments at different rotation speeds. The experiments plotted on the left side were conducted in 0.1 M KHCO_3 and the experiments plotted on the right side were conducted in 0.2 M KHCO_3 . As expected, a change in selectivity can be seen in both cases at a rotation speed above 400 rpm. Similar trends for the faradaic efficiency of products are being observed at both concentrations, albeit, the trends are more distinct in 0.2 M KHCO_3 . In both cases, there is an increase of hydrogen, carbon monoxide and formate with increasing rotation speed while methane and ethylene decrease. A decrease is also seen for CO_2RR products that are further reduced than CO beside methane and ethylene which are summarized as 'beyond CO'. In 0.2 M KHCO_3 formate, CO and C_2H_4 show slight changes while the change in the selectivity of H_2 and CH_4 is high. This might be related to the fact that the faster removal of OH^- from and higher supply of H^+ to the near surface area is leading to a lower pH. As stated in earlier paper, H_2 and CH_4 are the two product species that are largely depending on the pH.[10] It appears that there is a significant change of trends between a rotation speed of 800 rpm and 1000 rpm especially in 0.2 M KHCO_3 . This might be caused by a change of the hydrodynamics. To eliminate that this trend could be caused by an outlier, the experiment at 1000 rpm was reproduced successfully.

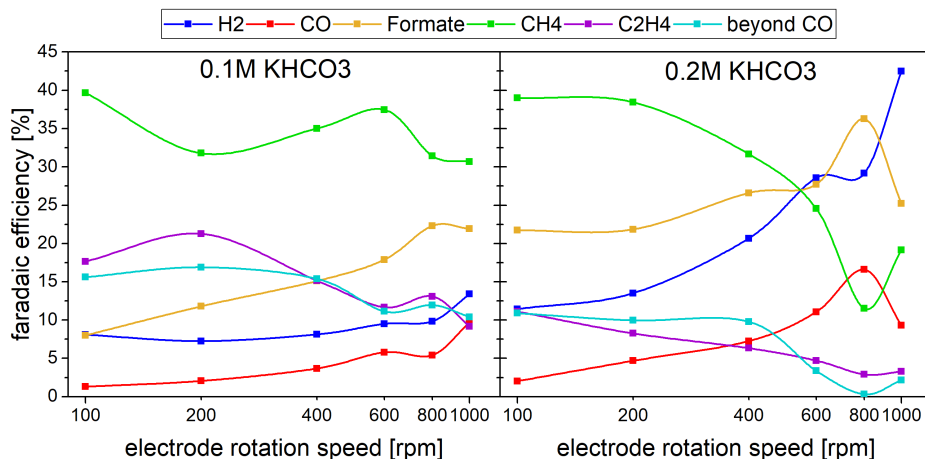


Figure 6.9: Changes in product selectivity due to changes of the electrode rotation speed in 0.1M and 0.2M KHCO_3

All experiments were conducted at an average of -1.45V vs. SHE, therefore, the total current lies in the same range for all experiments. No considerable change in total activity is seen, which also can be seen in the similar relation of the activity and the selectivity for the products.

6.2.2 Influence of Electrode Rotation Speed over Potential Range

To examine the dependence of the product distribution on the boundary layer thickness over a potential range, two different electrode rotation speeds that result in significantly different boundary layer thicknesses were picked. Experiments at 100 rpm (boundary layer thickness: $80\text{ }\mu\text{m}$) were compared to 800 rpm (boundary layer thickness: $24\text{ }\mu\text{m}$) using two different electrolyte concentrations (0.1 M and 0.2 M KHCO_3) over a potential range from -1.25V to -1.55V vs. SHE. The trends of the total current densities under all reaction conditions, are depicted in figure 6.10. The current flow starts to increase more significant around -1.40V vs. SHE. For 800 rpm a steady increase is given, while for 100 rpm a change of trends can be seen at approximately -1.43V vs. SHE in 0.1 M KHCO_3 and at -1.47V vs. SHE in 0.2 M KHCO_3 . These changes can most likely be attributed to mass transport limitations. Another aspect, that stands out is that the highest negative overpotential, at which the experiments were done, differs regarding the electrolyte concentration. This was due to the fact that limiting currents were reached at different potentials depending on the electrolyte concentration. All of the cyclic voltammetry sweeps that are shown in figure 6.2.2, were done before the experiment. To examine the ionic flow between the WE compartment cell and the CE compartment cell, the current between the reference electrode and the Pt-electrode was measured. This was done by switching the connections from the RCE and the Pt-electrode and doing a linear sweep. The measurement was repeated for

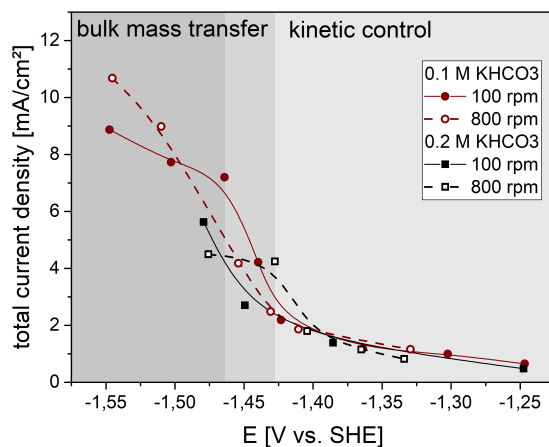


Figure 6.10: Total current densities in 0.1 M and 0.2 M KHCO_3 at 100 and 800 rpm

different electrolyte concentrations (0.1 M, 0.2 M and 0.5 M KHCO_3). The results are displayed in figure 6.2.2 and show that the slope of the current is directly proportional to the electrolyte concentration.

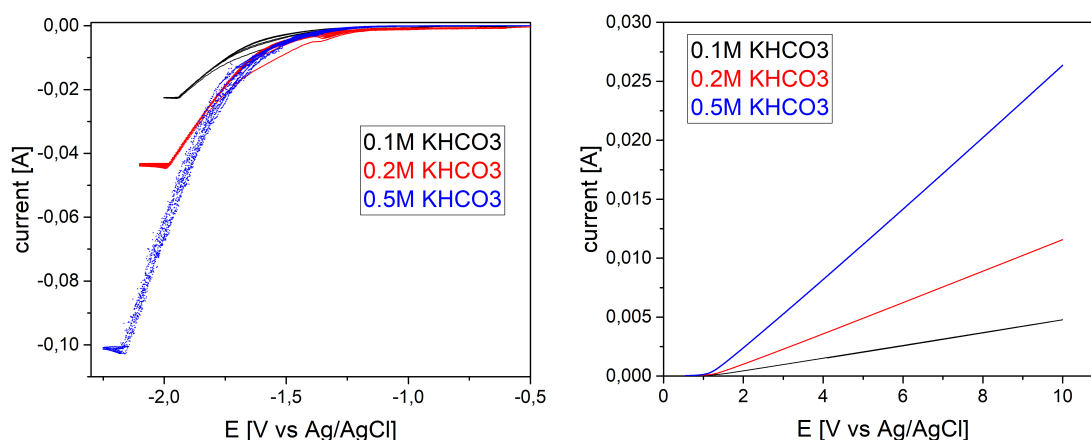


Figure 6.11: Limiting current depending on the electrolyte concentration and Linear sweep to examine current between Pt- and Ag/AgCl-electrode

A method to remain at a higher ion flow is to add a neutral salt such as KCl or K_2SO_4 , that does not affect the reaction, to maintain the salinity and keep a constant ion flow. This method was applied by Resasco et al. with different amounts of buffer to study buffer effects.[24] However, Singh et al. mentioned that this might cause a decrease of CO_2 in the electrolyte solution due to a "salting out" effect when the salinity becomes too high.[25] In chapter 7, an option to circumvent the issue of limited ion flow is presented by proposing a further developed cell design.

To take a closer look at the product distribution over the potential range the faradaic efficiency (selectivity) and partial current density (activity) of each product are plotted in figure 6.12. The following plots will be separated by the electrolyte concentration for a better comparison of the electrode rotation speeds. The electrode rotation speed of 100 rpm is shown as a solid line, whereas 800 rpm is represented with a dashed line. This graph helps to point out the general role of each product, when it comes to activity and selectivity in comparison to other products in different reaction settings. The specific dependence of each product on the rotation speed and electrolyte concentration will be discussed later. As seen before, products that are further reduced than CO , except for the main products CH_4 and C_2H_4 , are summarized to 'beyond CO '. The partial current density j of products was plotted in a linear way against the potential for a better depiction of the absolute current flow and onset potentials. In later graphs, the depiction will be changed to a logarithmic depiction, also known as Tafel plot, where the slopes are proportional to the production rate of products. At low overpotentials in 0.1 M and 0.2 M KHCO_3 hydrogen and formate are dominating with a combined faradaic efficiency of almost 70% in 0.1 M KHCO_3 and up to 85% in 0.2 M KHCO_3 . The only other product seen at that potential is CO . It has to be noted though, that the total current density is still low in that potential range under all reaction conditions (see figure 6.10). While hydrogen and formate production grows slightly with increasing potential, CO mostly remains at a same level. Starting at -1.35V vs. SHE products that share CO as an intermediate are starting to appear and increase with more negative potentials. The steep increase of the partial current density of those products lead to a fast change in selectivity. Most

dominant appears to be methane formation that reaches up to 60% faradaic efficiency at 0.2 M KHCO_3 and 100 rpm. Ethylene seems to follow a similar trend as methane. By increasing the rotation speed the selectivity and activity of hydrogen, formate and CO increase while methane, ethylene and beyond CO selectivity and activity decrease. Most products face a change of trends at around -1.43V/-1.47V vs. SHE (depending on the electrolyte concentration and rotation speed) with their current density decreasing or flattening to form a current plateau. This might indicate a mass transport regime at current densities above mentioned potential values.

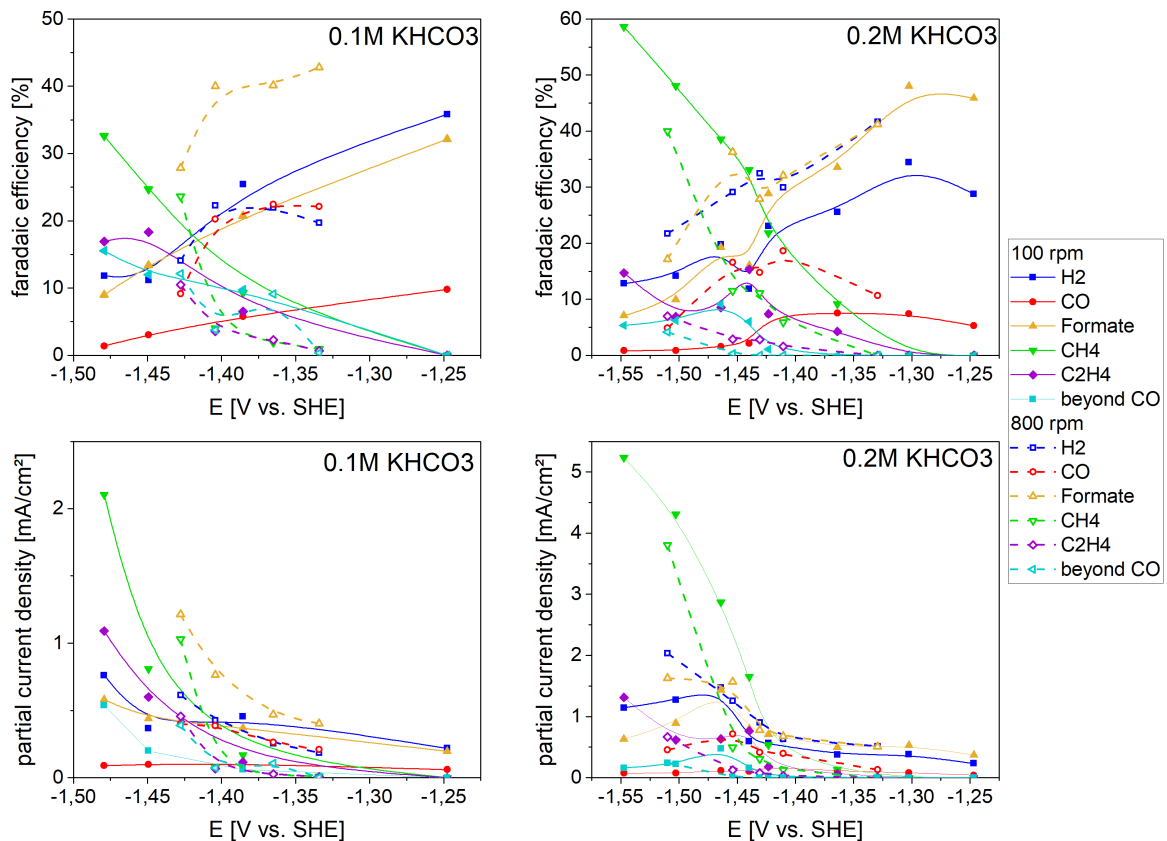


Figure 6.12: Faradaic efficiency and logarithmic partial current density at different electrode speeds paired with different electrolyte concentrations

Identifying Mass Transport Effects

To confirm the existence of mass transport limitations that were assumed to appear during experiments at potentials more negative than -1.43V/-1.47V vs. SHE the mathematical model for the CO_2RR was used. In figure 6.13 results of those calculations in exemplary reaction conditions of 0.1 M KHCO_3 and a potential of 1.47V vs. SHE at 100 and 800 rpm are depicted. The left graph shows the concentration gradients of the buffer species CO_2 , HCO_3^- , CO_3^{2-} , and K^+ are shown and on the right the concentration gradient of OH^- and H^+ are seen. The consumption of CO_2 as well as buffer reactions at the electrode surface lead to a decrease of its concentration from the bulk to the electrode surface. A similar decrease can be seen for the HCO_3^- concentration while the concentration of CO_3^{2-} is high near the surface and decreases towards the bulk. The pH at the electrode surface increases due to the consumption of protons, the production of OH^- , and buffer reactions. Because of the applied electric field a potential gradient occurs resulting in a negatively charged electrode surface.

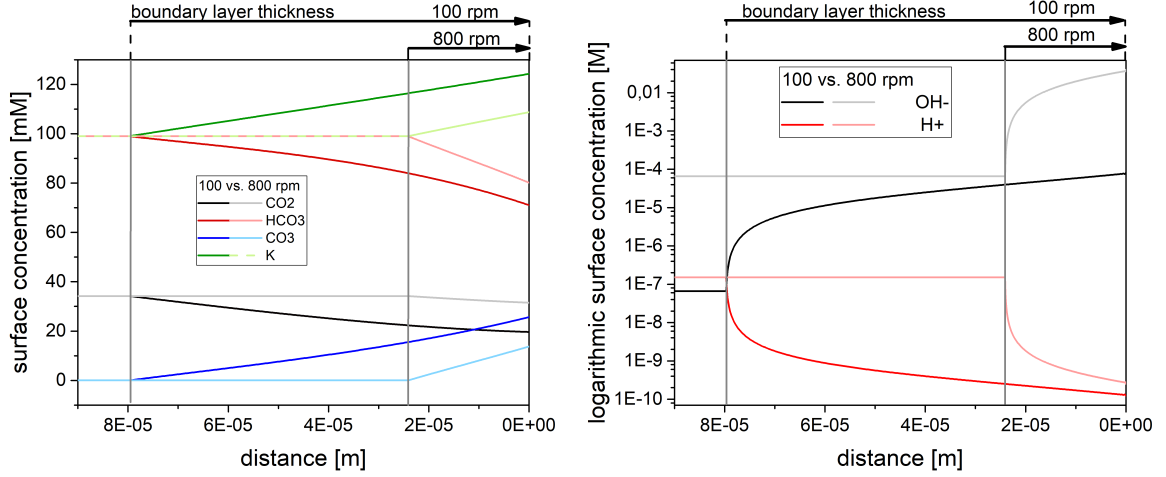
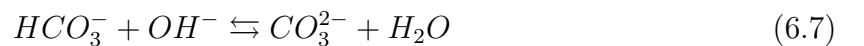


Figure 6.13: Concentration gradients of buffer species and the pH in the boundary layer at a steady state condition

By extracting the near surface concentration of species for all experiments the calculated concentration of species can be plotted. In figure 6.14 the concentration of CO_2 , HCO_3^- , CO_3^{2-} and OH^- at the outer Helmholtz plane are depicted. The concentration of CO_2 in the bulk solution was assumed to be 34.2 mM when bubbling the gas at a rate of 20 sccm.[11] Already at lower overpotentials a deviation from this value occurs at 100 rpm whereas at 800 rpm the concentration of the bulk value is almost reached near the electrode surface. It can be seen that the concentration of CO_2 is independent of the electrolyte concentration but highly influenced by the rotation speed. At 100 rpm and around -1.43V vs. SHE mass transport limitations are starting to increase significantly and a current plateau is reached at -1.50V vs. SHE. Looking at the rotation speed of 800 rpm, no significant limitation can be observed. Only a slight decrease of the CO_2 concentration towards higher overpotentials is noticeable. The bicarbonate concentration shows similar trends. However, in this case, as bicarbonate is the anion species of the electrolyte, two different initial concentrations are deployed. At an electrode rotation speed of 100 rpm the concentration of bicarbonate decreases, starting at a potential of -1.43V vs. SHE. However, in contrast to the concentration of CO_2 , a decrease of the bicarbonate concentration can be seen above -1.47V vs. SHE at a electrode rotation speed of 800 rpm too. This could be either attributed to mass transport effects that also occur at higher rotation speeds or happens due to the involvement of bicarbonate into increased buffer reactions at more negative potentials. Another option for the depletion of bicarbonate could be that it acts as a reactant in a possible direct reduction to formate which will be discussed later in detail. The increase of CO_3^{2-} can be attributed to a series of events starting at approximately -1.40V vs. SHE. Looking at the buffer equations that take place in solutions with a pH larger than 7 and considering the changes in the species CO_2 , HCO_3^- and OH^- some conclusions can be drawn.[11] Firstly, CO_2 is converted into bicarbonate with the OH^- which is produced during the reactions at the electrode surface.



The resulting bicarbonate then gets neutralized by the newly formed OH^- near the electrode surface.



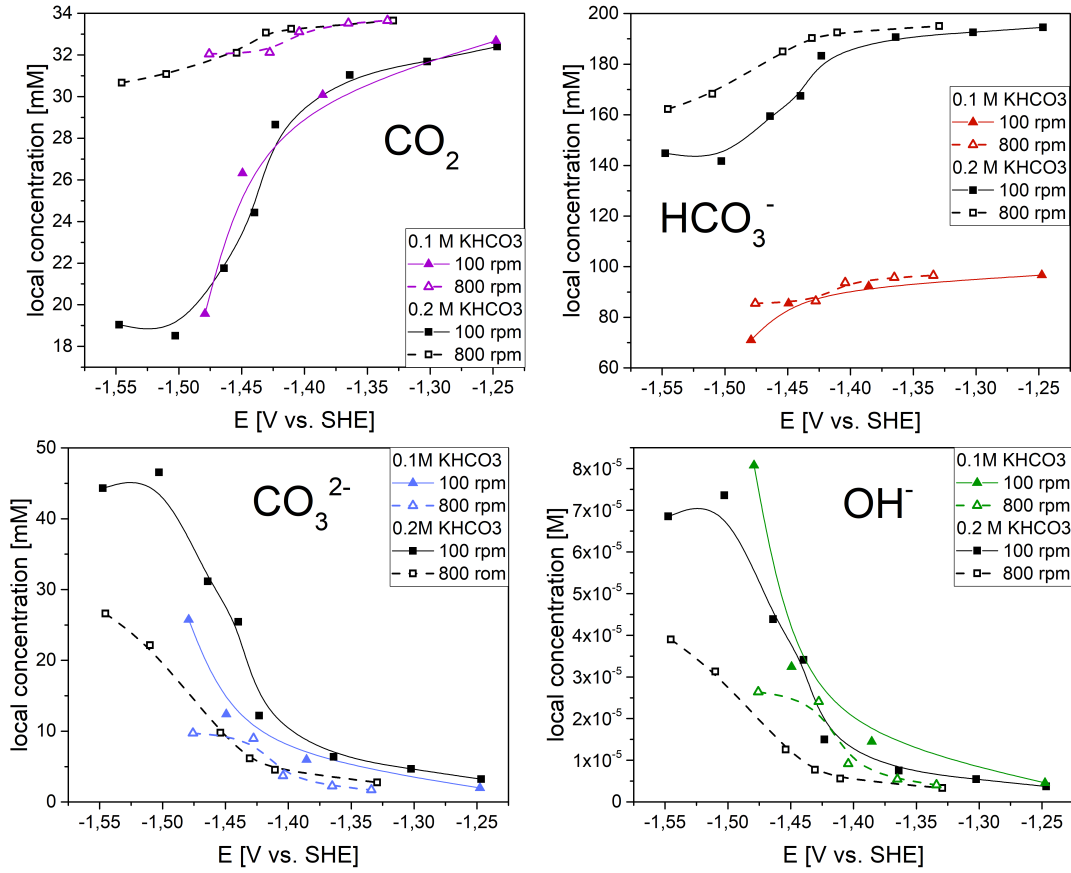


Figure 6.14: Concentration of CO_3^{2-} and HCO_3^- at the outer Helmholtz plane

Hence, when a higher production rate of CO_2 reduction products picks up at -1.40V vs. SHE, more OH^- is produced which means that the mentioned buffer reactions pick up and a higher amount of CO_3^{2-} is seen due to the equilibrium shift. This means that CO_2 is not only consumed by the faradaic reaction but also by the buffer reactions to stabilize the pH adding to the further depletion of CO_2 at the electrode surface. The increase in the rotation speed results in a faster removal of OH^- from the electrode surface, and thereby, a decrease of the surface concentration of OH^- and concomitant a decrease of the pH with more negative potentials (figure 6.15). It can also be noted, that a higher electrolyte concentration which equals higher buffer strength also lowers the pH. The stronger buffer reaction is seen in a decrease of OH^- and an increase of CO_3^{2-} with a higher electrolyte concentration. To underpin the conclusions that were drawn before, the local pH in different reaction conditions is plotted next to the concentration of buffer species in a potassium bicarbonate electrolyte as a function of the pH.[25] In this graph the area between a pH of 8.6 and 10 shows significant changes in the concentration mirroring some of the observations. With a rising pH a decrease of CO_2 is seen, whereas an increase of CO_3^{2-} takes place, HCO_3^- is stagnating in this area and OH^- increases, while naturally the concentration of protons decreases. To analyze the CO_2 RR properly, mass transport effects have to be exposed by uncovering the fine line between the depletion of CO_2 due to faradaic reactions and buffer effects. Also the role of bicarbonate and the possibility of a direct reduction has to be considered.

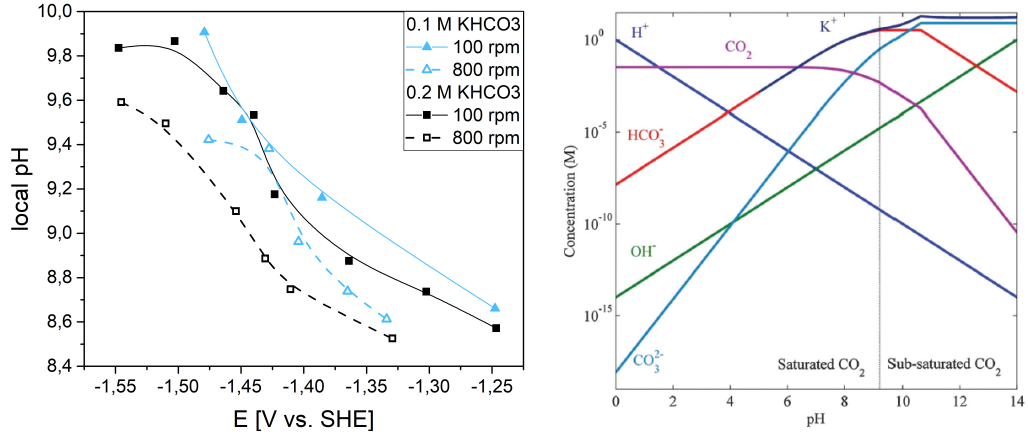


Figure 6.15: A) pH ($\hat{=}-\log[H^+]$) at the outer Helmholtz plane B) Concentration of buffer species in CO₂ saturated bicarbonate electrolyte at 298,5 K and 1 atm[25]

The mathematical model allows further to generate 3D plots of the concentration, potential and pH gradients over time and distance. For a better overview only the change of concentration at 100 rpm was plotted. It has to be noted that $c(0,0)$ can be found on the left for CO₂, HCO₃⁻ and the potential (decreasing quantities), while it is found in the front for OH⁻, CO and the pH (increasing quantities) for a suitable depiction of the gradients. It appears that the pH is stabilizing faster, however, this is due to the fact that the pH is a logarithmic quantity. The plane that is seen in the plot of the potential at $t(0)$ is an artifact of the code.

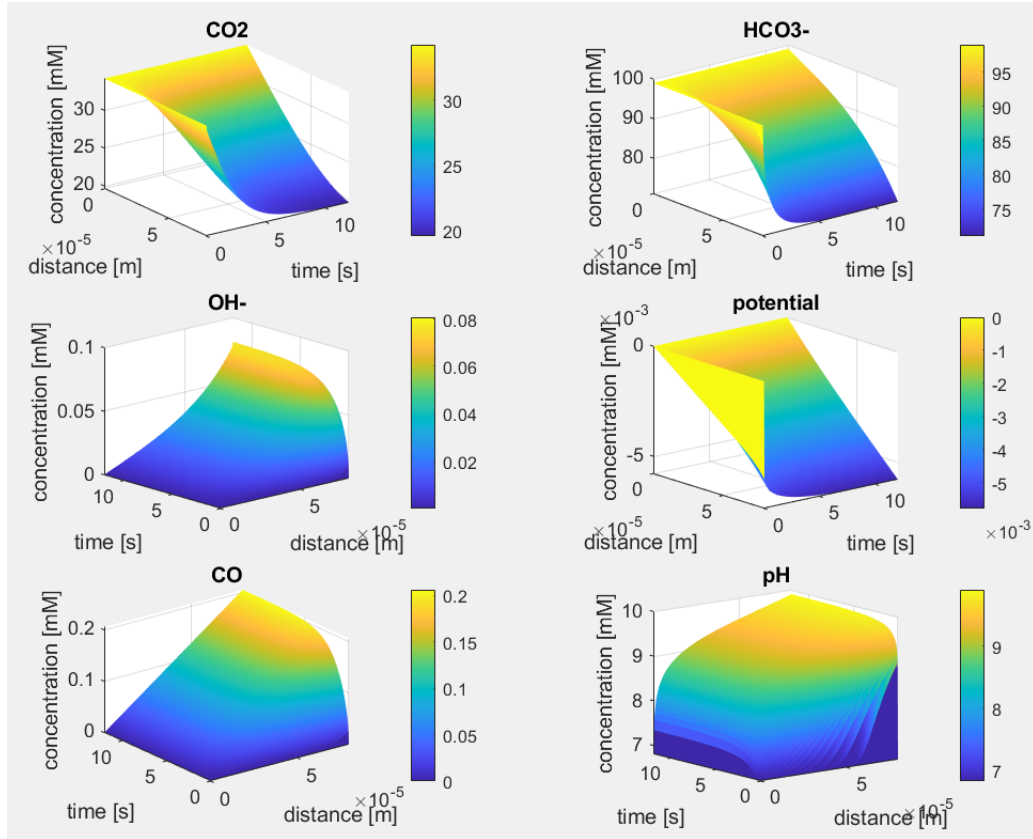


Figure 6.16: 3D plots of the concentration gradient of species and the pH gradient in the boundary layer over time

One weak spot of this code is represented in figure 6.17 where the concentration gradients of the main products are shown at 12 seconds when a steady state is already reached. In the code it is assumed that the bulk concentration of products remains at 0 mM.

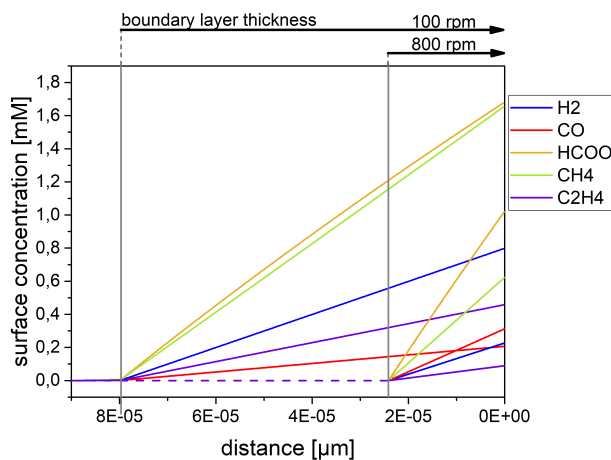


Figure 6.17: Concentration gradient of product species in the mass transfer boundary layer

Nevertheless, due to the accumulation of liquid products in the reaction solution the concentration of product species in the bulk increases. It was determined via quantitative NMR spectroscopy that most liquid products do not reach a concentration value above $1 \mu\text{mol}$ in the reaction solution which is why this change of concentration can be neglected.

In general, the mathematical model gives valuable insight into mass transport effects and shows the importance of surface concentrations. In the following analysis of products in detail, the surface concentrations calculated as described help to further rationalize experimental data.

Detailed view on different products

The overview that was given before, already lined out important areas with high current flow, crucial onset potentials and trends of product selectivities and activities. To understand the effects of the electrolyte concentration and rotation speed better, it is necessary to take a look at each of the products in detail. In the following, the trend of each products regarding the changes in rotation speed and electrolyte concentration will be commented. Detailed mechanistic considerations will be discussed in section 6.3.

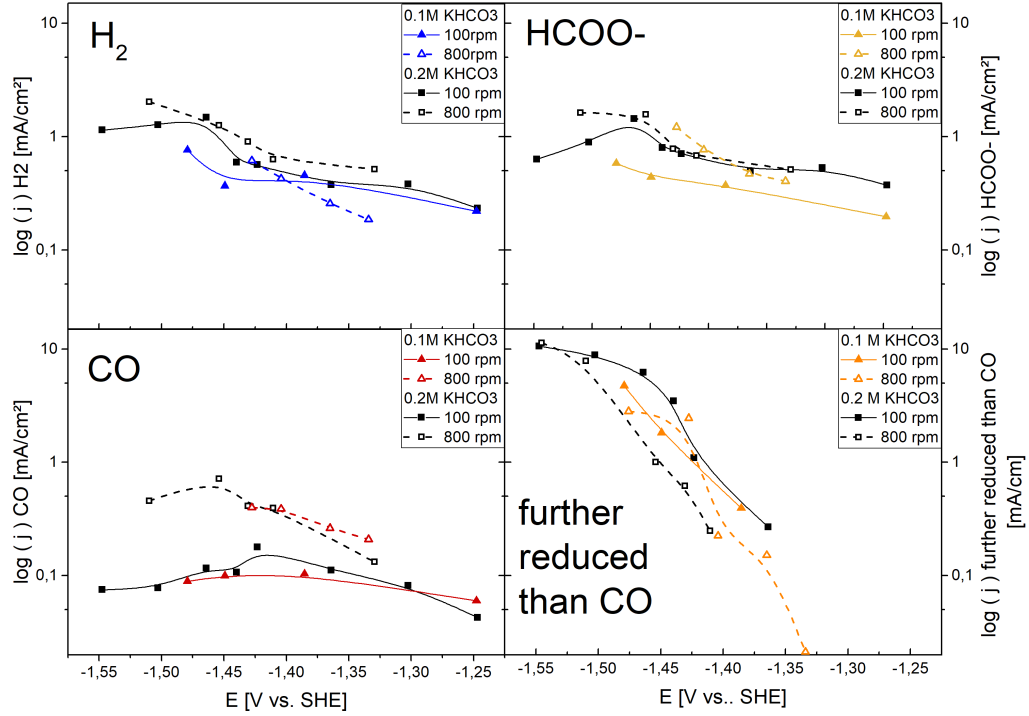


Figure 6.18: Partial current density of hydrogen, formate, CO and further than CO reduced

Hydrogen formation is, as already known, strongly dependent on the pH. With a lower pH, more protons are available, and following, a higher current density is reached for the HER. This means that in general, when mirroring the trends of the reigning pH, similar trends can be seen for the HER. The plateau of the current density, that is reach around 1.47V vs. SHE at 100 rpm in 0.2 M KHCO_3 , seems to be directly related to the stabilization of the pH under those conditions. In figure 6.19 an attempt to rationalize the data by plotting the relation between the current density of hydrogen and the concentration of the proton concentration at the outer Helmholtz plane is depicted. It can be seen that the trend of each rotation speed fall into one line. As the pH is depending on the rotation speed and the electrolyte concentration and a direct correlation can be seen between the HER and the pH and, the same conclusion can be drawn for the HER. However, when considering the mechanistic, it has to be said that the hydrogen evolution can also be driven by water

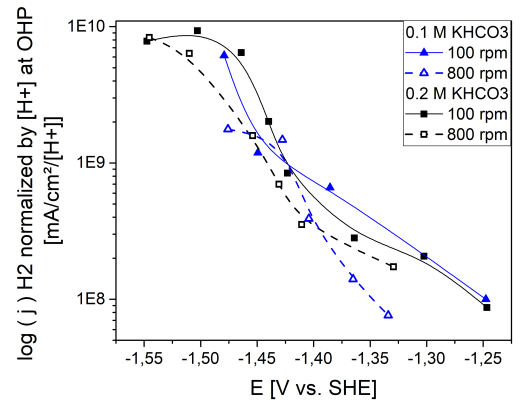


Figure 6.19: Partial current density of hydrogen normalized by the proton concentration at the OHP

reduction, which makes the analysis of this reaction more complex.

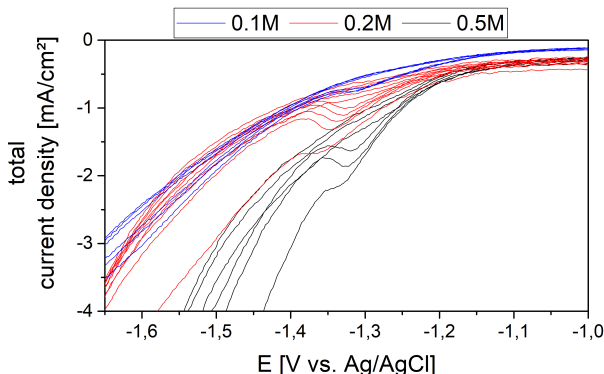


Figure 6.20: Reduction peak in CV sweeps attributed to the direct formation of bicarbonate to formate

the cyclic voltammograms (figure 6.20) that were conducted in this thesis before each chronoamperometry experiment. The peak is growing with higher bicarbonate concentration. Kortlever et al. ruled out the assumption of the CO absorption by investigating the possibility of direct reduction of HCO_3^- to HCOO^- . [27] In their research, a CV sweep was conducted in 0.1 M KHCO_3 without purging CO_2 , leading to the peaking of formate formation at exactly the potential where the reduction peak was found before. The slow dissociation of HCO_3^- to CO_2 diminishes the possibility that because of the buffer equilibrium CO_2 is the actual reduced species. However, this phenomenon, that is appearing at -1.30V vs. Ag/AgCl which equals a potential of approximately -1.10V vs. SHE, was not covered by the potential range that was investigated. Nevertheless, those conclusion offer valuable insights and the possibility of the direct reduction of bicarbonate to formate on copper to help mapping the mechanistic of this reaction.

The carbon monoxide production does not depend on the bicarbonate concentration, neither at low nor at high rotation speeds. However, the carbon monoxide formation is a function of the rotation speed with a decreasing CO production at a higher rotation speed. By looking at the near surface concentration of CO at the outer Helmholtz plane (OHP) (figure 6.21) that was calculated by the mathematical model presented before, some more conclusions can be drawn. The local CO concentration can be used as a metric of CO surface coverage. It has to be noted that compared to the partial current density, the local concentration of CO is plotted linearly instead of logarithmic. The local concentration is higher at 100 rpm which contradicts the values obtained for the partial current density. However, more products that are further reduced than CO are seen at this rotation speed, which explains why less CO is seen at the lower rotation speed.

In figure 6.18 it can be seen that the formate partial current density is only affected by the rotation speed at a low bicarbonate concentration, whereas at a higher concentration no effect of the rotation speed is seen. This is an indication that the bicarbonate concentration is a relevant factor for the mechanistic to produce formate. In earlier papers, it was discussed that the concentration of bicarbonate might have an influence on the formate formation. This discussion was based on a small reduction peak that can be found at low negative overpotentials which was at first attributed to the adsorption of CO molecules. [26] The reduction peaks mentioned were also found in

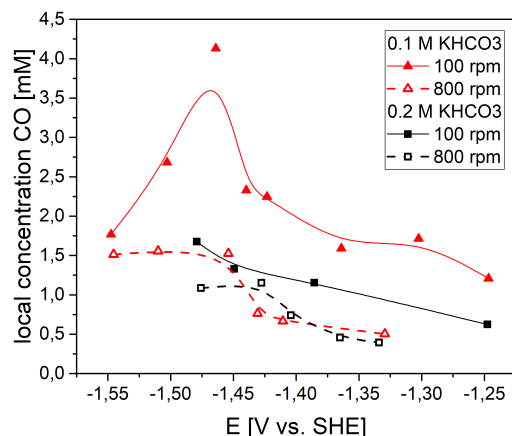


Figure 6.21: Local concentration of CO at OHP

The products that are further reduced than CO consume the most part of the current density. The rotation speed shows slight effects by lowering the partial current density at higher rotation speeds. Additionally, the mentioned mass transport effects at 100 rpm can be seen too. To break down the products that are further reduced than CO, two of the main products methane and ethylene will be looked at closer. The remaining part of the current density produces different oxygenates that will be discussed afterwards.

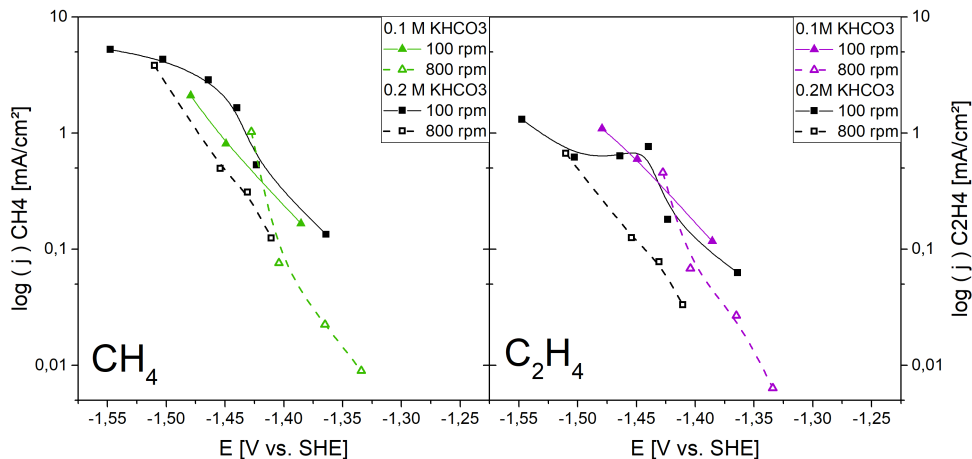


Figure 6.22: Partial current density of methane and ethylene

In figure 6.22 it can be seen that at 100 rpm and a higher bicarbonate concentration methane exhibits the highest production rate. At 800 rpm different trends are observable. While at 800 rpm and 0.1 M KHCO_3 lower partial current densities are seen until -1.40V vs. SHE where a change in trends can be seen and an acceleration of the methane production occurs. When looking at higher electrolyte concentration it can be said that the methane production is a function of the rotation speed as it is suppressed at 800 rpm. In the figures presented before, it was seen that less CO_2 is transported to the electrode surface due to mass transport limitations at 100 rpm and more negative overpotentials. Regardless, there is still an increase seen in methane formation in this area. A reason for this phenomenon could be, that it is less likely for two CO species to couple because of a decrease in its surface concentration. A hydrogenation of CO to CH_4 , on the contrary, is assumed to happen more frequently, which is why methane might be favored over C_2+ species in that regime. This is also an indicator for the pH dependence of methane as with a lower pH more protons for hydrogenation are available. This aspect, however, will be discussed later in detail. When looking at the ethylene formation in figure 6.22, there is barely any difference in the production rate at different HCO_3^- concentrations for the lower rotation speed. A different trend can be seen at 800 rpm, where a suppression of the formation of ethylene occurs at an electrolyte concentration of 0.2 M KHCO_3 . In general, similar trends can be seen for methane and ethylene production. One difference might be the flattening of the ethylene curve at 100 rpm in 0.1 M KHCO_3 which is related to the fact of increased hydrogenation instead of C-C coupling as mentioned. A closer look at eventual differences will be presented in the mechanism section (6.3). The oxygenates that share CO as a reaction intermediate were summarized in figure 6.23. Compared to methane and ethylene the partial current density of beyond CO products are lower. In 0.1 M KHCO_3 , an earlier onset potential is seen at a rotation speed of 800 rpm, whereas for 0.2 M KHCO_3 the opposite trend is seen.

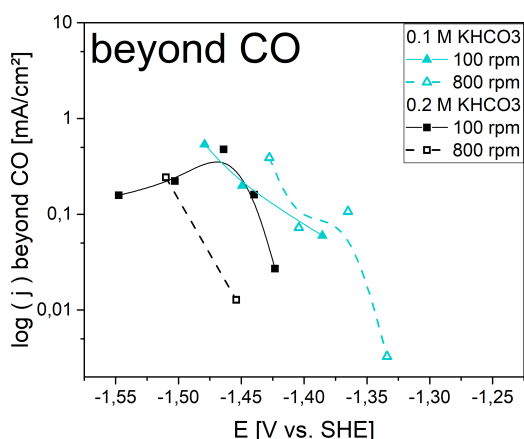


Figure 6.23: Partial current density of beyond CO products

To get a better understanding of those trends, the remaining products that share CO as reaction intermediate, beside methane and ethylene, are plotted in figure 6.24. In 0.1 M as well as 0.2 M KHCO_3 ethanol shows the highest activities that decreases with a higher rotation speed. At approximately -1.47V vs. SHE a peak can be seen for acetate and acetaldehyde in 0.2 M KHCO_3 and at 100 rpm. In 0.1 M KHCO_3 the same trend can be seen at 100 rpm. However, due to the current limitation in the diluted electrolyte no insight was gained in trends at potentials more negative than -1,47V vs. SHE. It can also be noted, that in this electrolyte concentration the onset potential of acetate and acetaldehyde seems to be earlier than in 0.2 M KHCO_3 .

In general, it can be said, that the partial current density of the products is suppressed at higher rotation speeds, and in 0.2 M KHCO_3 appear at more negative potentials. In 0.1 M KCHO_3 no clear trend can be observed regarding the onset potential.

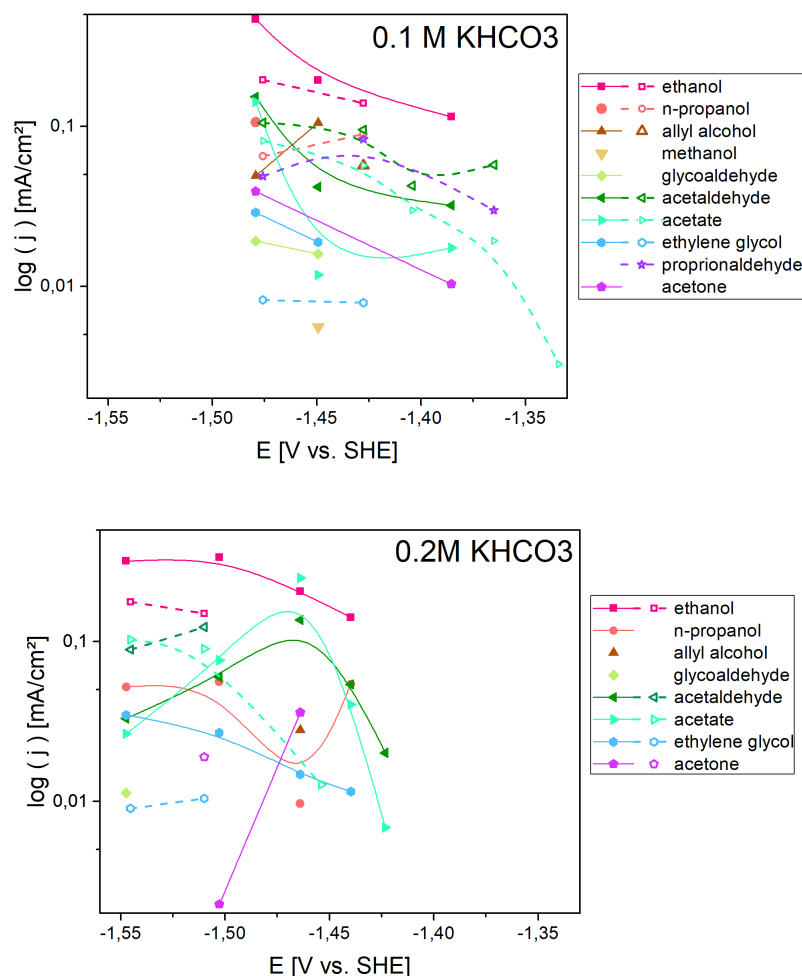


Figure 6.24: Partial current density of beyond CO products in 0.1 M and 0.2 M KHCO_3

As said, to understand mechanistic pathways to C_{2+} products, it helps to put oxygenates and hydrocarbons into relation as for hydrocarbons production additional C-O scission

and hydrogenation through proton-electron transfer steps are needed. The ratio of those two groups indicates which mechanism is dominating at the corresponding overpotential and is depicted in figure 6.25. It is compared to the oxygenates/hydrocarbons ratio of CO₂RR and COR experiments conducted by Wang et al. in a flow cell.[28] Similar results are seen as the ratio increasingly shifts toward hydrocarbons with more negative potentials. Higher amounts of oxygenates are seen at more diluted electrolyte concentration and lower rotation speed. Wang et al. concluded that the changes might derive from shifts of CO* and H* surface coverage depending on the overpotential and reaction conditions. With a higher surface coverage of H* more hydrocarbons could be produced.

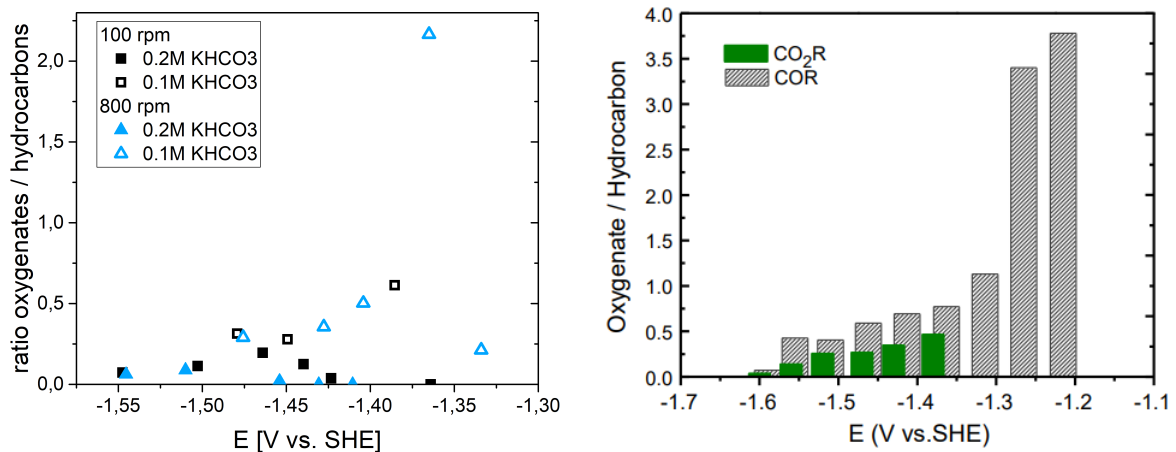


Figure 6.25: Ratio of $>2e^-$ oxygenates to hydrocarbons over potential range at different reaction conditions compared to the results of Wang et al.[28]

In figure 6.26 the products that are reduced further than CO are divided into three categories - C1, C2 and C3 products. To look at this categorization of products might help to understand the mechanism of C-C coupling. It can be seen that at more positive potentials and a more diluted electrolyte concentration C2 products dominate over C1 products. While the total faradaic efficiency of all beyond CO products increases towards more negative overpotentials, the ratio shifts towards C1 products, and additionally, the amount of C3 products increases. At an electrolyte concentration of 0.2 M KHCO₃ generally more C1 products are formed. C3 products are seen less at this concentration with a low faradaic efficiency at 100 rpm and barely no faradaic efficiency at 800 rpm. The difference that derives from different rotation speeds is a lower total faradaic efficiency.

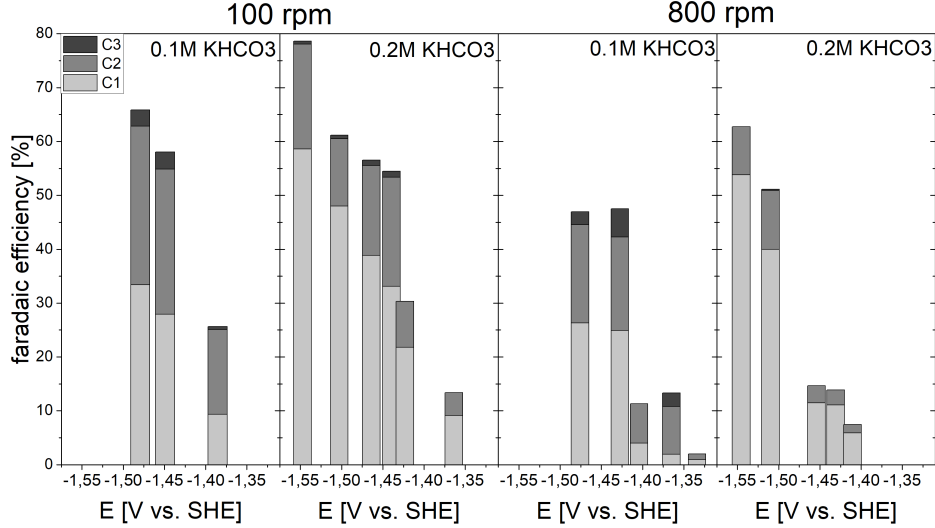


Figure 6.26: Comparison of C1, C2 and C3 products over potential range at different reaction conditions

To conclude, a combined consideration of the ratio oxygenates to hydrocarbons and categorization into C1, C2 and C3 products shows that higher amounts of C2 oxygenates can be found at lower negative overpotentials whereas higher negative overpotential favor C1, C3 and hydrocarbons. Deviations of the actual results might happen due to the resolution of the NMR spectra obtained. Improved quantification of products can be achieved by using a NMR instrument that exhibits a higher magnetic field leading to a better resolution of the NMR spectra.

6.2.3 Influence of the Electrolyte Concentration

In the earlier discussion some comparison was already done between 0.1 M and 0.2 M KHCO_3 . From the experiments described before it was seen that hydrogen, formate, methane and beyond CO seem to be affected by the bicarbonate concentration whereas CO and ethylene largely remained unaffected. To certify the trends seen before and to give an outlook on a more specific relation of the electrolyte concentration and the rotation speed, two measurements were done. One experiment was done at 100 rpm and one at 800 rpm, in an electrolyte with a 0.5 M concentration. The potential was fixed at -1.32V vs. SHE $\pm 30\text{mV}$. The results were then compared to results at a similar potential in 0.1 M and 0.2 M KHCO_3 . The averaged potential over the duration of the experiment are summarized in table 6.2.

conc(KHCO_3)	0.1 M	0.2 M	0.5 M
pH	6.82	7.12	7.52
E(100 rpm) [V vs. SHE]	1.313	1.302	1.305
E(800 rpm) [V vs. SHE]	1.353	1.329	1.334

Table 6.2: Average potential of experiments under different reaction conditions

In figure 6.3 the selectivities and activities of products generated in different electrolyte concentration and two different rotation speeds are compared. It can be seen that the total faradaic efficiency increases with higher electrolyte concentrations as well as higher rotation speeds.

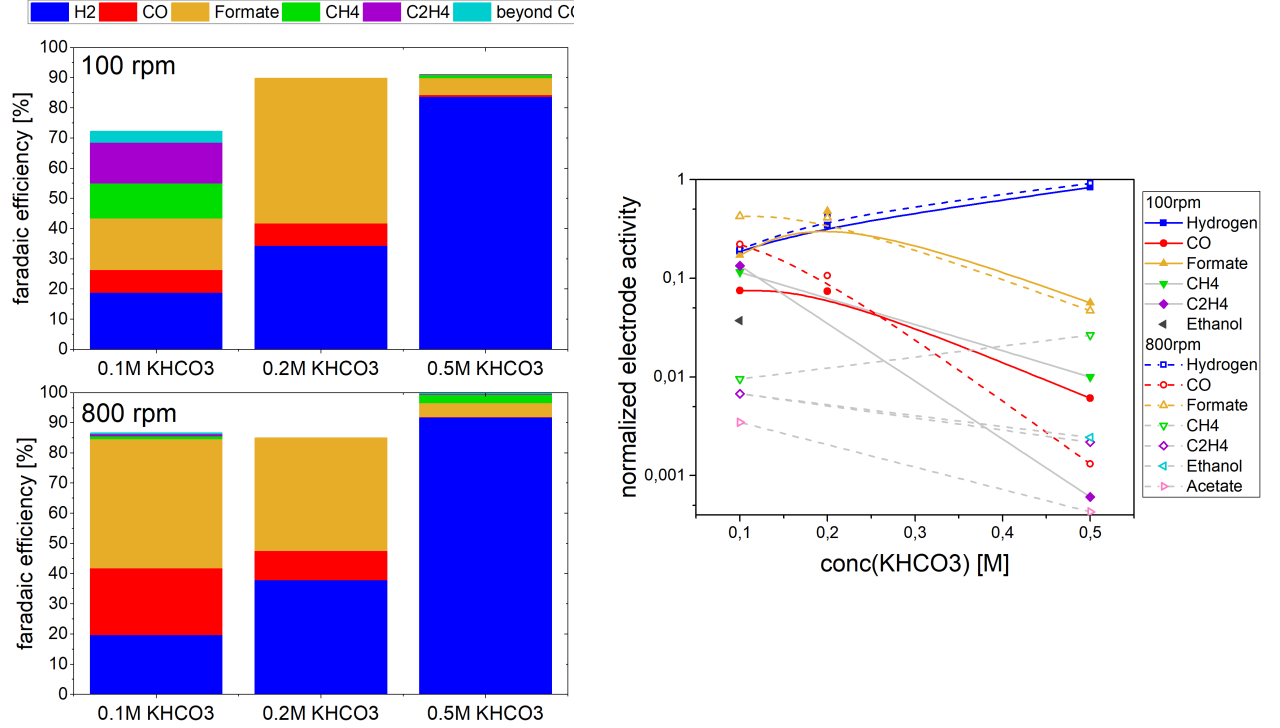


Table 6.3: Faradaic efficiency and normalized activity in different electrolyte concentrations (0.1 M, 0.2 M, 0.5 M KHCO₃)

It is striking that there is a significant increase of selectivity towards hydrogen at higher electrolyte concentration. This trend can be seen at both rotation speeds. It can be attributed to an increase in activity in hydrogen formation, where it can be clearly seen that hydrogen is a function of the electrolyte concentration, whereas only a slight increase is deriving from a higher rotation speed. When looking at the selectivity, the interpretation regarding trends for the formation of formate gets more challenging. The activity chart provides a better insight as the activity towards formate decreases with increasing bicarbonate concentration. A drop in activity can also be seen from 0.2 M KHCO₃ to 0.1 M KHCO₃ at 100 rpm while at 800 rpm the activity is plateauing. However, as similar trends can be seen for different rotation speed, it seems that bicarbonate is no function of the rotation speed. For CO, a decrease in its faradaic efficiency with higher electrolyte concentration and lower rotation speed can be observed. Taking a look at the activity, the same trends can be seen, however a steeper decline can be seen at 800 rpm. The lower FE value at 0.1M KHCO₃ for 100 rpm is probably caused by the fact that most CO is further reduced whereas at 800 rpm the percentage of further reduced CO is smaller. At higher electrolyte concentration a higher activity for CO production is seen at 100 rpm. The larger amount of protons at 0.5M KHCO₃ might be shifting the percentage of occupied sites from CO* towards higher H* occupation resulting of higher hydrogen amounts compared to CO. A weakening of the bonds of CO to the catalyst surface due to centrifugal forces might cause a faster desorption of CO at a higher rotation speeds leading to lower production rates. A decrease of activity can be seen for ethylene at higher electrolyte concentrations. While at 100 rpm, the activity is high in low bicarbonate concentrations it decreases immensely towards a high bicarbonate concentration. The decline in activity is less steep at a higher rotation speed. A research group showed that a change in the pH changes the onset potential of ethylene which is why this might take place.[22] To summarize the methane to ethylene ratio, at 0.5 M KHCO₃ more methane is seen at both

rotation speeds. At a lower concentration of 0.1 M KHCO_3 again methane is dominating at 800 rpm, however, at 100 rpm more ethylene is produced. At a electrolyte concentration of 0.2 M KHCO_3 neither was detected. In total, only products of $2e^-$ reaction can be found at 0.2 M KHCO_3 . Resasco et al. state in an earlier paper, that the anion identity and concentration only has an effect on H_2 and CH_4 formation, however, not on the formation of C_2H_4 , HCOO^- , CO and ethanol.[24] This does not conform with the trends reported here.

6.2.4 Influence of Surface Modifications of the Working Electrode

Two experiments were conducted with surface structured copper at two different rotation speeds to understand the role that the surface structure plays in different mass transport regimes. The copper cubes were prepared as described in section 4.3.1. The electrolyte concentration was kept at 0.2 M KHCO_3 and the potential at $1.28 \pm 0.5\text{V}$. For the copper cubes the current density recorded was approximately -11 mA/cm^2 whereas the current density with polycrystalline copper was only around -1 mA/cm^2 . This is due to the difference of the geometric area which Roberts et al. estimated to be about 20 times higher for CuCubes than 'flat' polycrystalline copper by running capacitive scans.[16] Most interesting in this experiment is the outcome of the ratio ethylene to methane. Methane is abundant in natural gas and therefore economically not on a competing level using this application, however, it is one of the main products on flat copper. Ethylene is used in many industrial applications and is usually deriving from fossil fuels. With this application an easy way beside the refinery would be found to produce ethylene and therefore it is of great interest to increase the selectivity towards ethylene. This might help to understand the mechanistic of C-C coupling and how to enhance it as ethylene contains two carbon species. Table 6.4 summarizes the ethylene to methane ration achieved in the experiments done on polycrystalline copper compared to results from CuCubes. The results make clear that on polycrystalline copper methane formation is favored whereas with surface structuring ethylene formation is dominating. It is further seen, that the ratio shifts to CH_4 production at a higher rotation speed, supporting the observations made before, that with higher rotation speed the C-C coupling is less facilitated.

	Polycrystalline Copper	CuCubes
100 rpm	0.14 - 0.34	200
800 rpm	0.10 - 0.30	38

Table 6.4: Ethylene to Methane ratio for polycrystalline copper and CuCubes in 0.2 M KHCO_3

Several studies reported that depending on the surface facet different activities are achieved. A common observation is that more ethylene is formed on 100 facets with lower onset potentials.[22] It has been shown that CuCubes offer more exposed 100 facets. Roberts et al. tested different active sites and came to the conclusion that 100 facets work best compared to 111 and 211 facets when it comes to the faradaic efficiency of ethylene. However, CuCubes even had better results as less methane was produced than on 100 facets. It was assumed that either a high density of ethylene active sites is available with CuCubes surface structuring or a new active site is formed that hasn't been found yet. Another possibility might be the influence of the pH as ethylene has an earlier onset potential at higher pH.[16]

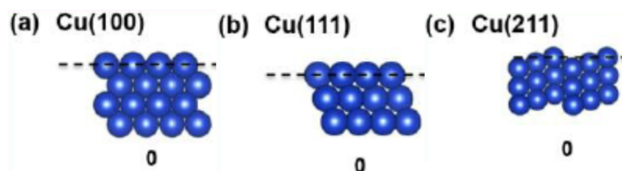


Figure 6.27: Surface facets of copper

It was mentioned earlier that a loss of activity of the electrode might happen due to surface restructuring under certain reaction conditions. To avoid this, surface structures like the CuCubes might be a good solution. It was discovered that CuCubes remained stable in experiments of six hours. [29] The high stability of this surface structure allowed to use the same electrode for both experiments without any extensive electrode preparation in between. As seen in figure 6.28 the faradaic efficiency of H_2 does not change with an increase in the rotation speed. Following the same trend as with polycrystalline copper, CO increases with higher a rotation speed as well as formate. For species that share CO as an intermediate, such as methane, ethylene, ethanol and n-propanol the faradaic efficiency decreases with higher rotation speed.

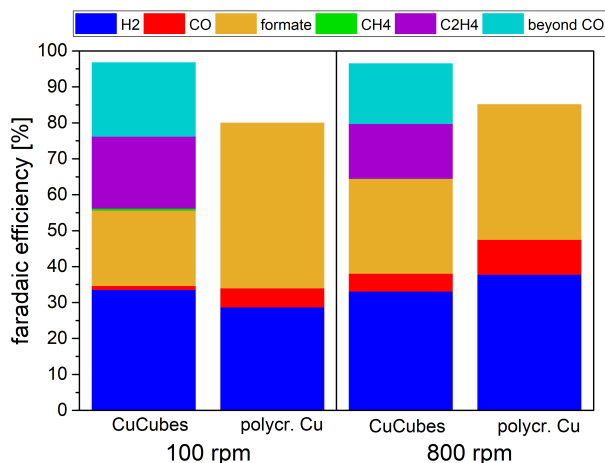


Figure 6.28: Comparison between polycrystalline copper and CuCubes

The effect that the change in rotation speed had on the product distribution on 'flat' polycrystalline copper was that beyond CO products were decreasing with an increasing rotation speed. The formation of nanocubes on the electrode surface also results in a porous surface structure. It is thought that the time of residence of reaction intermediates in the pores is longer than on flat surface whereby more C-C coupling can happen leading to longer chains. Due to the increase of the rotation speed the environment in the near surface area changes. The increase of CO might indicate that less CO diffuses into the pores also leading to a decreasing amount of further reduced products. Nevertheless, the rotation speed seem to have a less significant impact on CuCubes than on polycrystalline copper. In total, this provides a good preview on the trends seen regarding the influence of mass transport effects on structured copper surfaces. If the observed trend persists, this could be a promising way to generate higher amounts of ethylene at lower overpotentials with controlled mass transport.

6.3 Mechanistic Considerations

The four main steps of the electrocatalytic conversion of CO₂ can be simplified as followed:

- chemical adsorption of CO₂ molecules on the surface
- chemical activation of CO₂ into the intermediate radical CO₂* species
- multiple electron/proton transfer processes to form carbonaceous products
- desorption of products from electro-catalyst surface

Once the mass transport limitation can be neglected the generation of products depends on the rate limiting step and the velocity of the adsorption and desorption processes. It is still not validated at what point of the mechanistic pathway the rate limiting step occurs. In heterogeneous catalysis electron transfer reactions in the vicinity of the electrode surface are typically not the rate limiting step due to an abundance of electrons and resulting high electron transfer rates. A general agreement lies on the fact that CO is an important intermediate for the generation of further reduced products. It is further hypothesized that the adsorption of CO₂ is the rate-limiting step. This view was recently challenged by Schreier et al. who suggest that the rate limiting step does not depend on the CO intermediate but instead depends on the formation of the intermediate formyl (*CHO).[30] Earlier studies drew a correlation between the Tafel slope and the rate limiting step. While investigating the role of the pH on the reaction mechanism, it was stated that the lower the Tafel slope and the larger overpotential shift on the RHE scale are, the later in the mechanistic pathway the rate limiting proton-electron transfer step is happening.[28] All in all, the reaction mechanism depend strongly on the surface coverage of certain species. Schreier et al. calculated the coverage of species with a mathematic model.[30] The change of mass transport effects can influence this ratio of the surface coverage of different species. The effect not only derives from the supply of reactants but also of the 'sweeping away' or faster removal of species from the electrode surface with higher rotation speed of the working electrode. Crucial for the progress of the reaction is that nothing blocks or inhibits electrode surface which is known as 'catalyst poisoning'. Along the duration of an experiment the activity of the catalyst is ought to remain at the same level. As it was seen in this thesis, there is a reduction of catalyst activity over time for polycrystalline copper. Restructuring of the electrode surface, impurities or maybe even bigger multi-carbon molecules sticking to the electrode surface could be reducing the active area of the electrode. A higher level of reduction of the catalyst activity was seen at 800 rpm, however, this could also derive from a faster build-up of gas bubbles in the ion bridge at a higher rotation speed as discussed earlier. In the following, a classification will be deployed to make suggestions for different pathways that are concluded from the results discussed earlier. The 2e⁻ products H₂, HCOO⁻ and CO will be discussed first, which are assumed to be the first step of the reaction pathway or, in the case of hydrogen formation, a competitive reaction. While formate is thought to be terminal processes, CO is leading to further reduced products. Next, methane and ethylene will be looked at, which are two of the main products. Those two products are giving more insights into the influence of the pH on product formation and also can help to understand under what reaction conditions C-C coupling is favored over CO hydrogenation. Finally, beyond CO products will be discussed, which are minor products formed via electron or proton-electron transfer reaction with more than 2e⁻ involved. Those products will be further divided into C1, C2 and C3 products as well as oxygenates and hydrocarbons for the evaluation of results.

The classification into the amount of carbon atoms can help to understand the process of C-C coupling. The division into oxygenates and hydrocarbons helps to give an overview on the reaction conditions needed for C-O scission and proton-electron transfer step that lead to hydrocarbons.

6.3.1 HER, CO and Formate - $2e^-$ transfer reactions

All of the products in this first group were formed through a $2e^-$ transfer reaction and are competing reactions in the first step of the CO_2 RR. The reaction mechanism for those products, presented by Bohra et al., are depicted in figure 6.29 and will be discussed in the following.

The main competing reaction of the CO_2 reduction is the hydrogen evolution reaction (HER). This reaction lowers the faradaic efficiency of products and is therefore undesired. To reduce the partial current density that is lost through this side reaction, it is crucial to understand the way this product is formed and which reaction conditions suppress the formation of hydrogen. The HER can be driven by different mechanisms, a Volmer-Tafel or Volmer-Herovskyy mechanism (figure 6.29). It can be formed through water reduction, proton reduction or is bicarbonate mediated. Water reduction is seen as the dominant path over proton reduction at higher pH values due to a lower proton concentration. Goyal et al. showed that between 0.1 M and 0.2 M $KHCO_3$ a change in the HER formation mechanism from water reduction to bicarbonate mediated HER is taking place by investigating mass transport effects during CO_2 reduction on a Au rotating disc electrode.[32] It was concluded that the pH gradient and the rotation speed have a significant effect on the HER. The hydrogen production was suppressed at higher rotation speeds in diluted electrolyte concentrations in their studies. They concluded that the rotation speed dependence is a way to ascertain the dominant path to the HER. However, those results seem to be counterintuitive as a less alkaline pH caused by increased transport of protons to the electrode surface and simultaneous removal of newly formed OH^- should lead to an increase in HER. In this thesis, a high dependence of the HER on the pH was seen. A higher production of hydrogen occurred in higher concentrated bicarbonate electrolytes with a larger buffer strength which is coherent with their results. However, no suppression of the HER at higher rotation speed was seen in the experimental section of this thesis. This increase is more distinct in the higher electrolyte concentration.

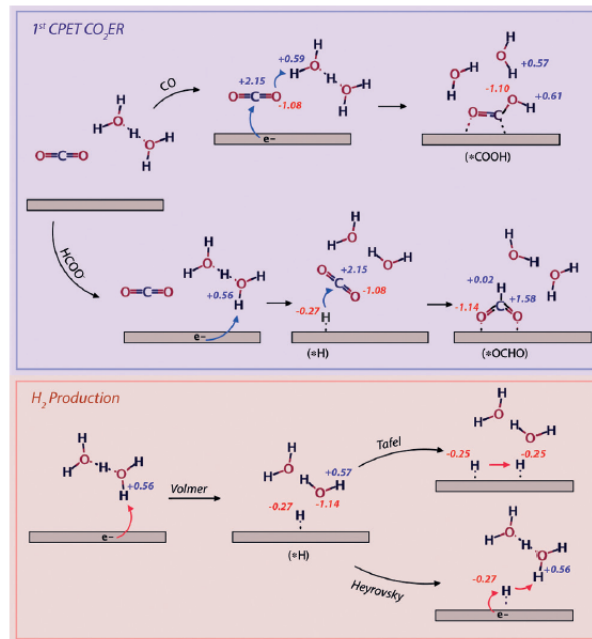


Figure 6.29: Reaction mechanism for $2e^-$ products of CO_2 RR [31]

To conclude, for the inhibition of the HER while driving the CO_2 RR, the right reaction conditions have to be found. HER is inhibited by high CO^* coverage at the electrode surface which reduces the H^* coverage. More alkaline conditions are needed to reach this

goal. Through the bubbling of CO_2 and the buffer reactions happening in aqueous solutions the pH of suitable electrolytes end up at a near neutral pH. Therefore, electrolytes with low buffer strength have to be used to reach a more alkaline pH at the electrode surface by avoiding complete neutralization of newly formed OH^- . Further, the right mass transport regime has to be used as high CO_2 supply is favored at the electrode surface but also higher rotation speeds promote a lower pH at the electrode surface.

Kuhl et al. stated that 2e^- products hold the lowest kinetic barriers which conforms with the fact that formate and CO are the only CO_2RR products that appear at low overpotentials.[13] To understand the difference in the pathway between CO and formate Feaster et al. described the mechanism in detail.[33] With a joint experimental and theoretical investigation the correlation between $^*\text{COOH}$ binding energy and CO formation on different metals as well as $^*\text{OCHO}$ binding energy and formate formation was reported. With the results of their experiments they concluded that $^*\text{OCHO}$ appears to be a terminal pathway. The direct reduction of bicarbonate to formate was already elaborately discussed in the result section where Kortlever et al. repeated the CV sweeps in KHCO_3 with and without purging CO_2 . A peak appeared at same point in both occasions with a peak in formate production. This indicates that formate is formed through the reduction of bicarbonate and promoted by higher electrolyte concentrations.[27] The formate peak in the CV sweeps was also seen in the result section as well as an enhancement of formate production with increased mass transport. The increased transport of KHCO_3 to the electrode surface might be one of the reasons for this trend undermined by the fact that an increase of the electrolyte concentration also increases the partial current density of formate. However, looking at the discussion that included 0.5 M KHCO_3 in section 6.2.3 formate production is decreased significantly in this electrolyte concentration. A reason could be a change of the pathway from HER by water reduction to a bicarbonate mediated HER as a competitive reaction to the formation of formate.

As a major part of produced CO is further reduced right away, the partial current density of CO exhibits the lowest values among 2e^- transfer products. It has been seen that CO is a function of the rotation speed and consequently of the boundary layer thickness. With a higher rotation speed more CO is detected. When looking at the calculations of the near surface concentration of CO, a higher concentration is seen at lower rotation speeds and in more diluted electrolyte concentrations. Therefore, the amount of CO seen depends strongly of the reaction conditions and the ability of the metal to further reduce CO. To promote C_{2+} products the pathway towards CO has to be dominating over formate production. Bohra et al. mention the importance of lateral adsorbate-adsorbate interaction in their theoretical studies CO_2RR on Ag and imply that the presence of $^*\text{OCHO}$ weakens the H^* binding strength and thereby enables the formation of $^*\text{COOH}$. [31] This highlights the importance of the cross-disciplinary use of theoretical and experimental studies.

6.3.2 Methane CH_4 and Ethylene C_2H_4 - pH and C-C coupling

Methane and ethylene have been the two CO_2RR products that were essential in revealing the importance of the pH on product selectivity. Hori et al. were the first to mention the influence that the local pH has during the electrochemical CO_2RR as they were conducting experiments in the pH range between 6 to 12. The discovery was mainly based on the observation that the pH influences the selectivity between CH_4 and C_2H_4 as the presumably do not share the same reaction path.[2][10] The study suggests that methane

is pH dependent due to the simultaneous transfer of one proton and one electron for the rate determining step whereas ethylene, in contrast, is independent of the pH because the rate limiting step only requires one electron transfer. However, in 2015 Schouten et al. discovered that C_2H_4 probably follows two pathways by using CuCubes. One of those pathways shares a common intermediate with methane while the other pathway does not.[22] The shared pathway is found on 111 and 100 surface facets, whereas in the second pathway CO is selectively reduced to C_2H_4 at relatively low overpotentials. This happens presumably through the formation of a surface-adsorbed CO dimer. It was stated that the surface at which the second pathway appears seems to be a dominant crystal facet in polycrystalline copper. Schreier et al. based the formation of methane on the presence of a surface bound formyl intermediate (CHO_{ads}) which is the reported key intermediate for methane electrogeneration on Cu.[30] Ethylene is contemplated to be produced by the coupling of two CO_{ads} or the coupling of one CO_{ads} with one CO in solution and therefore strongly depends on a high CO surface coverage. A third mechanism could take place where C-C coupling happens through the coupling of CO and formaldehyde. In the literature, formaldehyde has not been detected as a product to the best knowledge yet due to different aspects. The high volatility, as mentioned before, is one of the reasons. Further, the NMR peak of formaldehyde is obscured by the water peak and accordingly suppressed in the H-NMR which makes it easy to overlook this product. The detection could be done with C-NMR spectroscopy, however, regarding the challenges mentioned and a poorer detection limit of C-NMR compared to H-NMR spectroscopy, some difficulties are faced. To increase C-C coupling at low overpotentials the coverage of C1 species has to be at a sufficient high level and kinetically favorable conditions should be available. Specific surface facets appearing on nano structured copper cubes which are thought to be 100 facets have been identified as promoters of C-C coupling. Alkaline conditions are also to be favored.

In this thesis, the two factors - mass transport and different electrolyte concentrations - gave further insight into this matter. As methane depends on the pH, the different electrolyte concentrations leading to different buffer strength should lead to a different behaviour than ethylene in different bicarbonate concentrations. Also, because of the shift of the surface pH due to changes in the electrode rotation speed the different boundary layer thicknesses should affect methane and ethylene differently. In the results, similar trends between methane and ethylene were seen. However, to get a closer look at the differences, the partial current densities were plotted together in figure 6.30. In 0.1 M $KHCO_3$ at 100 rpm very similar results were obtained for both species. When increasing the rotation speed in this diluted electrolyte concentration, no significant changes were seen. By increasing the electrolyte concentration, however, the trends change. At more positive potentials than -1.43V vs. SHE and at 100 rpm, an increase of the partial current density for methane is seen, while no significant changes are seen for ethylene. The stronger buffer effects for the increased electrolyte concentration keep the pH at a lower value even though if more OH^- is produce. This could therefor affect the CO hydrogenation.

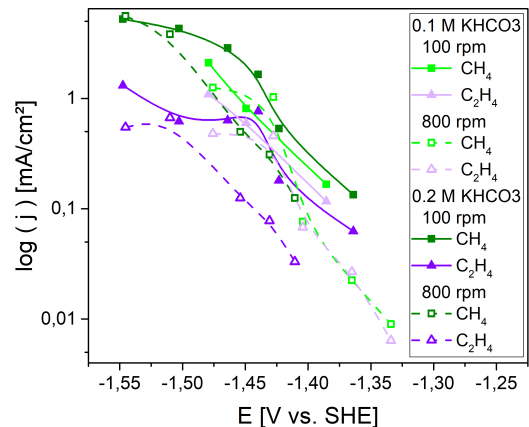


Figure 6.30: Partial current density of methane and ethylene

tion towards methane and have no significant effect on the C-C coupling towards ethylene. At potentials more negative than -1.43V vs. SHE both curves are flattening, although ethylene production seems to be affected more. Increasing the rotation speed to 800 rpm at the concentration of 0.2 M KHCO_3 suppresses both, methane and ethylene. However, ethylene seems to be affected more significantly, which again can be attributed to the reduction of C1 species at the electrode surface that could take part in C-C coupling to promote the formation of more C_{2+} species. Therefore, a good balance has to be found between reducing mass transport effects and reducing or 'sweeping away' of those C1 species by applying rotation to the working electrode. The mentioned importance of surface facets of copper was also investigated in the result section supporting the hypothesis that CuCubes promote ethylene production and therefore C-C coupling.

6.3.3 Beyond CO - pathway to multicarbon products

One of the main observations is that beside the main products methane and ethylene all of the beyond CO reduced products are oxygenates except for ethane which was detected during experiments on surface structured copper. Those oxygenates consist of a wide variety of chemical species as aldehydes, ketones, carboxylic acids and alcohols were detected. The key is to understand the mechanistic pathway leading to those products to control the selectivity. Different hypothesis were presented in the past, one of those is looking at the different surface sites that are present on polycrystalline copper surfaces which might be the cause for the wide range of products as each site produces different types of oxygenates. It was also hypothesized, that the same surface site can catalyze the formation of different C1 oxygenates that are combined through C-C coupling in various ways. Structural influences were discussed by using CuCubes which expose a high amount of 100 surface facets. The selectivity was changed by using different surface facets, however, a wide variety of beyond CO products were detected. Therefore, it is more likely that the same surface site is capable of generating different oxygenates at once. Kuhl et al. suggested that a repetitious step involving 2H^+ and 2e^- was leading to the different products depending on the number of how often this step was repeated.[13] In general, proton-electron transfers to oxygen ends of reaction intermediates are facile, while those transfer steps to carbon ends or C-O bond scission involving steps are more difficult to take place. The high amount of oxygenates with hydroxyl and carbonyl moieties indicates that the C-C coupling step probably occurs before at least one C-O bond is broken, confirming the statement before. It is known that the hydrogenation of oxygen atoms primarily happens electrochemically, involving an e^- transfers instead of direct $^*\text{H}$ transfer steps on the electrode surface. Therefore, the surface coverage of H^* and CO^* species is crucial. The more H^* is present, the more hydrocarbons are formed. To come back to the main focus of the thesis, the mass transport effects, the hypothesis before doing the experiments of this thesis was that with higher rotation speed which results in a lower boundary layer thickness is promoting the formation of species with two or more carbon atoms. This theory was based on the elimination of mass transport effects, and therefore, a higher concentration of CO_2 at the electrode surface. The actual outcome was different as seen in the result section, however, it delivers important insights into the reaction proceedings. The decrease of beyond CO products at higher rotation speeds might be caused by the faster removal of CO from the surface of the electrode due to the high rotation speed before it can be further reduced to C_{2+} products. Also, the change of pH due to the removal of produced OH^- from the electrode surface definitely has an effect on the reaction mechanism regarding the importance of the pH in this reaction. It was

found that alkaline conditions are promoting C_{2+} products. So, considering that a higher rotation speed causes a more acidic pH this would lead to less beyond CO products which was the trend seen in the result section. When looking at the influence of the potential at which the experiment takes place the assumption was made due to earlier studies that lower overpotentials generate higher selectivity for C_{2+} products and oxygenates whereas more negative potentials are generating more C1 and C3 products and hydrogenates. This could be due to the increasing coverage of adsorbed H at more negative overpotentials or that the Heyrovsky mechanism, which uses one H_{ads} and one H-atom from the solution for H-H bond formation, is dominating. Another discovery done in earlier studies was that aldehydes are formed at an earlier onset potential than alcohols. Hori et al. were the first to do experiments on Cu with various aldehydes as starting materials while CO_2 was purged in 0.1 M $KHCO_3$. For each aldehyde the corresponding alcohol was detected.[10] The aldehydes might be formed through a cannizzaro type disproportion reaction which could take place through a homogeneous chemical reaction in the electrolyte when alkaline conditions are given.[34] In this thesis, however, it was seen that depending on the electrolyte concentration and rotation speed the onset potentials were varying. More data over a larger potential range has to be collected to draw final conclusions in this matter.

To summarize, the reduction of CO_2 to high energy dense C_{2+} products urges the use of more diluted and weakly buffered electrolytes and mass transport regimes where a sufficiently alkaline pH is maintained to suppress the formation of hydrogen and formate but concomitant not significantly reduce C1 species at the electrode surface that could further take part in C-C coupling while still a high supply of reactants is provided.

Chapter 7

Conclusion and Outlook

7.1 Thesis Summary

To conclude, with the combination of a new cell set-up and a mathematical model, which is a good tool for data analysis and the validation of reproducibility, a valuable set of data was generated for the reduction of carbon dioxide. The insights this technique gave into the influence of mass transport effects on product selectivity during electrochemical CO₂ reduction helps to get one step closer to understanding and improving phenomena happening in the near surface area of the working electrode. With the gas-tight electrochemical RCE cell, a stable control of the boundary layer thickness and mass transport effects was achieved. Additionally, it was shown that with the experiments of the reduction of potassium ferricyanide a good agreement was found between the determined boundary layer thickness and the calculated boundary layer thickness based on theoretical studies. Further, with the experimental results of the electrochemical CO₂ reduction, a confirmation was achieved of the fact that a change in mass transport affects the product distribution. 17 different products were detected in the set of data that was collected. The dependence of each product on mass transport and electrolyte concentration was closely discussed. An outlook was given on the effect of 0.5 M KHCO₃ compared to the investigated concentrations of 0.1 M and 0.2 M KHCO₃ as well as on the change of product distribution through surface structuring to animate for additional investigation in linking those aspects with mass transport evaluations. The developed MatLab code offered a great opportunity to analyze the concentration gradient of reaction and product species and the influence of their near surface concentrations on the reaction outcome. Combined with a good estimate on the pH gradient this is giving a closer insight on mass transport effects and their influence on reaction pathways.

7.2 Future Directions

It is important to always question the own ideas and remain critical in thinking. That way this field will see more great results and advance further towards the industrialization of the electrochemical reduction of carbon dioxide to value added products as an alternative to fossil resources. In the following a few thoughts are added on how to improve the cell design presented in this work. Further, some experimental methods will be discussed to gain more insight into the mechanistic of the CO₂ reduction.

7.2.1 Cell Design

The cell that was designed in this thesis was delivering good results to put the boundary layer thickness into relation with the product selectivity during electrochemical CO₂ reduction. However, there are a few things that can be improved. The main constraint of this design is the limited ion flux between the working and counter electrode due to the small cross-section of the ion bridge. To overcome this issue the cell body was changed to a combination of the rotation cell presented in this thesis (WE side) and the compression cell introduced by Kuhl et al. (CE side).[13] In figure 7.1 the enhanced design is depicted.

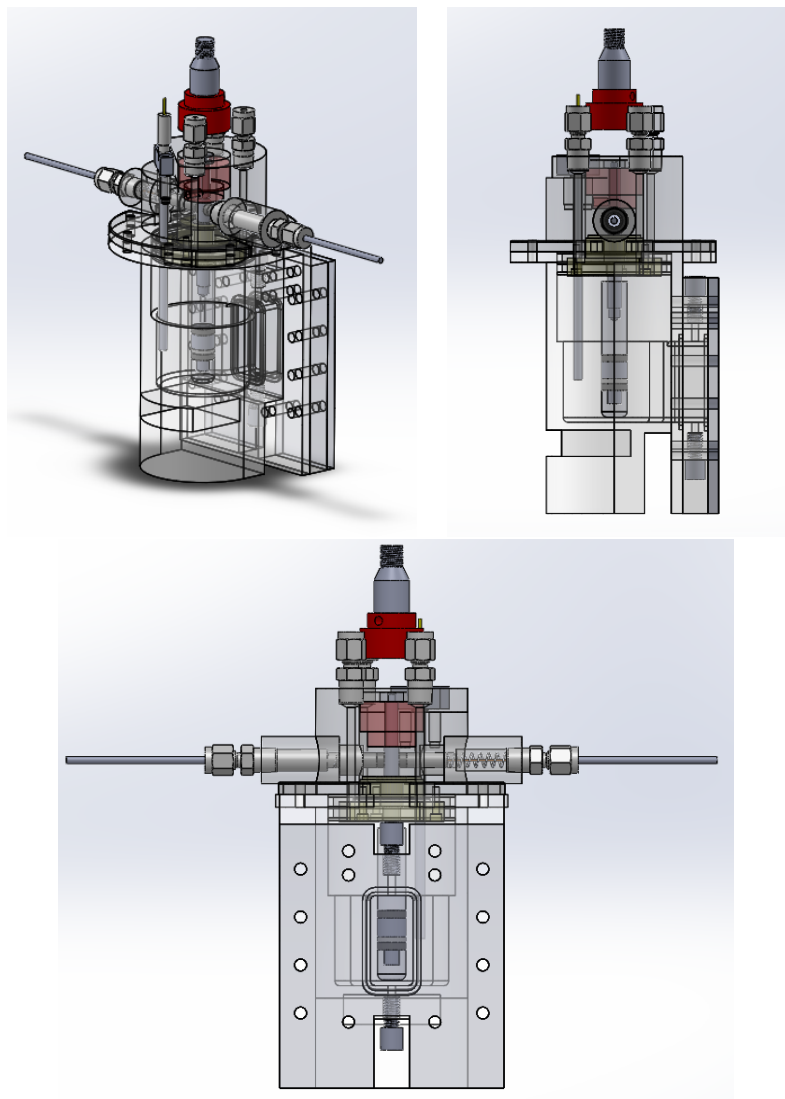


Figure 7.1: Further developed cell design

One of the main changes is that the cross-section of the membrane was made wider and the distance between WE and CE decreased. Additionally, the trapping of bubbles becomes less likely with the presented design. The working electrode compartment was further developed in a way that less electrolyte volume has to be used on each side. As a comparison, in the rotation cell the electrolyte volume on the WE side was 82 mL and on the CE side 22 mL, whereas in this set-up the volume comes down to approximately 65 mL on the WE side and 8 mL on the CE side. This enhances the detection of liquid products as the concentration increases. Further, the Teflon rods that are encapsulating

the electric brush plungers were supposed to be glued to the Teflon shell body of the working electrode cap. Due to the complex assembly and the necessity of exchanging the brush plungers at times, because of the abrasion of the carbon tips, the Teflon rods were plugged in and fixed with a layer of flexible thermoplastic (Parafilm). No gas-leaks were detected, which was why this set-up was suitable for the intended application of this thesis as no elevated pressure was applied. However, to improve the set-up, the Teflon rods were threaded to ensure the fixation of those parts through screwing them to the WE cap instead of using adhesives. To add the possibility of regulating the temperature inside the cell, a pocket for a heating unit was extruded right below the WE compartment.

7.2.2 Experimental

The results of this thesis show that the selectivity of products during the CO₂RR can be controlled with known mass transport conditions. Now many different set of experiments regarding different reaction conditions and catalyst modifications that have formerly been conducted can be repeated in this reaction environment. For example, further surface modifications can be applied that were, for example, tested by Wang et al.[35] Instead of CuCubes, which will have to be investigated further, CuFlowers were generated. Attention can be paid to the processes happening inside the pores and how different mass transport regimes influence this behavior by changing the environment near the surface, and therefore, eventually changing the supply for the pores. Morales-Guio et al. introduced a promising method to generate higher amounts of C₂₊ alcohols by using a bimetallic catalyst of gold particles on polycrystalline copper.[36] To achieve higher yields or control the selectivity of those alcohols, defined mass transport control as described in this thesis could be used. To gain more insights into reaction pathways, it would help to do experiments with the same reaction conditions, although use known intermediates as starting materials instead of CO₂. CO reduction was done by some research groups with important observations on reaction pathways of further reduced products.[28]

7.2.3 Modelling

The modelling as it was described in this thesis already works well to estimate surface concentrations of reactants and product species as well as the pH gradient. This helps for mechanistic considerations. However, the changing concentrations of species during the reaction might reach a level at which they change the surface environment influencing different reaction pathways. To include changing boundary conditions might be challenging, however, it could have an influence on predicting the reaction conditions and outcomes more accurately. Additionally, introducing 2D modelling along the electrode surface from the center to the edge might further improve the accuracy of the model. If we consider the direction of flow close to the electrode, surface species might be affected by a constant exchange with the electrode. More sophisticated calculations would have to be used. This adds to the point that a combination of experimental and computational are of good use. The calculation of binding energies of different species on copper with the influence with a controlled mass transport might help to understand the mechanistic.

7.3 Final Remarks

There are still many questions to answer in the field of electrochemical CO₂ reduction. Nevertheless, this technology is on a promising path to play an important role in the transformation and storage of renewable energies. The scalability of this technology will help to make it a central player for decentralization for either the punctual removal of CO₂ from industrial sources and the combined energy storage or the application in remote areas to provide autonomy regarding their energy supply. The interplay between the transformation and storage of renewable energy, reduction of the emission of the greenhouse gas CO₂ and the generation of value added products that usually derive from fossil resources compose a fascinating technology that will be at a feasible economic level in the near future.

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Appendix

MatLab Code for CO2RR

```
1 %electrochemical CO2 Reduction on Copper
2 %Author: Martina Ruescher
3
4 clear all; close all; clc; tic
5
6 %CONSTANTS & ...
   VARIABLES-----
7 global D F R E z T
8
9 F = 96486; % [A*s/mol]
10 R = 8.314; % [kg*m2/(s2*mol*K)]
11 T = 293; % [K]
12
13 %Electrolyte Concentration & Viscosity
14 run viscosity_u0.m; %load concentration & viscosity
15 n = 3; %defines which electrolyte conc and viscosity %CHANGE
16 c_el_v(1,n); %concentration electrolyte
17 c_el_v(2,n); %viscosity
18
19 %Diffusion Coefficient
20 Dst = ...
   [1.91,1.19,0.923,5.27,1.957,0,4.50,2.03,1.454,1.49,1.87,0.84,1.3,...
21    1.1,0.84,1.089,1.22]*10^(-9);
22 vst = 0.891;
23
24 %Stokes-Einstein D /T=const
25 Const = zeros(1,17);
26 for i=1:17
27     Const(i) = Dst(i).*vst/T;
28 end
29
30 %Calculate effective value of D
31 D = zeros(1,17);
32 for i=1:17
33     D(i) = Const(i)/c_el_v(2,n)*T;
34 end
35
36 %Potential (ION ...
   Flux)-----
37 %boundaryL: macroscopic systems - electroneutrality
   %sum(z(i)*u(i)=0 --> pot = 0 -->migration term=0
38 %boundaryR: microscopic system (Poisson)
   %diff(pot,x,2)=(-1)*rho/E
39
40
41
42 %E = E0(vacuum)xEr(in water at 25 C )
43 E = 8.854e-12*78.3; % [C/(Vm)]
44 z = [0;-1;-2;-1;1;0;0;0;-1;0;0;0;0;0;0;-1;0]; %valency of each species
45
46 %DEFINE ...
   FUNCTION-----
47 m = 0; %symmetry (cartesian:0,cylindrical:1,spherical ...
   coordinates:2)
```

```

48 tend= 20;
49
50 %Boundary Layer Thickness
51 rpm=[25,    50,    100,   150, 200, 400,  600,  800, 1000, 1600];
52 %w^-0.54:
53 d = [143,  108,    81,   59,  53,  35,  28,  24,  21,   ...
      16]*10^(-6);
54 %w1-0.7:
55 d_i=[296,  182,   112,   84,  69,  43,  32,  26,  22,   ...
      16]*10^(-6);
56
57 x  = linspace(0,d(1),300);           %space %CHANGE
58 t  = linspace(0,tend,301);           %time
59 sol = pdepe(m,@concgradpde,@concgradic,@concgradbc,x,t); %pdepe solver
60
61 u1 = sol(:,:,1); %CO2
62 u2 = sol(:,:,2); %HCO3-
63 u3 = sol(:,:,3); %CO3(2-)
64 u4 = sol(:,:,4); %OH-
65 u5 = sol(:,:,5); %K+
66 u6 = sol(:,:,6); %potential
67 u7 = sol(:,:,7); %H2(1)
68 u8 = sol(:,:,8); %CO(2)
69 u9 = sol(:,:,9); %HCOO-(3)
70 u10 = sol(:,:,10); %CH4(4)
71 u11 = sol(:,:,11); %C2H4(5)
72 u12 = sol(:,:,12); %EtOH(6)
73 u13 = sol(:,:,13); %nPrOH(7)
74 u14 = sol(:,:,14); %Allylalcohol(8)
75 u15 = sol(:,:,15); %MeOH(9)
76 u16 = sol(:,:,16); %Acetate(10)
77 u17 = sol(:,:,17); %Ethylenglycol(11)
78 x100 = x*10^6; %distance
79 u18 = u12+u13+u14+u15+u16+u17; %beyondCO
80 u19 = 14+log10(u4*1E-3); %pH
81
82 extract1=[u1(301,300),u2(301,300),u3(301,300),u5(301,300),u4(301,300),...
83          u6(301,300),1,1,u7(301,300),u8(301,300),u9(301,300),...
84          u10(301,300),u11(301,300),u12(301,300)+u13(301,300)+...
85          u14(301,300)+u15(301,300)+u16(301,300)+u17(301,300)+u18(301,300)];
86 extract3=[u1(301,:);u2(301,:);u3(301,:);u5(301,:);u4(301,:)];
87 extract3=extract3';
88 extract4=[u7(301,:);u8(301,:);u9(301,:);u10(301,:);u11(301,:)];
89 extract4=extract4';
90 extract5=[u7(:,300),u8(:,300),u9(:,300),u10(:,300),u11(:,300)];
91 %PLOTTING
92 %3D plot of concentration gradient over time and distance
93 figure(1)
94 subplot(3,2,1)
95 surf(x,t,u1,'LineStyle','none')
96 title('CO2')
97 xlabel('distance [m]')
98 ylabel('time [s]')
99 zlabel('concentration [mM]')
100 subplot(3,2,2)
101 surf(x,t,u2,'LineStyle','none')
102 title('HCO3-')
103 xlabel('distance [m]')
104 ylabel('time [s]')

```

```

105 zlabel('concentration [mM]')
106 subplot(3,2,3)
107 surf(x,t,u4,'LineStyle','none')
108 title('OH-')
109 xlabel('distance [m]')
110 ylabel('time [s]')
111 zlabel('concentration [mM]')
112 subplot(3,2,4)
113 surf(x,t,u6,'LineStyle','none')
114 title('potential')
115 xlabel('distance [m]')
116 ylabel('time [s]')
117 zlabel('potential [V]')
118 subplot(3,2,5)
119 surf(x,t,u8,'LineStyle','none')
120 title('CO')
121 xlabel('distance [m]')
122 ylabel('time [s]')
123 zlabel('concentration [mM]')
124 subplot(3,2,6)
125 surf(x,t,u19,'LineStyle','none')
126 title('pH')
127 xlabel('distance [m]')
128 ylabel('time [s]')
129 zlabel('concentration [mM]')
130 %3D plot of concentration gradient of products
131 figure(2)
132 subplot(3,2,1)
133 surf(x,t,u7,'LineStyle','none')
134 title('H2')
135 xlabel('distance [m]')
136 ylabel('time [s]')
137 zlabel('concentration [mM]')
138 subplot(3,2,2)
139 surf(x,t,u8,'LineStyle','none')
140 title('CO')
141 xlabel('distance [m]')
142 ylabel('time [s]')
143 zlabel('concentration [mM]')
144 subplot(3,2,3)
145 surf(x,t,u9,'LineStyle','none')
146 title('HCOO')
147 xlabel('distance [m]')
148 ylabel('time [s]')
149 zlabel('concentration [mM]')
150 subplot(3,2,4)
151 surf(x,t,u10,'LineStyle','none')
152 title('CH4')
153 xlabel('distance [m]')
154 ylabel('time [s]')
155 zlabel('concentration [mM]')
156 subplot(3,2,5)
157 surf(x,t,u11,'LineStyle','none')
158 title('C2H4')
159 xlabel('distance [m]')
160 ylabel('time [s]')
161 zlabel('concentration [mM]')
162 %2D concentration gradient of buffer species
163 figure(12)

```

```

164 hold on
165 plot(x100,u1(301,:))
166 plot(x100,u2(301,:))
167 plot(x100,u3(301,:))
168 plot(x100,u5(301,:))
169 xlabel('distance [ m ]')
170 ylabel('concentration [mM]')
171 legend('CO2','HCO3','CO3','K')
172 hold off
173
174 %PRINT TO ...
175     TEXTFILE--(optional)-----
176 %Define FILENAME in calculated_data_to_textfile.m
177 %f = u1;
178 %run Calculated_data_to_textfile.m
179
180
181 %PDEPE SOLVER DEFINITION
182 %initial conditions-----
183 function u0 = concgradic (x)
184 run viscosity_u0.m; %load values for bulk concentration
185
186 for o = 2          %(1)0.05M, (2)0.1M (3)0.2M (4)0.5M... %CHANGE (2x)
187     u0 = ubulk(:,o);
188 end
189 end
190
191 %boundary conditions-----
192 %p(x,t,u)+q(x,t)*f(x,t,u,diff(u,t) = 0;
193 function [pl,ql,pr,qr] = concgradbc(xl,ul,xr,ur,t)
194 global F y
195 run Openfile_curr_eff_01M_100rpm.m %loads current efficiencies from file
196 %CHANGE fID in Openfile
197 run viscosity_u0.m; %loads electrolyte conc and viscosity
198
199 for m=1              %CHANGE
200     y = d(m,1);      %potential
201     Q =(d(m,2));     %current density
202
203     for i=1:length(d)
204         cef(i)=d(m,i); %current efficiencies
205     end
206 end
207
208 %zeff&cef
209 %H2(1)CO(2)HCOO(3)CH4(4)C2H4(5)EthOH(6)nPropOH
210 %(7)Alalk(8)MetOH(9)AcO(10)Etglyk(11)Glyoxal(12)
211 C_CON = (cef(1,4)/zeff(2)+cef(1,5)/zeff(3)+cef(1,6)/zeff(4)+...
212         2*cef(1,7)/zeff(5)+2*cef(1,8)/zeff(6)+3*cef(1,9)/zeff(7)+...
213         3*cef(1,10)/zeff(8)+cef(1,11)/zeff(9)+2*cef(1,12)/zeff(10)+...
214         2*cef(1,13)/zeff(11));
215
216 OH_FORM = (2*cef(1,3)/zeff(1)+2*cef(1,4)/zeff(2)+cef(1,5)/zeff(3)+...
217         8*cef(1,6)/zeff(4)+12*cef(1,7)/zeff(5)+12*cef(1,8)/zeff(6)+...
218         18*cef(1,9)/zeff(7)+16*cef(1,10)/zeff(8)+...
219         6*cef(1,11)/zeff(10)+7*cef(1,12)/zeff(10)+...
220         10*cef(1,13)/zeff(11));
221     o = 2; %CHANGE

```

```

222 pl = ...
        [ul(1)-ubulk(1,o);ul(2)-ubulk(2,o);ul(3)-ubulk(3,o);ul(4)-ubulk(4,o);
223         ul(5)-ubulk(5,o);ul(6)-ubulk(6,o);ul(7)-ubulk(7,o);ul(8)-ubulk(8,o);
224         ul(9)-ubulk(9,o);ul(10)-ubulk(10,o);ul(11)-ubulk(11,o);
225         ul(12)-ubulk(12,o);ul(13)-ubulk(13,o);ul(14)-ubulk(14,o);
226         ul(15)-ubulk(15,o);ul(16)-ubulk(16,o);ul(17)-ubulk(17,o)];
227 ql = [0;0;0;0;0;0;0;0;0;0;0;0;0;0;0;0;0];
228 pr = [C_CON;0;0;(-1)*OH_FORM;0;0;-cef(1,3)/zeff(1);
229        -cef(1,4)/zeff(2);-cef(1,5)/zeff(3);
230        -cef(1,6)/zeff(4);-cef(1,7)/zeff(5);
231        -cef(1,8)/zeff(6);-cef(1,9)/zeff(7);
232        -cef(1,10)/zeff(8);-cef(1,11)/zeff(9);
233        -cef(1,12)/zeff(10);-cef(1,13)/zeff(11)].*(-Q*10/F);
234 qr = [1;1;1;1;1;1;1;1;1;1;1;1;1;1;1;1;1];
235 end
236
237 %MAINFUNCTION
238 function [c,f,s] = concgradpde(x,t,u,DuDx)
239 global F D rho z E T R
240
241 %Homogenous reactions for source term
242 %rate constant
243     k3f = 5.93e3*0.001; %3b forward
244     k3r = 1.34e-4;      %3b reverse
245     k4f = 1e8*0.001;    %4b forward
246     k4r = 2.15e4;       %4b reverse
247 %rate laws
248     %u1-CO2, u2-HCO3, u3-CO3, u4-OH
249     r3f = k3f*u(1)*u(4);
250     r3r = k3r*u(2);
251     r4f = k4f*u(2)*u(4);
252     r4r = k4r*u(3);
253 %mass balances
254     dCO2 = -r3f + r3r;
255     dHCO3 = r3f - r3r - r4f + r4r;
256     dCO3 = r4f - r4r;
257     dOH = -r3f + r3r - r4f + r4r;
258 %for poisson equation
259 rho = F * ((-1)*u(2)+(-2)*u(3)+(-1)*u(4)+u(5)+(-1)*u(9)+(-1)*u(16));
260
261     for i=1:17
262         c(i,1) = 1;
263     end
264     f1= [D(1,1);D(1,2);D(1,3);D(1,4);D(1,5);D(1,6);D(1,7);
265          D(1,8);D(1,9);D(1,10);D(1,11);D(1,12);D(1,13);
266          D(1,14);D(1,15);D(1,16);D(1,17)].*DuDx;
267     f2= [D(1,1)*z(1,1)*F/(R*T)*u(1);    D(1,2)*z(2,1)*F/(R*T)*u(2);
268          D(1,3)*z(3,1)*F/(R*T)*u(3);    D(1,4)*z(4,1)*F/(R*T)*u(4);
269          D(1,5)*z(5,1)*F/(R*T)*u(5);    1; D(1,7)*z(7,1)*F/(R*T)*u(7);
270          D(1,8)*z(8,1)*F/(R*T)*u(8);    D(1,9)*z(9,1)*F/(R*T)*u(9);
271          D(1,10)*z(10,1)*F/(R*T)*u(10); D(1,11)*z(11,1)*F/(R*T)*u(11);
272          D(1,12)*z(12,1)*F/(R*T)*u(12); D(1,13)*z(13,1)*F/(R*T)*u(13);
273          D(1,14)*z(14,1)*F/(R*T)*u(14); D(1,15)*z(15,1)*F/(R*T)*u(15);
274          D(1,16)*z(16,1)*F/(R*T)*u(16);D(1,17)*z(17,1)*F/(R*T)*u(17)].*DuDx(6);
275     f = f1 +f2;
276     s = [dCO2;dHCO3;dCO3;dOH;0;rho/E;0;0;0;0;0;0;0;0;0;0;0];
277 end

```

Subfile 'Openfile_curr_eff_01M_100rpm.m'

```

1  fID='var_pot_100rpm_0.1MKHCO3.txt';           %CHANGE (loop if necessary)
2  a=fopen(fID,'rt');
3  data = textscan(a,'%s','delimiter','/n');
4  data=data';
5  for i=15:length(data{1,1})
6      for n=i-14
7          U(n,:)=strsplit(data{1,1}{i,1});
8      end
9  end
10 str=string(U);
11 d=str2double(str);
12 fclose(a);

```

Subfile 'var_pot_100rpm_0.1MKHCO3.txt'

```

1  Cu
2  Potential current_density H_{2} CO Formate CH_{4} C_{2}H_{4} Ethanol ...
   n-Propanol Allylalcohol Methanol Acetate Ethyleneglycol
3  4
4  11
5  0.1
6  79.7359*10^(-6)
7  -1.479  -6.447  0.1181  0.0138  0.0899  0.3263  0.1692  0.0721  ...
   0.0164  0.0076  0 0.0220  0.0045
8  -1.449  -3.274  0.1120  0.0304  0.1338  0.2470  0.1832  0.0592  0 ...
   0.0321  0.0017  0.0036  0.0058
9  -1.386  -1.787  0.2546  0.0578  0.2072  0.0934  0.06541 0.0640  0 ...
   0 0 0.0098  0
10 -1.248  -0.610  0.3583  0.0981  0.3213  0 0 0 0 ...
   0 0 0 0

```

Subfile 'viscosity_u0.m'

```

1  %filename: viscosity_u0.m
2  c_el_v=[0, 0.05, 0.1, 0.202,0.305,0.409,0.515,1.064;
3          0.89,1.009,1.015,1.027,1.04, 1.053,1.067,1.145];
4  %c_el_v(1,:) - concentration electrolyte
5  %c_el_v(2,:) - viscosity
6  c_KHCO3 = [0.05; 0.1; 0.2; 0.5; 1; 2];
7  %initial concentration of reactant and product species
8  ubulk = [0.0342, 0.0342, 0.0342, 0.0342, 0.0342, 0.0342;
9           0.05, 0.099, 0.199, 0.499, 0.994, 1.976;
10          7.7e-6, 3.1e-5, 1.2e-4, 7.6e-4, 0.003, 0.012;
11          3.3e-8, 6.6e-8, 1.3e-7, 3.3e-7, 6.6e-7, 1.3e-6;
12          0.05, 0.099, 0.199, 0.499, 0.994, 1.976;
13          0, 0, 0, 0, 0, 0;
14          0, 0, 0, 0, 0, 0;
15          0, 0, 0, 0, 0, 0;
16          0, 0, 0, 0, 0, 0;
17          0, 0, 0, 0, 0, 0;
18          0, 0, 0, 0, 0, 0;

```

```

19         0,      0,      0,      0,      0,      0;
20         0,      0,      0,      0,      0,      0;
21         0,      0,      0,      0,      0,      0;
22         0,      0,      0,      0,      0,      0;
23         0,      0,      0,      0,      0,      0;
24         0,      0,      0,      0,      0,      0].*1000; %at t=0
25
26 %u0(1) - CO2,u0(2) - HCO3, u0(3) - CO3, u0(4) - OH; u0(5) - K,
27 %u0(6) -potential,H2(7)CO(8)HCOO(9)CH4(10)C2H4(11)EthOH(12)nPropOH,
28 %(13)Alalk(14)MetOH(15)AcO(16)Etglyk(17),Glyoxal(18)
29 zeff=[2, 2, 2, 8, 12, 12, 18, 16, 6, 8, ...
        10];
30 %H2(1)CO(2)HCOO(3)CH4(4)C2H4(5)EtOH(6)nPrOH(7)Aly(8)MeOH(9)AcO(10)Egl(11)

```

MatLab Code for Reduction of Potassium Ferricyanide

```

1 %CVSimulations for redox reaction Fe(III) <-> Fe(II) on a glassy ...
   carbon RDE
2 %Author: Martina Ruescher
3 %species: (1)[FeCN6]3- (2)[FeCN6]4- (3)K+ (4)ClO4- (5)potential
4
5 clear; clc; tic %timecounting starts
6
7 global F R T D A bulk n K1 K2 alp E0 Ei dt w d dv
8
9 %-----Constants-----
10 n      = 1; %number of exchanged electrons
11 F      = 96485.333; %Faraday's constant [As/mol of e-]
12 R      = 8.314459848; %Gas constant [J/(K*mol)]
13 T      = 293.15; %temperature [K]
14 vst    = 0.891; %dynamic viscosity water at 298K
15 dv     = 1; %dynamic viscosity at 293.15K
16 A      = 0.196e-4; %surface area [m2]
17 bulk   = [0.01; 2.19e-8] *1000; %bulk concentration [mol/m2]
18 Dst    = [7.2e-10,6.4e-10]; %Diffusionscoeff at 298K[m2/s]
19 Const  = Dst .* vst / 298; %Einstein-Stokes
20 D      = Const / dv .* T; %Diffusioncoeff at 293.15K [m2/s]
21 z      = 3; %valency
22 NA     = 6.022e23; %Avogadro number [mol-1]
23 e      = 1.602e-19; %electron charge
24
25 %-----Variables-----
26 Emax   = 0.9; %upper vertex of potential [V]
27 Emin   = -0.5; %lower vertex of potential range [V]
28 E0     = 0.22; %standard potential [V]
29 alp    = 0.5; %symmetry factor
30 K1     = 6e-6; %forward constant
31 K2     = 2e-6; %backward constant
32
33 %-----LOOP-----
34 for q = 1:4
35
36 rpm    = [0,200,400,800]; %rounds per minute
37 w      = 2*pi*rpm(1,q)/60; %rotation
38 tend   = 28; %end time
39
40 if q==1

```

```

41 d      = 6*(D(1,1)*1/0.1)^(1/2); %boundary layer thickness without ...
    rotation
42 else                                     %multiple of (Dt)^1/2 1/t=scanrat
43 d      = 0.201*w^(-1/2)*dv^(1/6)*D(1,1)^(1/3); %LEVICH RDE
44 end                                     %boundary layer thickness with rotation
45
46 m      = 0;                            %geometrical factor
47 xn      = 100;                          %number of distance steps
48 x{q}    = 1:xn;                         %defining distance cell
49 x{q}    = linspace(0,d,xn);             %distance vector
50 dt      = 0.1;                          %time steps
51 tn      = tend/dt;                      %number of time steps
52 t       = 0:dt:tend;                    %time vector
53
54 %-----Function-----
55 sol     = pdepe(m,@concgradpde,@concgradic,@concgradbc,x{q},t);
56
57 %-----Results-----
58 u1{q}   = sol(:, :, 1);                  %FeCN3- (Fe3+)
59 u2{q}   = sol(:, :, 2);                  %FeCN4- (Fe2+)
60 u3{q}   = sol(:, xn, 1);
61 u4{q}   = sol(:, xn, 2);
62 u5{q}   = sol(280, :, 1);
63 Ix{q}   = zeros(1,280);
64 %-----Calculating-Current-----
65 %Loop
66 for p=1:280
67     i=p+1;
68     Ei(1)=0.9;
69
70     if ((1≤p) && (p≤140))
71         Ei(i) = 0.9-0.01*p;
72     else
73         Ei(i) = -0.5+0.01*(p-140);
74     end
75
76 %Current at t==0
77 Ix{q}(1) = n*A*K1*u4{q}(1)*exp((alp)*(F/(R*T)*(Ei(1)-E0)))...
78     -n*A*K2*u3{q}(1)*exp(-(1-alp)*(F/(R*T)*(Ei(1)-E0)));
79 %Current at t=[1;tend]
80 Ix{q}(i) = n*A*K1*u4{q}(i)*exp((alp)*(F/(R*T)*(Ei(i)-E0)))...
81     -n*A*K2*u3{q}(i)*exp(-(1-alp)*(F/(R*T)*(Ei(i)-E0)));
82 end
83 end
84
85 %IMPORT DATA FROM EXEL
86 fid='30D4D510.xlsx';
87 a=fopen(fid,'rt');
88 T1=readtable(fid,'Sheet','0rpm');
89     Iexp1=T1.WE0(1:end);
90     Uexp1=T1.Pot0(1:end);
91
92     Iexp2=T1.WE200(1:end);
93     Uexp2=T1.Pot200(1:end);
94
95     Iexp3=T1.WE400(1:end);
96     Uexp3=T1.Pot400(1:end);
97
98     Iexp4=T1.WE800(1:end);

```

```

99     Uexp4=T1.Pot800(1:end);
100 fclose(a)
101
102 extract1=[Ei;Ix{1};Ix{2};Ix{3};Ix{4}];
103 extract1=extract1';
104 extract2=[Uexp1,Iexp1,Uexp2,Iexp2,Uexp3,Iexp3,Uexp4,Iexp4];
105
106 %PLOTTING-----
107 %CURRENT VS POTENTIAL
108 figure (1)
109     hold on
110     plot(Ei,Ix{1})
111     plot(Uexp1,Iexp1)
112     title('U-I-Sim (0 rpm) vs. U-I-Exp')
113     xlabel('Potential [V]')
114     ylabel('Current [A]')
115     hold off
116 figure(2)
117     hold on
118     plot(Ei,Ix{1})
119     plot(Ei,Ix{2})
120     plot(Ei,Ix{3})
121     plot(Ei,Ix{4})
122     plot(Uexp1,Iexp1,'o')
123     plot(Uexp2,Iexp2,'x')
124     plot(Uexp3,Iexp3,'s')
125     plot(Uexp4,Iexp4,'*')
126     title('Current-Potential Simulated')
127     xlabel('Potential [V]');
128     ylabel('Current [A]');
129     legend('0s','200s','400s','800s','0ex','200ex','400ex','800ex')
130     hold off
131 figure(3)
132     hold on
133     plot(Uexp1,Iexp1,'o')
134     plot(Uexp2,Iexp2,'x')
135     plot(Uexp3,Iexp3,'s')
136     plot(Uexp4,Iexp4,'*')
137     title('Current-Potential Experimental')
138     xlabel('Potential [V]');
139     ylabel('Current [A]');
140     legend('0rpm','200rpm','400rpm','800rpm')
141     hold off
142
143 %CONCENTRATION as function of TIME and DISTANCE
144 %concentration ferricyanide at rpm 800
145 figure(4)
146     surf(x{4},t,u1{4},'LineStyle','none')
147     xlabel('distance [m]')
148     ylabel('time [s]')
149     zlabel('concentration [mMol]')%[Fe(CN)6]3-
150 %concentration ferricyanide at rpm 0
151 figure(5)
152     surf(x{1},t,u1{1},'LineStyle','none')
153     xlabel('distance [m]')
154     ylabel('time [s]')
155     zlabel('concentration [mMol]')%[Fe(CN)6]3-
156 figure(5)
157     plot(x{1},u3{1});

```

```

158     title('concentration at tend rpm 0')
159     xlabel('distance')
160     ylabel('concentration Ferricyanide')
161 figure(6)
162     plot(x{4},u3{4});
163     title('concentration at tend rpm 800')
164     xlabel('distance')
165     ylabel('concentration Ferricyanide')
166 figure(7)
167     hold on
168     plot(Ei,Ix{1})
169     plot(Uexp1,Iexp1)
170     plot(Ei,Ix{2})
171     plot(Uexp2,Iexp2)
172     plot(Ei,Ix{3})
173     plot(Uexp3,Iexp3)
174     plot(Ei,Ix{4})
175     plot(Uexp4,Iexp4)
176     xlabel('Potential [V]')
177     ylabel('Current [A]')
178     title('U-I-Simulated vs. U-I-Experimental')
179     legend('Sim 0rpm','Exp 0rpm','Sim 200rpm','Exp 200rpm',...
180           'Sim 400rpm','Exp 400rpm','Sim 800rpm sim','Exp 800 rpm');
181     hold off
182 figure(8)
183     hold on
184     plot(Ei,Ix{1})
185     plot(Uexp1,Iexp1)
186     title('U-I-Sim (0 rpm) vs. U-I-Exp')
187     legend('s','x')
188     hold off
189 figure(9)
190     hold on
191     plot(Ei,Ix{2})
192     plot(Uexp2,Iexp2)
193     title('U-I-Sim (200 rpm) vs. U-I-Exp')
194     legend('s','x')
195     hold off
196 figure(10)
197     hold on
198     plot(Ei,Ix{3})
199     plot(Uexp3,Iexp3)
200     title('U-I-Sim (400 rpm) vs. U-I-Exp')
201     legend('s','x')
202     hold off
203 figure(11)
204     hold on
205     plot(Ei,Ix{4})
206     plot(Uexp4,Iexp4)
207     title('U-I-Sim (800 rpm) vs. U-I-Exp')
208     legend('s','x')
209     hold off
210
211 toc %timecounting ends
212
213 %INITIAL conditions-----
214 function u0 = concgradic (x)
215 global bulk
216     u0 = bulk;

```

```

217 end
218
219 %BOUNDARY conditions-----
220 %p(pot,t,u)+q(pot,t)*f(pot,t,u,diff(u,t) = 0;
221
222 function [pl,ql,pr,qr] = concgradbc(xl,ul,xr,ur,t)
223 global bulk A F n K1 K2 alp R T E0
224
225         if ((0≤t) && (t≤14))
226             Ex = 0.9-0.1*t;
227         else
228             Ex = -0.5+0.1*(t-14);
229         end
230 Ex
231 I=n*A*F*K1*ur(2)*exp((alp)*(F/(R*T)*(Ex-E0)))...
232     -n*A*F*K2*ur(1)*exp(-(1-alp)*(F/(R*T)*(Ex-E0)));
233 Q=I/A; %Q... curr.dens. [j if not defined else in MatLab imaginary ...
    number]
234
235 pl=[ul(1)-bulk(1);ul(2)-bulk(2)];
236 ql=[0;0];
237 pr=[-Q/F;Q/F];
238 qr=[1;1];
239 end
240
241 function [c,f,s] = concgradpde(x,t,u,DuDx)
242 global D
243     c = [1;1];
244     f = [D(1,1);D(1,2)].*DuDx;
245     s = [0;0];
246 end

```