Electrochemical Reduction of CO₂ to Ethylene

Spectroscopic Evaluation of Copper Electrodes

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ELECTROCHEMICAL
REDUCTION OF CO₂ TO
ETHYLENE
SPECTROSCOPIC EVALUATION OF COPPER
ELECTRODES

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ELECTROCHEMICAL REDUCTION OF CO₂ TO ETHYLENE – SPECTROSCOPIC EVALUATION OF COPPER ELECTRODES

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Chapter 1.

Introduction

This chapter provides motivation and background information for the work in the field of electrochemical reduction of CO₂. After stating the importance of the subject, reaction mechanism on Cu electrodes is discussed. Finally, a brief overview of the thesis outline is given.

1.1 Motivation for CO₂ recycling

Excessive CO₂ emission by human activities is a serious environmental threat and a leading cause of global climate change¹. Anthropogenic emissions of CO₂ accelerated at the start of the industrial age in the mid-18th century and are now increasing the atmospheric concentration of CO₂ by 1–2 parts per million by volume (ppmv) annually². As can be seen from figure 1, due to the tremendous consumption of fossil fuels, the annual CO₂ emission steadily increased in the past 60 years. The continuously increasing concentration of CO₂ in the atmosphere to levels as high as 410.31 ppm has created serious environmental, social and global ecological issues. Consequently, this has resulted in global warming, acid rain, acidification of soils and rising of sea levels³⁻⁵.

This makes it imperative to find methods to mitigate CO₂ emissions and also to replace an increasing portion of fossil fuels by renewable sources to meet global energy demand. Therefore, control and utilization of CO₂ have become urgent issues to the entire international community.

Different strategies to reduce CO₂ emissions must be employed and can be divided in three categories. These categories include 1) improving energy efficiency of the chemical industry, 2) carbon capture and storage, and 3) using non- or low-carbon renewable energy sources, (e.g., solar, wind). Of these technologies, in the second option, CO₂ is used as a carbon source to produce new, high-value products and in essence zero CO₂ emission is feasible.

CO₂ can be converted through diverse routes, including chemical⁶, biochemical⁷, photochemical⁸, electrochemical⁹, or biological¹⁰ transformations. Among these CO₂ conversion technologies, electrochemical reduction has numerous advantages over others and is considered to be the most promising¹¹. These advantages include¹²: 1) operating under ambient temperature and pressure, 2) possibility of driving the electrochemical conversion of CO₂ toward the desired products via controlling

external potential, electrocatalysts and electrolyte, 3) minimal chemical consumption by recycling the electrolytes, 4) straightforward scale-up and low cost equipment, and 5) direct consumption of electrons for product formation and possibility of using renewable sources like solar and wind energies.

In electrochemical CO₂ reduction, the electrochemical reaction is independent of the electricity source. To avoid extra CO₂ emissions and replace the use of fossil fuels, the electrocatalytic reduction of CO₂ should be powered by electricity from renewable energy sources such as solar energy, hydropower and wind energy. In this way, the anthropogenic carbon cycle can be closed and intermittent renewable electricity can be stored, resulting in net reduction of greenhouse gas emissions. In this way, carbon-based chemicals could be produced to replace those currently derived from petroleum. Significant technical progress has been made in recent years, and preliminary technoeconomic analysis of CO₂ electrochemical reduction has demonstrated the commercial feasibility of the technology.

Figure 1. Correlation of global temperature with CO₂ concentration from 1958 to 2017¹³.

1.2 Importance of CO₂ reduction

Several important products can be formed during heterogeneous electrochemical reduction of CO₂ including CO, formic acid, oxalic acid, methanol, methane, formaldehyde, ethanol and ethylene¹⁴. These products can be used as commodity chemicals as well as fuels, thus allowing CO₂ to be recycled into compounds that can act as energy carriers. Among these products, ethylene has the highest commercial value.

The performance of a catalyst is commonly evaluated by the following crucial parameters¹⁵: (1) onset potential or overpotential (η), which is the difference between the onset potential and the standard reduction potential. As the reduction reaction has to overcome the kinetic energy barrier, the onset potential is always more negative than the standard potential of CO₂RR. (2) Faradaic efficiency (FE). This is defined as the ratio between the useful energy output (energy stored in a desired product) and total energy input. FE describes the product selectivity during the reduction reaction, which is closely related to the reduction mechanism. (3) Current density (CD), calculated as current divided by the geometric surface area of working electrode, reflects the transformation rate of CO₂. This parameter is a crucial indicator of the performance of the cell. More importantly, the partial current density for a specific product is calculated via multiplying the overall current density by the FE of the product and is a measure of the product formation rate. (4) Stability, degradation rate of CD over the period of system operation. (5) Tafel slope, derived from the Tafel plot, which represents overpotential verses logarithm of the partial current density of a specific product. It is an indicator for the reaction pathway and the rate-determining step. (6) turnover frequency (TOF), a measure of per-site activity of catalyst.

Note that these parameters are not only dependent on the properties of the catalyst as the working electrode, but also on experimental parameters related to electrolyte, CO₂ pressure, reaction temperature, etc.

To be feasible, the activation barrier for CO₂ reduction should be minimized compared to hydrogen evolution, driving CO₂ reduction selectively at low overpotential (high energy efficiency) with high reaction rates (high turnover number). High energetic efficiency is achieved through a combination of high selectivity (high FE) and low overpotentials (Figure 2). One hypothesis is that this can be achieved by use of a catalyst that can lower the energy of formation of the CO₂^{•-} radical anion intermediate.

Figure 2. Qualitative reaction scheme for CO₂ conversion. η represents the overpotential.¹⁶

Though electrocatalytic reduction of CO₂ possesses many advantages, this field still faces challenges of (1) large overpotential (low energy efficiency), (2) slow electron transfer kinetics even at high electrode potential resulting in low current densities, (3) unsatisfactory selectivity and costly separation steps, and (4) rapid deactivation of the catalyst (lifetime of less than 100 h) leading to a shift in the product selectivity towards hydrogen evolution reaction, restricting practical use and commercialization. Over the last few years, researchers have focused on the exploration of different electrocatalysts with the aim of addressing these key challenges. Despite reports of new studies showing improved Faradaic efficiencies and lower overpotentials, the conditions to enable implementation of a large-scale

industrial process are still unclear. Generally, in order to minimize investment costs, industrial reactors are operated at commercially relevant geometric current densities above 100 mA /cm² with at least 50% Faradaic efficiency for the required products¹⁷. To date, efforts to increase the current densities have been very successful, with current densities exceeding 600 mA/cm² achieved using gas diffusion electrodes(GDEs). High CO₂ reduction selectivity is important for future commercialization of these technologies because expensive separation processes can be avoided, decreasing the overall cost of scale-up.

1.3 Heterogeneous catalysis in aqueous media at metal electrodes

In effort to find catalysts to lower the overpotentials and control the selectivity, both homogeneous and heterogeneous catalysts have been applied to the electrochemical reduction of CO₂¹⁸⁻¹⁹. Most homogeneous catalysts suffer from significant drawbacks, such as i) leaching from the electrode posing difficulty to separate the catalyst from the products and to recycle, ii) high cost, iii) toxicity and iv) poor chemical stability, which hinders their practical application. They are, however, usually more selective than heterogeneous catalysts²⁰. Nevertheless, due to the disadvantages of homogeneous catalysts, development has been mainly focused on heterogeneous catalysts such as metal/metal alloys and non-metal catalysts.

1.4 Classification of metals

The first study to quantify both gaseous and liquid products, was reported by Hori and co-workers.²¹ This led to a classification of metal electrodes into four groups. Based on this, metals electrodes are classified depending on the tendency to bind various intermediates and final products.

Pb, Hg, In, Sn, Cd, and Bi give formate as a major product. These metals have moderate binding affinity toward the formate intermediates (*OCHO and *COOH).

Au, Ag, Zn, Pd, and Ga primarily produce CO as final product of CO₂RR. Such selective production of CO requires strong adsorption of *COOH while possessing low binding energy of *CO species. As a result of weakly bound *CO to the electrode surface, CO desorbs from the electrode as a major product. On Ni, Fe, Pt, and Ti, CO is strongly adsorbed and highly stabilized on the electrode surface. This practically inhibits further reduction of CO₂ under atmospheric pressure in aqueous media and instead almost exclusively reduction of water to hydrogen is observed.

Among various metals, Cu stands out in uniquely producing a number of hydrocarbons such as ethylene and methane, aldehydes, and alcohols with high current density. The product distribution on Cu ranges widely, depending on electrolyte, potential and temperature. This distinct behavior can be explained on the basis of heat of adsorption²². Pt and Ni, for instance, have high heats of CO adsorption while Au and Ag have much smaller heat of adsorption. The heat of adsorption on Cu is intermediate among these metals, leading to CO adsorption with moderate strength. Thus, achieving a balance of the barriers for activation of CO₂ and hydrogenation of *CO lead to effective formation of hydrocarbons. Cu is thus the only pure metal that reduces CO₂ to products requiring more than two electron transfers with substantial Faradaic efficiencies.

1.5 Cu

Polycrystalline Cu electrodes uniquely reduce CO₂ to high value-added hydrocarbon and alcohols, which are widely used industrially. Since Hori et al.²¹ found that CO₂RR on copper electrodes leads to formation of hydrocarbons, mainly ethylene and methane, different types of products and the reaction mechanisms have been investigated. Besides these hydrocarbons, CO, formic acid and oxygenates such as ethanol and propanol are also formed on Cu. In a study by Jaramillo and co-workers²³, using more sensitive product detection techniques for liquid products, a total of 16 products were observed with five detected for the first time. This included

the formation of eleven distinct C₂ oxygenated products including aldehydes, ketones, alcohols, and carboxylic acids. Figure 3 provides an overview of the current efficiency of each product as a function of applied potential and is divided into three groups to distinguish between major, intermediate, and minor products. Despite these efforts, poor selectivity and activity degradation are still two remaining challenges for practical application of Cu electrodes.

Figure 3. Product current efficiency on polycrystalline copper in CO₂-saturated 0.1 M KHCO₃ as a function of potential is shown for major, intermediate range, and minor products²³.

As discussed above, numerous carbon-containing products can be produced during the electrochemical CO₂RR, among which ethylene has a high commercial value. Ethylene is a key building block of the chemical industry and representative

for products with a reasonably high added value. It is produced on a large scale as an important precursor for commercially useful chemical products such as ethylene oxide, ethylene glycol, ethyl benzene, etc. and much of it is turned into polyethylene, which is used in plastic packaging. Ethylene has a global production volume of 158 million tons in the year 2020. Much effort has been devoted to advance the prospects of producing ethylene from CO₂ electroreduction.

1.6 Mechanism

In CO₂RR, water acts as the source of protons, and CO₂ is reduced at the cathode, while the oxygen evolution reaction takes place at the anode. However, CO₂ activation and reduction at the cathode is a significant challenge and does not take place easily due to the high heat of formation of -393 kJ/mol. Furthermore, as the first electron transfer step, i.e. the formation of the intermediate species CO₂^{•-} by an electron transfer to a CO₂ molecule, is highly unfavorable. The consequence is that, due to the enormous energy requirement to rearrange a linear molecule to a bent radical anion, the single electron reaction of CO₂ to CO₂^{•-} occurs only at a highly negative potential of -1.9 V versus the standard hydrogen electrode (SHE) in aqueous media under standard conditions²⁴. The high overpotential would lead to a serious waste of electric power and formation of hydrogen during the reaction, reducing the selectivity of CO₂ reduction. Following this key reaction step, there are several concerted proton (H⁺) and electron transfer processes that are more favorable to occur at less negative potentials. The primary reactions for the major products and important intermediates that occur at the copper electrode during the reduction of CO₂ are given below (all potentials are given with respect to the reversible hydrogen electrode (RHE)). These values are estimated from thermodynamics data in aqueous media at 25°C²⁵. The actual electrode potentials to drive the reductions are much more negative than these equilibrium values, mainly due to formation of CO₂^{•-}.

Heterogeneous electrochemical reduction of CO_2 occurs at electrode-electrolyte interfaces. This heterogeneous catalytic reaction contains three main steps: (1) adsorption of CO_2 on the surface of a catalyst, (2) electron and proton transfer to CO_2 , (3) rearrangement of product species followed by desorption.

In the first step, tremendous energy is needed to reorganize the linear CO_2 molecule to a bent radical anion. To overcome this, proton-assisted approach to CO_2 reduction, lowers the thermodynamic barrier significantly. Transition-metal complexes can have accessible multiple redox states that promote such proton-assisted, multi-electron pathways. In addition, in the aqueous system, hydrogen dominates as the major side-product of CO_2RR . This is in fact due to lower overpotentials of the hydrogen evolution reaction compared to CO_2RR . Therefore,

owing to the small difference in thermodynamic potential of the above equations, it is a great challenge to reduce CO_2 to desirable products with considerable selectivity.

At less negative potentials, CO_2 is reduced to CO and HCOOH . Then, at more-negative potentials, the absorbed CO is further reduced to hydrocarbons and alcohols. Contrary to CO , HCOOH is not further reduced at a Cu electrode. The electrochemical reduction of CO with a similar product distribution to CO_2 reduction suggest that the CO_2RR proceeds *via* CO as intermediate species²⁶. The exact reaction mechanism of carbon monoxide reduction to either ethylene or methane is still subject of dispute.

1.7 Types of electrode

Bulk metals have been studied intensively as CO_2 reduction electrocatalysts and their properties have been reviewed in detail by Hori²⁶. Due to the several attractive qualities over bulk catalysts, nanostructured metallic electrocatalysts have been subject of several recent investigations. To improve the electrocatalytic CO_2 reduction performance, diverse morphologies of Cu nanostructures including oxide-derived electrodes, nanoparticles, nanocubes, nanowires, porous hollow fibers, roughened surfaces prepared by electrodeposition, electropolishing, or plasma treatments have been investigated. The main advantage of nanostructured catalysts is that they are capable of providing more active sites because of their enhanced surface areas compared to smooth Cu ²⁷. Under-coordinated surface sites are usually abundant on nanostructured materials, such as corners, edges and steps, and defects, such as vacancies and grain boundaries. Since the catalytic activity of heterogeneous catalysts is proportional to the number of surface active sites, greater abundance of active surface sites can boost the performance. Moreover, various types of low-coordinated sites have different catalytic behavior than smooth surfaces. Thus, they can have a role in shifting the selectivity. According to recent studies, Cu nanostructures can have a promoting effect on ethylene formation²⁸⁻²⁹. In addition to

catalytic activity, nanostructured electrocatalysts have been shown to improve catalytic stability³⁰. This is due to the fact that nanostructured electrocatalysts are able to accommodate impurities much better because of their enhanced surface area.

1.8 Outline of this thesis

The focus of this thesis is on the improvement of ethylene selectivity in electrochemical reduction of CO₂ on copper electrodes. With the help of in situ spectroscopy techniques, mechanistic aspects of this reaction are carefully examined.

First, the experimental procedures and details of the equipment and set-ups is described in chapter 2. Besides, a brief theoretical background about the fundamentals of each technique is provided. The techniques discussed mainly includes gas chromatography, ATR-FTIR Spectroscopy, Raman Spectroscopy. Other characterization techniques are also discussed briefly, which include electrochemical surface area measurements. Finally, the methods for preparation of various electrodes are reviewed extensively.

In chapter 3, the effect of partial pressure of CO₂ (P_{CO_2}) on the product distribution of CO₂RR on rough Cu₂O films is investigated. Interestingly, enhanced selectivity towards formation of hydrocarbons was observed at low P_{CO_2} . After extensive examination of the effect of potential, film roughness and electrolyte buffer capacity, we concluded that this observation is due to an effect of the local pH. We concluded that the P_{CO_2} affects the local pH and plays a determining role in selectivity.

In chapter 4, the previous chapter was extended to a study of the partial pressure of CO (P_{CO}) and investigation of the effect of CO₂/CO mixtures on product selectivity. Moreover, the effect of the electrolyte anion (directly affecting electrolyte pH) on CORR product distribution was studied. To further understand the effect of anion on mechanism, ATR-SEIRAS was employed to monitor the CO adoption on Cu electrodes.

Introduction

In chapter 5, in situ ATR-SEIRAS was employed to study the interfacial phenomena on Cu electrode during CO₂RR. With the help of isotopic labeling (¹³CO₂ and D₂O), various intermediates and products were identified at different potentials. A highly detailed interpretation of spectra is presented in this chapter, and the presence of the CO₂ dimer radical-anion on roughened copper surfaces is explored.

In chapter 6, effects of addition of CuSO₄ to the electrolyte on surface morphology, roughness and product distribution was investigated. It was revealed that due to addition of CuSO₄, during CO₂RR, in situ electrodeposition of rough Cu nano-structures occurs. As a result, an improved selectivity towards ethylene at an optimum CuSO₄ concentration was observed. In situ Raman spectroscopy was employed and a correlation between CO coverage and activation of ethylene pathways was observed. In addition, Cu-OH, present at highly negative potentials, was found to have detrimental effects on ethylene formation.

In chapter 7, in situ Raman spectroscopy was applied to reveal the mechanistic pathways and oxidation state of the Cu electrode during CO₂RR. Employing isotopic labeling (¹³CO₂ and D₂O) allowed to distinguish oxides, hydroxide and a stable C-containing species on Cu at highly negative potentials. In addition potential-dependent features associated with carbonates, bicarbonates, CO, and most importantly hydroxide species were resolved.

Finally, in chapter 8, a summary of the findings and a perspective is provided.

Chapter 2.

Theory and experimental methods

This chapter outlines the principles and details of experimental setups of the most important used techniques in this thesis. The techniques include (micro) gas chromatography, ATR- Infrared spectroscopy and Surface Enhanced Raman spectroscopy.

2.1 Gas chromatography

Fundamentals

Gas chromatography is one of the most widely used separation techniques for analyzing hydrocarbon mixtures. The basic units of a gas chromatograph include the chromatographic column and the detector. The column separates the gas mixture into its components and the detector records the concentrations of the separated components.

The basis of the separation is the difference in the interactions of individual compounds with the stationary phase as they are moved through a long column by a carrier gas, usually helium or nitrogen. The time taken from injection to emergence is known as the retention time, and is characteristic for each substance under any given set of conditions. Compounds with greater affinity for the stationary phase spend more time in the column and have a longer retention time than samples with a higher affinity for the mobile phase. This affinity mainly depends on the intermolecular interactions and the polarity of the stationary phase. As a result, each component moves along the chromatographic column with different speed.

To measure a sample with an unknown concentration, a standard sample with known concentration (calibration gas) is injected into the instrument. This is repeated for at least 3 various concentrations for each compound. The standard sample peak retention time and the obtained areas are used to make a calibration graph. By using this calibration curve, the concentration of test sample can be calculated.

The Faradaic efficiency (FE) is defined as the ratio between the amount of product actually detected by the GC and the amount of product theoretically formed based on the charge passed through the cell during electrolysis. The FE or selectivity for each product in CO₂RR was calculated according to the following equation:

$$\text{FE}(\%) = \frac{nZF}{Q} \times 100$$

n is the amount of the generated products (number of moles, mol); Q is the total charge passed through the cell (coulombs, C); F is the Faraday constant (96 485 C/mol); Z is the number of electrons required to obtain 1 molecule of the product. The number of electrons required to form 1 molecule of CO, CH₄, C₂H₄ and C₂H₆ are 2, 8, 12 and 14, respectively.

Setup

All electrochemical measurements were carried out using a Bio-Logic VSP potentiostat. A home-made two compartment electrochemical cell using a three electrode assembly was used to carry out the electrochemical reduction of CO₂ (See figure 1). The as-prepared cuprous oxide films with the thickness equivalent to a total charge of 3C (Coulomb) were used as the working electrode, unless another thickness is mentioned. Glassy carbon (SIGRADUR® G) was used as the counter electrode and was separated from the working electrode using an anion exchange membrane (Selemion AMV, AGC, Inc.). Ag/AgCl in 3 M NaCl was used as a reference electrode. The distance between the working and reference electrodes was kept small (3 mm) to reduce solution resistance. The IR compensation was automatically applied by using ohmic drop determination-current interrupt technique. All potentials were converted to the Reversible Hydrogen Electrode (RHE) scale by:

$$V_{\text{vs. RHE}} = V_{\text{measured vs. Ag/AgCl}} + 0.198 + 0.059 * (\text{pH of solution}).$$

The electrolyte solutions of KHCO₃ (Sigma- Aldrich, 99.99% metals basis) were prepared with deionized water (Millipore MilliQ, 18.2 MΩ cm), in concentrations ranging from 0.05 M to 0.5 M. The gas mixture (CO₂/CO and He) was continuously purged through a glass frit at a rate of 20 ml min⁻¹ for 30 minutes before each experiment, using two mass flow controllers, to attain steady CO₂ concentration in the electrolyte. The pH of the electrolytes of various concentrations of KHCO₃ and P_{CO2} was monitored. The flow rate was decreased to 5 ml min⁻¹ during the

electrochemical reduction experiments. The reactor effluent was then vented directly into the gas sampling loop of a micro-gas chromatograph (micro-GC) equipped with a pulsed discharge detector (PDD) every 4 minutes. The micro-GC was equipped with two different columns (Molsieve plot and Rt-Q Bond) for separation of H_2 , O_2 , CO , CO_2 and hydrocarbons. The mass balance was typically closed within +90 %, and therefore the electrolyte was not analyzed for liquid phase products, which based on other studies most likely contains some formate/formic acid, as will be further addressed in the description of the results in various chapters.

Figure 1. Experimental setup used to evaluate the electrochemical CO_2 reduction of the Cu foils. Inside the reactor, from right to left, the Cu electrode Teflon holder is seen from back (The Cu foil is facing the CE). In the middle, the reference electrode is visible by the yellowish capillary. Next, to the left, is the holder for glassy carbon CE, which can be seen as the black square behind the membrane. To the far left, a frit bubbler is seen while purging the electrolyte with CO_2 .

2.2 ATR-FTIR Spectroscopy

Fundamentals

Surface enhanced infrared absorption spectroscopy (SEIRAS) is based on the phenomenon that a significant increase in intensity of $10\text{-}10^3$ times can be obtained on roughened surfaces of metals, as compared to polished surfaces. Such enhancement factors are enough to enable detection of sub-monolayer adsorbates and intermediates and their configurations on metallic electrode surfaces under operando conditions. In addition, infrared spectroscopy is a suitable technique to provide important experimental evidence to address preferred reaction pathways, selectivity and effects of the reaction environment on CO₂RR catalysis.

This enhancement effect is based on the similar well established mechanism of surface enhanced Raman spectroscopy (SERS) and is attributed to electromagnetic and chemical origins³¹. However, unlike SERS, the SEIRA phenomenon is much less substrate specific.

IR absorption spectroscopy, uses the absorption of IR photons to detect molecular vibrations with a changing dipole moment. IR spectra can be measured in transmission mode, reflection mode or attenuated total reflection (ATR) mode. To enable operando IR spectroscopy under potential control, the experiment is typically conducted in ATR mode in a Kretschmann-like configuration³².

In the ATR mode, the electrocatalyst is deposited on an ATR crystal which serves as an internal reflection element (IRE) made of high-refractive materials (Si, Ge, or ZnSe). The IR beam is illuminated from below and undergoes a reflection at the interface of sample with the IRE. This results in formation of an evanescent wave with a low penetration depth (d_p , see figure 3) of typically $0.5\text{-}2.0\text{ }\mu\text{m}$ into the sample, depending on the angle of incident of IR beam and refractive index of the IRE and the sample. The evanescent wave penetrates the electrolyte medium and

decays exponentially with distance, enabling the selective monitoring of the catalytic interface.

Metal island thin films suitable for SEIRAS measurements have been deposited on the IREs in a wide variety of ways, such as chemical (electroless deposition) and sputtering techniques. The metal film must be thin enough so that the evanescent wave can reach the electrolyte. Moreover, the film should be non-uniform and made of islands, to enable the electromagnetic mechanism of SEIRA resulting from the polarization of these metal islands by the electromagnetic field of the incident radiation.

Setup

All electrochemical experiments were performed in a custom-made three-electrode cell, with the Cu film being used as the working electrode. A graphite rod, rather than a Pt wire, was used as counter electrode to eliminate any possible Pt contaminations on the working electrode, while a Ag/AgCl electrode (3 M NaCl, BASi) was used as reference electrode. A VersaSTAT 3 potentiostat was used to perform electrochemical measurements. The experiments were conducted in a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen-cooled MCT detector and a Veemax III ATR accessory (See figure 2). Prior to each experiment, the electrolyte was bubbled with purging gas (CO_2 , $^{13}\text{CO}_2$ or CO) for 15 minutes to saturate the solution. The Cu films were activated by three activation cycles between 0.6 and -0.6 V in the electrolyte, in order to improve the signal. A reference spectrum was recorded and spectra were taken with 4 cm^{-1} resolution during a CV with a typical scan rate of 3 mV/sec, under continuous purging.

Figure 2. Experimental setup used for in-situ ATR-SEIRAS experiments. The Teflon cell is mounted on top of the Veemax III ATR accessory. On the top of cell, on the lid, gas inlet and outlet, and reference electrode and graphite rod as CE are observed.

Figure 3. Schematic of the electrochemical cell used for in-situ ATR-SEIRAS experiments. Thin Cu film is deposited onto an infrared-transparent ATR crystal, and is used as the working electrode. The graphite rod, reference electrode and gas inlet are seen inserted into

the electrolyte. The penetration depth (d_p) of evanescent wave resulting from the internal reflection of IR beam, is shown to surpass the Cu film and reach the electrode/electrolyte interface.

2.3 Raman Spectroscopy

Fundamentals

Raman spectroscopy detects the inelastically scattered light as a result of incident monochromatic light, typically provided by a laser. Following the interaction of the exciting laser light with the surface of the electrode, a small fraction of photons which undergo inelastic scattering contains information of the vibrational modes of the samples, i.e. the Raman spectrum.

Surface enhanced Raman Spectroscopy (SERS) offers a surface-enhancement of several orders of magnitude on certain rough metal surfaces, typically of metals such as Ag and Au. Such surface-enhancement mainly originates from enhanced local electromagnetic fields, which significantly decay with distance from the electrode and make this technique well suited to investigate interfacial electrochemical reactions. Electromagnetic enhancement is regarded as the major contributing mechanism with an enhancement contribution of 10^4 - 10^6 . On the other hand, chemical enhancement due to charge transfer between metal and adsorbed molecules on plasmonic nanostructures has a smaller contribution of 10 - 100 ³³.

In addition to issues addressed by infrared spectroscopy, SERS is suitable to identify catalytically active sites due to its ability to probe the catalyst surface in higher oxidation states. For example, operando SERS can be used to discriminate the presence of CuO, Cu₂O, Cu(OH)₂ and Cu(0) as the active surface for CO₂RR. The Raman signals corresponding to metal-adsorbate modes are in the wavenumber range of $< 1000 \text{ cm}^{-1}$.

In summary, SERS has been proven to be exceptionally useful for studying interfacial catalytic CO₂RR by providing information on surface adsorbed species and transformations in oxidation state.

Setup

Raman spectroscopy was carried out using an Avantes AvaRaman spectrometer with an Intertec laser as excitation source at $\lambda = 785$ nm. In-situ experiments were performed in a homemade Teflon flow cell with Pt mesh as counter electrode and Ag/AgCl in 3 M NaCl as a reference electrode. The electrolyte was continuously purged externally (outside the cell) with CO₂ throughout the experiment and was pumped using a Watson-Marlow 101U pump at 1 mL/min (See figure 4). The Raman probe, separated from the electrolyte by a quartz window was mounted on a μ m optical screw to optimize the distance to the electrode surface. The beam travels through 4 mm of solution to get to the catalyst surface. An acquisition time of 10 seconds was selected to record each spectrum.

Figure 4. Schematic of the electrochemical setup used for in-situ SERS experiments. The electrolyte compartment placed outside the cell and before the pump, is continuously purged with CO₂.

2.4 Electrochemical surface area determination

The relative surface roughness factors of the electrochemically active surfaces were calculated by measuring the double layer capacitance values in 0.1 M KCl. Pt mesh was used as a counter electrode and Ag/AgCl was used as reference electrode. After reducing the layers in 0.1 M KHCO_3 , cyclic voltammetry (CV) was performed with different scan rates (5, 20, 40, 60, 80, 100 mVs^{-1}) in the potential range in which no Faradaic processes occur. The slope of the (difference in) current density vs. scan rate gave the capacitance value which was normalized to smooth copper, to obtain the surface roughness factors.

2.5 Electrode preparation

Electrodeposition of Cu_2O films

Cuprous oxide films were electrodeposited onto copper foils (Alfa Aesar, 99.99%) from Cu^{2+} containing solutions prepared using 0.4 M CuSO_4 (Sigma Aldrich, 99%) and 3 M lactic acid (Sigma Aldrich) at 60°C, according to a published procedure described elsewhere³⁴. A one-compartment, three electrode cell with Cu foil as working electrode, Pt mesh as counter electrode and Ag/AgCl (3M NaCl) as the reference electrode were used (See figure 5). Copper foils were prepared by mechanical polishing and then electropolishing (in 85% phosphoric acid, potentiostatically at 3 V vs. a graphite foil counter electrode), followed by cleaning ultrasonically in ethanol and water. The pH of the solution was adjusted to 12 using NaOH (Sigma Aldrich, 98%). Galvanostatic deposition was performed at 0.8 mA cm^{-2} using a potentiostat/galvanostat (PAR, Versastat 3) until a desired film thickness was achieved.

Figure 5. Schematic of the experimental setup used for electrodeposition of Cu_2O .

Cu sputtering on ATR crystals

Cu thin-film electrodes were prepared by magnetron sputtering from a copper source, directly onto the reflecting plane of a 45° silicon ATR crystal. The sputtering was carried out using an argon flow of 25 ml/min, and applying a power of 30 W. These relatively mild conditions result in a sputtering rate of 0.044 nm/s. Since the time of sputtering was set at 270 s, a film thickness of 12 nm was produced after 270 s. The resistance of each film tested across a 1.5 cm length of the layer was around $8\ \Omega$. Surface characterization of the copper film was carried out using atomic force microscopy (AFM). The working mode of the applied AFM system (Cypher, Oxford Instruments), was amplitude modulation, with a NSC36 double side probe coated cantilever, and the measurements were carried out in air.

Chapter 3.

Effect of partial pressure on product selectivity in Cu-catalyzed electrochemical reduction of CO₂

Abstract

The influence of CO₂ partial pressure on electrochemical reduction of CO₂ using oxide-derived electrodeposited copper surfaces in a conventional two compartment cell configuration, is discussed. Contrary to what has been reported in the literature for polished copper surfaces, demonstrating a linear decrease in the Faradaic efficiency (FE) as a function of decreasing partial pressure, the (FE) and partial current density of both ethylene and methane are improved when the CO₂ partial pressure is decreased below 1 atm, and an optimized ethylene efficiency of ~45% is

achieved in the range of ~ 0.4 – ~ 0.6 atm at -1.1 V vs. RHE. Such optimum in ethylene FE, ranging from ~ 10 – 45% , is obtained at a variety of applied voltages (-0.7 to -1.1 V vs. RHE), but only at relatively low concentrations of KHCO_3 of less than 0.25 M. Since a low KHCO_3 concentration induces only a low buffer capacity, we conclude that a rise of local pH induced by a decreased CO_2 partial pressure explains improved selectivity towards ethylene. If the CO_2 partial pressure decreases below ~ 0.4 atm, not only the availability of CO_2 limits ethylene selectivity, but also a fall in local pH, associated with the decreasing partial current density in formation of ethylene. Calculations of local concentrations of CO_2 and the pH corroborate these hypotheses. These findings contribute to, and substantiate the current understanding of the significant role of local pH conditions on the selectivity of CO_2 electroreduction products, and suggest high ethylene selectivity over oxide derived Cu electrodes can be obtained for diluted CO_2 feed compositions if the electrolyte has a relatively low buffer capacity.

3.1 Introduction

The accumulation of CO_2 in the atmosphere is generally accepted to have significant impact on climate conditions. A promising methodology for reducing carbon dioxide is conversion of CO_2 into fuels or commodity chemicals through an electrochemical process based on renewable electricity³⁵. Among the metal electrodes used, copper is the most extensively studied since it is capable of producing hydrocarbons from CO_2 with high Faradaic efficiencies^{21, 23, 36-37}. Although a broad mix of hydrocarbons and minor products have been reported, the main products at relatively high potentials are ethylene and methane^{23, 38-39}. Ethylene is a desired product in electrochemical reduction of CO_2 , given the large market potential and use as feedstock for several industrial processes. In particular oxide-derived copper electrodes have been reported to show a high Faradaic selectivity towards ethylene⁴⁰⁻⁴³. Furthermore, significant progress has recently been made in increasing the current density towards ethylene by utilization of highly basic

electrolytes in combination with advanced gas diffusion electrodes. Generally these studies have evaluated the cell performance using highly purified feeds (>98%). Yet direct utilization of flue gas would imply that the CO₂ partial pressure is only ~0.15 Bar. Furthermore, the single-pass electrochemical conversion of CO₂, even in gas-diffusion-based reactors, is still low⁴⁴, and recycling is required to increase the overall process efficiency. Thus, in practical applications, diluted concentrations of CO₂ can be expected.

Kenis et al. have nicely evaluated the effect of sub-atmospheric partial pressures on the performance of Ag-based gas diffusion electrodes, and showed that the decrease in partial current density for CO was less than 45% when switching from a pure CO₂ feed to a feed of 10% CO₂ in inert gas⁴⁴. Furthermore, Kyriacou et al.⁴⁵ have conclusively shown that on smooth copper surfaces in 0.5 M KHCO₃, the Faradaic efficiency (FE) and the rates of formation of the reduction products, including ethylene, diminish linearly with decreasing P_{CO2}, while the efficiency in hydrogen evolution increases.

Lum et al.⁴⁶, in their study focusing on the effect of surface roughness of copper electrodes in 0.1 M KHCO₃, observed that the FE in methane formation improves when the P_{CO2} decreases from 1.0 to 0.8 or to 0.6 atm.

Finally, the effect of CO partial pressure on the formation of several products of electroreduction, has been investigated in detail⁴⁷⁻⁵⁰. In a study by Wang et al.⁵⁰, a major decrease in partial current densities of CO reduction products is observed as a function of decreasing partial pressure of CO. Li et al.⁴⁷ examined the effect of the local CO concentration on ethylene selectivity both theoretically and experimentally, and interestingly showed that constraining CO, favored ethylene production.

As discussed above, research on the subject of variations in partial pressure of CO₂ has been mostly restricted to smooth copper electrodes or gas diffusion electrodes. Herein, we examine for the first time the effect of partial pressure on

performance of rough, oxide-derived copper electrodes in the electrochemical reduction (CO₂R) of CO₂. This paper begins by investigating the effect of partial pressure at variable applied potential. It will then go on to correlate effects of partial pressure as a function of buffer (KHCO₃) concentration, which highly affects the local surface pH. The third part deals with the effect of surface roughness, a factor also known to be responsible for the rise of local pH. The impact of the mentioned factors on local pH, proton activity and consequently hydrocarbon selectivity will be discussed on the basis of several results of calculation of the local concentration of CO₂ and pH near the electrode.

3.2 Experimental section

Detailed description of materials and methods used for this study can be found in chapter 2.

Modelling methodology

The modelling approach was analogous to the one reported by Gupta et al.⁵¹. In such 1-D model, a 3-region system is considered, being '*Bulk*', '*Boundary Layer*' and '*Electrode Surface*' in a batch, isothermal, and non-stationary situation. This is representative of the experimental set-up used in the present study. Only the cathodic half-cell is described in the model, as it is considered to be the limiting reaction in the whole electrochemical process (in the anodic half-cell, the oxygen evolution reaction takes place). The thickness of the '*Boundary Layer*' region is given by the input parameter δ , which is taken to be 100 μm , in accordance with previous literature⁵¹⁻⁵²; for the current density j , the experimentally determined value of 25 mA.cm⁻² was used.

At the '*Bulk*' region, the equilibria of all dissolved species, CO_{2(aq)} and KHCO₃, were considered. The equation of state for the calculation of the CO₂ saturation concentration in pure water was taken from Duan et al.⁵³. Then, the salt-out effect due to the presence of an electrolyte is also considered using the model from

Schumpe⁵⁴, having as output a saturated concentration of $\text{CO}_{2(\text{aq})}$, given a certain pressure, temperature and initial KHCO_3 concentration. Bulk equilibria for the buffered system $\text{CO}_{2(\text{aq})}$ – KHCO_3 were calculated having as input $\text{CO}_{2(\text{aq})}$ (after salt-out effect) and KHCO_3 initial concentrations. It is assumed that the ‘*Bulk*’ region is unaffected by the electrochemical reaction at the ‘*Electrode Surface*’, and neither by the transport effect in the ‘*Boundary Layer*’.

At the ‘*Boundary Layer*’ region, two phenomena are taking place: diffusion of all species (modelled with Fick’s 2nd Law), and homogeneous equilibrium reactions for the buffered system $\text{CO}_{2(\text{aq})}$ – KHCO_3 . All necessary data for these two effects were taken from Gupta et al.⁵¹, for a constant temperature. It is assumed that diffusion is the only transport mechanism for the reactive species to reach the ‘*Electrode Surface*’ region. Resulting equations are a set of Partial Differential Equations (PDE), solved with the PDE method in Matlab R2019A. Initial conditions (at instant zero and all spatial domains) consider that the concentration of all species is equal to the concentrations at the ‘*Bulk*’ region (from the equilibrium calculations). Boundary conditions at $x=0$ (considering the border with ‘*Bulk*’ region to be $x=0$, at all-time domains) assume that concentrations are equal to the ‘*Bulk*’ region equilibrium concentrations. Boundary conditions at $x=\delta$ (considering the border with ‘*Electrode Surface*’ region to be $x=\delta$, at all time domains) presume that a Neumann boundary condition is applied. Consumption or formation rates for the set of electrochemical reactions (only affecting $\text{CO}_{2(\text{aq})}$ and OH^-) are used in this boundary layer.

At the ‘*Electrode Surface*’ region, the $\text{CO}_{2(\text{aq})}$ consumption and OH^- formation rates are calculated from the given Faradic Efficiency values taken from the experimental data. All products formed at the electrode are considered not to affect the modelled system and have been neglected. Since Faradaic Efficiency values are constant with respect to current density, reactant concentration, or other variables, the $\text{CO}_{2(\text{aq})}$ consumption and OH^- formation rates are therefore constant. The only

considered products are: H_2 by hydrogen evolution, and CH_4 , C_2H_4 , and CO by CO_2R .

3.3 Results and discussion

Electrochemical deposition of Cu_2O films

The XRD patterns of the as prepared Cu_2O films with varying thickness and a reduced electrode are shown in Figure 1. It can be seen that with an increase in thickness, the intensity of the Cu_2O (110), (111), (100) and (220) diffraction lines increases while the intensity of the peaks associated with metallic copper (the substrate) decrease. The observed change in orientation (for the 9C sample) is believed to be the result of pH and Cu^+ variations during electrodeposition⁵⁵. Furthermore, XRD patterns of the reduced copper electrode signify that the surface of the oxide film had been fully reduced to metallic copper during CO_2R , consisting of Cu (111), (220) and (200). The predominant orientation of Cu is (200). SEM images of oxide-derived copper with the thickness of 3C, before and after electrochemical reduction, are shown in Figure S1 of the supporting information. A rough surface is obtained consisting of pyramidal shapes, showing cracks after electrochemical reduction. This is in agreement with the observations of Kas et al.²⁷.

Figure 1. XRD of Cu₂O electrodes with increase in thickness. The diffraction pattern shown at the bottom was obtained after electrochemical reduction.

CO₂R in 0.1 M KHCO₃ at various partial pressures and potentials

Electrochemical measurements were initially conducted at fixed potentials varying from -0.7 V to -1.1 V vs. RHE in 0.1 M KHCO₃ electrolyte as function of a P_{CO₂} ranging from 0.05 to 1 atm. The most striking observation to emerge from this study is the trend of FE of C₂H₄ and CH₄ as function of P_{CO₂} (See Figures 2a and b). What stands out is that upon decreasing P_{CO₂}, the FE_{C₂H₄} continuously increases until reaching a maximum at P_{CO₂}=0.4 atm, followed by a sharp drop at P_{CO₂}=0.05 atm. Furthermore, in the case of CH₄, the FE_{CH₄} strongly increases between 0.4 and 0.2 atm, until it sharply falls between P_{CO₂}=0.2 atm and P_{CO₂}=0.05 atm. On the other hand, the FE of CO linearly diminishes with decreasing P_{CO₂}, as previously reported in the literature⁴⁵⁻⁴⁶.

Figure 2. Faradaic efficiency vs. P_{CO_2} of (a) C_2H_4 , (b) CH_4 , (c) CO and (d) H_2 under varying applied potentials (scale off-set to 30% for clarity) in 0.1M $KHCO_3$. The solid lines are there to guide the eye. Error bars represent the standard deviation from three independent measurements.

The sharp decline in FE of ethylene is correlating to a sharply increasing H_2 efficiency below 0.4 atm (Figure 2d, note that the y-axis scales between 30-100%). The trend in FE of hydrogen production approximately mirrors the FE of C_2H_4 , suggesting an inverse correlation between hydrogen and ethylene production. Finally, the various results reported in Figure 2 indicate that the FE towards ethylene is strongly potential dependent, -1.1 V vs RHE being optimal, while the formation of CO and hydrogen are favored at relatively low potential. This is further illustrated in Figure S2, which shows the partial current density vs. potential (V vs RHE) of C_2H_4 , CH_4 , CO and H_2 under varying P_{CO_2} in 0.1M $KHCO_3$. Please note that the total

current density during the experiments was relatively constant, at $28 \pm 2 \text{ mA.cm}^{-2}$ (see Figure S2).

CO₂R in various KHCO₃ electrolyte concentrations

To evaluate whether the strong dependency of the ethylene FE shown in Figure 2 is depending on electrolyte concentration (and pH), we varied the KHCO₃ concentration and evaluated the pH as a function of P_{CO_2} , as shown in Figure 3. Figure 3 shows that the higher the KHCO₃ concentration is, the stronger is the buffer capacity, leading to higher values of the bulk pH at variable partial pressure of CO₂. At the same time, the higher the pressure of CO₂, the lower the pH of the bulk solution appears to be, as expected from equilibrium calculations.

Figure 3. Dependency of pH of the CO₂ saturated solutions on the KHCO₃ concentrations at different partial pressures. The solid lines guide the eye and are second-order polynomial fits. The $\text{FE}_{\text{C}_2\text{H}_4}$ is also shown for $P_{\text{CO}_2}=0.4 \text{ atm.}$ and at -1.1 V vs. RHE , demonstrating a significant drop as a function of increasing KHCO₃ concentration. Error bars of faradaic efficiency curve represent the standard deviation from three independent measurements.

Figure 3 shows that an inverse trend between concentration of the KHCO_3 solution (and solution pH) and FE towards ethylene at $P_{\text{CO}_2}=0.4$ atm exists. While the pH of the solution increases as a function of increasing KHCO_3 concentration, the $\text{FE}_{\text{C}_2\text{H}_4}$ decreases. However, the pH near the electrode surface significantly deviates from that of the solution, as will be discussed in more detail in the discussion of the model data. More experimental data of the combinations of P_{CO_2} and concentration of electrolyte are shown in Figures 4a-d. With increasing buffer strength of the electrolyte, the trend in $\text{FE}_{\text{C}_2\text{H}_4}$ as a function of P_{CO_2} changes from an optimum at ~ 0.4 atm, to an almost continuous trend with the highest KHCO_3 concentration at 0.5 M.

Figure 4. The effect of varying KHCO_3 electrolyte concentrations at -1.1 V vs. RHE on Faradaic efficiency of (a) C_2H_4 , (b) CH_4 , (c) CO and (d) H_2 . The solid lines are there to guide the eye.

Figure 4b reveals that with increasing the electrolyte concentration, the maximum in FE_{CH_4} increases, and takes place at gradually increasing values of P_{CO_2} at higher $KHCO_3$ concentrations. The FE_{CO} decreases with decreasing P_{CO_2} for all $KHCO_3$ electrolyte concentrations investigated (Figure 3c), with the highest FE at the lowest concentrations. Again the FE of hydrogen evolution shows an inverse correlation with ethylene (Figure 3d), and is the lowest at the lowest concentration of $KHCO_3$ electrolyte.

CO₂R on different cuprous oxide film thicknesses

The third, and last correlation investigated, was how the combination of variation in surface roughness and CO₂ partial pressure affect the FE. Sample surface roughness, relative to that of smooth copper, is reported in Table 2. As the oxide layer thickness increases, the roughness factors of the in-situ formed nanoparticulate copper surface increase as well, in agreement with the data of Kas et al.²⁷.

Table 2. The capacitance values and surface roughness factors of the films as a function of initial thickness of the films

Charge passed through (C/cm ²)	Capacitance (mF)	Surface Roughness Factor
Electropolished copper	0.26	1
1	2.8	11
3	4.56	18
5	6.87	26
7	10.86	42
9	11.33	44

Figure 5. Faradaic efficiency vs. P_{CO_2} of (a) C_2H_4 , (b) CH_4 , (c) CO and (d) H_2 for various oxide layer thicknesses at -1.1 V vs. RHE in 0.1 M KHCO_3 . The solid lines are there to guide the eye.

CO_2R on copper electrodes with different oxide thicknesses was conducted at -1.1 V vs. RHE in 0.1 M KHCO_3 at various partial pressures of CO_2 . Figure 5 shows that a thicker film with higher surface roughness, leads to a lower optimum FE in ethylene and methane at partial pressures of CO_2 in the range of 0.2-0.8 atm or 0.05 to 0.3 atm, respectively, while the formation of hydrogen is favored by the increasing thickness of the film. These observations are in agreement with previous studies, also showing a decrease in ethylene selectivity when the surface roughness increases^{52, 56-578}, but these have not been discussed in detail. We assume that multiple layers of copper, will lead to a certain porosity of the film, and therefore lower accessibility of CO_2 towards the reduced copper sites closest to the electrode inner surface. While

the local pH will be high in/near these porous films, the low concentration of CO_2 likely limits the formation of ethylene. This is in agreement with the low amount of methane formed for thicker films, which is also restricted by the availability of CO_2 . Detailed studies and modeling of mass transport in porous layers is required to corroborate this hypothesis.

It remains striking that the FE of C_2H_4 and CO is much lower for smooth copper surfaces than obtained for the thinnest modified, oxide-derived film (See Figure 6 and compare to Figure 5). The methane FE is much higher than observed for oxide derived surfaces, and in agreement with other CO_2/CO electroreduction studies on smooth copper surfaces. A linear dependency of the ethylene selectivity as a function of partial pressure of CO_2 is observed^{45, 48, 50}.

Hydrogen evolution continuously increases with a decrease in P_{CO_2} below 0.8 atm.

Figure 6. Faradaic efficiency vs. P_{CO_2} of C_2H_4 , CH_4 , CO and H_2 for electropolished Cu electrode at -1.1 V vs. RHE in 0.1M KHCO_3 . The solid lines are there to guide the eye.

Modelling

To provide additional insight in the trends of local concentrations of CO_2 and protons (pH) near the electrode surface, several calculations were performed

following the modelling methodology described in the experimental procedures. For several concentrations of KHCO_3 , the concentration of CO_2 at the electrode surface and the local proton concentration are plotted as a function of partial pressure of CO_2 in Figures 7a and b, respectively.

Figure 7. The effect of the CO_2 partial pressure at a boundary layer condition of $100 \mu\text{m}$ and total current density at the electrode of $25 \text{ mA}\cdot\text{cm}^{-2}$ on a) the concentration of CO_2 near the electrode surface, and b) the local concentration of protons. Trend lines are provided for different initial KHCO_3 concentrations.

As is demonstrated in Figure 7a, the concentration of CO_2 near the electrode surface decays as a function of partial pressure, and the trend is not strongly dependent on the initial KHCO_3 concentration. Generally, for all KHCO_3 concentrations taken into consideration, a depletion in the CO_2 concentration can be discerned starting from a CO_2 partial pressure of 0.4 atm. For the 0.50 M KHCO_3 series, depletion in CO_2 concentration can be observed at 0.2 – 0.4 atm, rising slightly at 0.05 atm. Depletion of CO_2 can be correlated to the minimum in proton concentration at CO_2 partial pressures of 0.2 – 0.6 bar in Figure 7b. These two observed facts correlate to the high FE towards ethylene (and rise in methane FE) in the CO_2 partial pressure range of 0.2 – 0.6 atm, as is evident from the experimental results shown in Figures 2 and Figure 4. While decreasing the partial pressure

evidently results in a lower local concentration of CO_2 (which should lower ethylene selectivity), this also results in an increasing basicity (lower H^+ concentration in Figure 7b) near the electrode surface. This overcompensates for the lower CO_2 concentration, and leads to better selectivity in ethylene. The decreasing trend in H^+ concentration is further stimulated by the exceptionally high consumption of H^+ , which accompanies CO_2R to C_2H_4 : 12 moles of H^+ per mole of C_2H_4 are consumed (or 12 moles of OH^- formed), while hydrogen evolution only converts 2 moles of H^+ per mole of H_2 produced. Since the CO_2 concentration depletes at low partial pressures, ethylene can no longer be formed, explaining the lower FE towards ethylene at partial pressure below 0.4 Bar, and the rise in local concentrations of H^+ , as shown in Figure 7b. It is interesting to note that for all studied concentrations of KHCO_3 , such minimum in proton concentration in Figure 7b increases in absolute value of proton concentration as the buffer capacity goes up. This trend is in accordance with the experimental results for ethylene selectivity. A higher proton concentration results in a lower ethylene formation rate (and rate of CH_4 formation, which also has a high H^+ consumption per mol of C-product).

The modeling results thus strongly suggest that the local pH (proton concentration) near the surface of the electrode is strongly correlated to the selectivity towards ethylene in the electrochemical reduction of CO_2 .

Methane vs ethylene selectivity: surface coverage effects

As indicated by the experimental and modeling results of the present study, surface coverages of Cu-H and Cu-CO appear to have a decisive role in determining methane and ethylene selectivity. Hydrocarbons are then formed through a Langmuir Hinshelwood-type of mechanism. The trends in formation of methane vs ethylene can be explained if we take a deeper look into two extreme conditions, namely electrolyte concentrations of 0.05 M vs. 0.5 M. At the concentration of 0.05 M, the highest FE_{CH_4} occurs at $P_{\text{CO}_2}=0.2$ atm. At such a low P_{CO_2} , sufficient amount of H_{ads} can be formed (even though the local pH is high) relative to CO_{ads} . This

induces methane formation and reduces the rate of formation of ethylene (2 CO molecules are required *per* mole of ethylene). On the other hand, at a concentration of 0.5 M, where the local pH value is retained close to the bulk pH value (around 7.45), a much higher surface coverage with H_{ads} can be expected, and the optimized value of CO_{ads} requires a higher P_{CO_2} . The significant increase of FE_{CH_4} as a function of increasing bicarbonate concentration is consistent with the literature^{26, 58}.

An analogous reasoning can be proposed for the formation of ethylene, where the surface concentration of CO_{ads} (assuming CO dimerization is the limiting step for the formation of ethylene) needs to be significantly higher than for the formation of CH_4 . Therefore the optimum in production of ethylene occurs at relatively higher partial pressures of CO_2 , than the optimized formation of CH_4 . This is in agreement with existing literature, such as a previous study of Raciti et al.⁵⁹, who also demonstrates a high local pH is needed for maximal selectivity toward multi-carbon products.

3.4 Conclusions

In general, our results confirm that the local pH, i.e. the pH near the surface of the electrode, is largely affecting the selectivity of roughened, oxide-derived copper electrodes in the electrochemical reduction of CO_2 towards ethylene. What is new, is that for the utilized roughened electrodes, the selectivity towards C_{2+} products does not depend linearly on partial pressure of CO_2 . We have demonstrated experimentally, and by modeling, that the partial pressure of CO_2 has a small, yet significant effect on local pH, in particular when the buffer capacity of the applied electrolyte ($KHCO_3$) is limited (at low concentrations of $\sim 0.05M$). This implies that the partial pressure not only *directly* affects the near-surface concentration of CO_2 (required for the formation of CO and consecutively CH_4 and C_2H_4), but also *indirectly* affects the local pH, which is essential in determining product selectivity.

3.5 Appendix

Figure S1. SEM images of oxide-derived copper with the thickness of 3C (a) before and (b) after electrochemical reduction.

Figure S2. Partial current density vs. potential (V vs RHE) of (a) C_2H_4 , (b) CH_4 , (c) CO and (d) H_2 under varying P_{CO_2} in 0.1M $KHCO_3$. The solid lines are there to guide the eye.

Chapter 4.

Optimizing CO coverage on rough copper electrodes: effect of the partial pressure of CO and electrolyte anions (pH) on selectivity toward ethylene

Abstract

Electrochemical reduction of CO on rough copper electrodes is known to produce commercially viable hydrocarbons and alcohols. In this study, we show that in inert gas, an increase in partial pressure of CO results in a linear increase in Faradaic Efficiency (FE) for ethylene, at various potentials ranging from -0.7 to -1.1 V *vs* RHE. On the contrary, when the partial pressure of CO is increased in a mixture of CO/CO₂, a potential dependent optimum in ethylene formation is found for the partial pressure of CO in the range of 0.5 (at -1.1 V) to 0.8 (at -0.8 V) atm. We also present the result of CO reduction in electrolytes with different anions. The optimized FE towards ethylene increases from 5.2% in KH₂PO₄ to 43.2% in KOH. The observed differences in selectivity are attributed to anion buffering capacity, pH

and conductivity of the electrolyte. Using in-situ attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS), we probed CO coverage in the presence of the different anions. Comparison of the adsorbed CO band area in different electrolytes revealed an increase of CO coverage with increase in pH, confirming CO coverage and pH are coupled. Collectively, the data herein outline the critical role of reactant partial pressures and the significant effect of anion composition (pH) on the surface coverage of CO and concomitant selectivity in electrochemical reduction of CO₂.

4.1 Introduction

The electrochemical reduction of CO₂ (CO₂RR) to hydrocarbons and alcohols has been subject of numerous studies since its discovery by Hori and coworkers²¹. Since the recognition of CO as the key intermediate in CO₂RR, many studies have also focused on reduction of CO. Studying CORR has the advantage that few reaction intermediates and steps are involved. In addition, with the elimination of dissolved CO₂ acting as buffer, CORR allows for a wider range of pH conditions to be examined.

CO gas streams are industrially available in the form of syngas, and CO is also a side product of steel manufacturing, ranging in CO concentration from 10-60%, often also consisting of CO₂^{47, 60-61}. Conversion of these abundant gas mixtures to hydrocarbons avoids costly purification steps. This underlines the importance of investigating electrocatalytic activity of gas mixtures containing CO or CO/CO₂. A number of reports have investigated the effect of CO partial pressure (P_{CO}) in inert gas on product selectivity of copper electrodes, with different outcomes. Schreier et al.⁴⁸ or Li et al.⁴⁹ demonstrated that with decreasing P_{CO} , ethylene partial current density either declined⁵ or was unvaried⁶, whereas both studies reported improved methane production rates as the P_{CO} was decreased. Wang et al.⁶² found a major decrease in ethylene and methane partial current density at low P_{CO} . A recent study by Li et al.⁴⁷ examined the effect of local CO concentrations on ethylene selectivity,

both theoretically and experimentally. They showed that constraining CO, favored ethylene production. However, they also found that at certain small local CO concentrations, partial current density and selectivity towards ethylene decreases.

In CORR a wide range of pH values can be investigated. Different values of pH can be achieved by changes in the composition of anions in solution. The buffering strength of the anion in the electrolyte, highly influences selectivity towards hydrocarbons. CORR on copper is also known to greatly depend on pH. However, the pH dependence varies for different products⁶³. Increasing the electrolyte alkalinity is known to enhance the selectivity towards ethylene, while suppressing the competitive hydrogen evolution reaction⁶⁴⁻⁶⁶. The dramatic pH impact on selectivity towards C₂ or C₁ pathways has been explained by differences in rate-determining proton–electron transfer steps⁶⁷. Electron transfer during CO dimerization, or a second proton assisted electron transfer, are rate determining steps in formation of C₂ products or methane, respectively⁶⁸⁻⁶⁹.

In our previous study, we studied the effect of CO₂ partial pressure (P_{CO_2}) on CO₂RR using oxide-derived copper electrodes⁷⁰ and reported improved ethylene formation by decreasing P_{CO_2} . So far, however, there is little published data on the performance of such electrodes in the reduction of CO/CO₂ gas mixtures⁷¹⁻⁷². The importance and originality of this study are the exploration of the effect of CO/CO₂ partial pressures on selectivity towards hydrocarbons. We also show that the electrolyte anion greatly influences the activity and selectivity towards C₁ and C₂ pathways. Besides, we employ ATR-SEIRAS to understand dynamic evolution of adsorbed CO, including atop-adsorbed and bridge-adsorbed CO, as a function of potential and applied anion in the electrolyte. We demonstrate that the CO surface coverage can be moderated by the ration of CO and CO₂ in the feed gas, as well as the establishment of the local pH by variation of the anion.

4.2 Experimental section

Materials and Film Deposition

Cuprous oxide films were prepared by electropolishing (in 85% phosphoric acid, potentiostatically at 2.1 V vs. a graphite foil counter electrode) of copper foils (Alfa Aesar, 99.99%), followed by electrodeposition. A Cu^{2+} containing electrodeposition solution was prepared using 0.4 M CuSO_4 (Sigma Aldrich, 99%) and 3 M lactic acid (Sigma Aldrich) at 60°C, according to a published procedure³⁴. A one-compartment, three electrode cell with Cu foil as working electrode, Pt mesh as counter electrode and Ag/AgCl (3M NaCl) as the reference electrode were used. The pH of the solution was adjusted to 12 using NaOH (Sigma Aldrich, 98%). Galvanostatic deposition was performed at 0.8 mA cm^{-2} using a potentiostat/galvanostat (PAR, Versastat 3) until a film thickness equivalent to 3 Coulomb was achieved. Cu thin-film electrodes were prepared by magnetron sputtering on a silicon ATR crystal, as described in our previous work⁷³. The electrolyte solutions of KHCO_3 (Sigma Aldrich, 99.99% metals basis), KClO_4 (Alfa Aesar, 99-100.5%), KOH (Sigma Aldrich, 99.99%), K_2HPO_4 (Sigma Aldrich, $\geq 98\%$) and KH_2PO_4 (Sigma Aldrich, $\geq 98\%$) were prepared using deionized water (Millipore MilliQ, 18.2 M Ω cm). In order to prepare 0.1 M phosphate buffer with pH=5.9, 0.0098 M of K_2HPO_4 was added to 0.0902 M KH_2PO_4 in equivalent aliquots.

Electrochemical Measurements

All electrochemical measurements were carried out on a Bio-Logic VSP potentiostat. A home-made glass two compartment electrochemical cell using a three electrode assembly was used to carry out the CO_2/CO electrochemical reduction. The as-prepared cuprous oxide films with the thickness of 3 Coulomb were used as the working electrode. Glassy carbon (SIGRADUR® G) was used as the counter electrode and was separated from the working electrode using an anion exchange membrane (Selemon AMV, AGC, Inc.). Ag/AgCl in 3 M NaCl was used as a

reference electrode and potentials were converted to the Reversible Hydrogen Electrode (RHE) scale by $V_{\text{vs. RHE}} = V_{\text{measured vs. Ag/AgCl}} + 0.198 + 0.059 \cdot (\text{pH of solution})$.

The gas mixture (CO_2 , CO and He) was continuously purged through a glass frit at a rate of 20 ml min^{-1} for 30 minutes before each experiment using two mass flow controllers, to attain a steady CO_2/CO concentration in the electrolyte. The flow rate was then decreased to 5 ml min^{-1} during the electrochemical reduction. The reactor effluent was vented directly into the gas sampling loop of a micro-gas chromatograph (micro-GC) equipped with a pulsed discharge detector (PDD) every 4 minutes. The micro-GC was equipped with two different columns (Molsieve plot and Rt-Q Bond) for separation of H_2 , CO, CO_2 and hydrocarbons.

In-situ ATR-SEIRAS

All electrochemical experiments were performed in a custom-made three-electrode cell, with the sputtered Cu film used as the working electrode. A graphite rod was used as counter electrode, while a Ag/AgCl electrode (3 M NaCl, BASi) was used as reference electrode. A VersaSTAT 3 potentiostat was used to perform the electrochemical measurements. The experiments were conducted in a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen-cooled MCT detector and a Veemax III ATR accessory. Spectra were taken with 4 cm^{-1} resolution during a CV with a scan rate of 2 mV/sec , under continuous purge of pure CO.

4.3 Results and discussion

Effect of P_{CO} on CORR

To investigate the effect of CO coverage on product distribution, the CO partial pressure was varied at several fixed potentials. Figure 1 shows the faradaic efficiency of ethylene, ethane and methane as a function of P_{CO} between -1.1 V and -0.7 V . Based on Fig 1a, an increase in partial pressure of CO results in a linear increase in Faradaic Efficiency for ethylene. This is in line with theoretical and experimental studies that propose higher CO coverage to facilitate CO dimerization^{47, 74-76}.

Consequently, this favors formation of C_2 products, in particular ethylene. Moreover, the highest FE was obtained at -0.8 V and 1 atm of CO.

These observations for the trend in formation of ethylene are also valid for ethane (Figure 1b), a minor product with marginal Faradaic Efficiency (FE), with the exception that in the range of 0.8 to 1.0 atm the FE decreases, in particular at -0.7 and -0.8 V.

Figure 1. Faradaic efficiency vs. P_{CO} in inert gas of a) ethylene, b) ethane and c) methane under varying applied potentials in 0.1M $KHCO_3$. The solid lines are there to guide the eye.

Similar to ethane, the other minor product, methane (Figure 1c), also displayed optimum selectivity at a P_{CO} of 0.8 atm, but now the highest FE is obtained at -1.1 V. Such trends in methane and ethane formation support previous observations implying that a Langmuir–Hinshelwood mechanism can be in play⁷⁷. Based on this mechanism, both CO and H compete for surface sites and increasing the P_{CO} improves coverage and activity towards formation of carbon-containing products. The optimum in P_{CO} for ethane and methane formation is in agreement with the hypothesis that the formation of these products also requires a significant quantity of activated H on the surface.

Reduction of mixtures of CO and CO_2

To assess the influence of CO_2 on the electrochemical reduction of CO, the partial pressure of CO was varied and the total pressure balanced to 1 atm with CO_2 , rather than He. When comparing Figs 1a and 2a, at the potentials of -0.7 V and -0.8 V, a

quite similar increasing trend in formation of ethylene is observed when the P_{CO} is increased, and comparable FE towards ethylene are obtained (at -0.8 V and 1 atm the FE is again ~30%). In agreement with literature, CO_2 is not electrocatalytically activated at -0.8 V, and hence CO_2 acts as an inert gas. As shown in Figure 2a, at potentials more negative than -0.8 V, an optimum in production of ethylene as a function of P_{CO} becomes apparent, shifting towards lower P_{CO} in the potential series of -0.9, -1.0 and -1.1 V, with the highest ethylene FE of ~45% at P_{CO} =0.5 atm and at V =-1.1 V.

Figure 2. (a) Faradaic efficiency of ethylene vs. P_{CO} (P_{CO} =0 equals P_{CO_2} =1), (b) Faradaic efficiency of methane vs. potential (V vs. RHE). Experiments were performed in 0.1 M $KHCO_3$. Voltages indicated by the legend in Fig. 1b.

These data suggest that at potentials more negative than -0.8 V, the reduction of CO_2 is dominating product formation. It is generally accepted that at values less negative than -0.8 V, only CO can be electrochemically activated over Cu surfaces, whereas activation of CO_2 requires higher overpotentials. Turning to Fig 2b, methane formation was observed to be the highest at P_{CO} =0.8 atm (and P_{CO_2} =0.2 atm) at the two most negative potentials, again showing similar trends and values as compared to Fig. 1c.

The observations for the formation of ethylene at potentials more negative than -0.8 V are very similar to observed by varying the partial pressure of CO₂ in inert balance gas⁷⁰, also showing an optimum in FE of ethylene at $P_{\text{CO}_2} \sim 0.5$ atm, see Fig. 3a. Fig 3a shows the results from this work and previously published data on P_{CO_2} ⁷⁰, measured at -1.1 V vs RHE (see also Supplementary Figures S2 and S3). The relatively low FE towards ethylene induced by reduction of CO, could be related to the large difference in aqueous solubility of CO (1 mM) and CO₂ (33 mM)⁷⁸.

The trend in ethylene production rate in Fig 3a is partly consistent with a recent study on CO₂/CO co-feeds which assigned the highest rate of ethylene formation to reduction of CO₂ in a mixture with CO, followed by pure CO₂ and finally pure CO⁷¹.

Figure 3. Comparison of Faradaic efficiency of (a) ethylene and (b) methane vs. P_{CO} ($P_{\text{CO}} + P_{\text{He}} = 1$) or P_{CO_2} ($P_{\text{CO}} + P_{\text{CO}_2} = 1$) or P_{He} ($P_{\text{He}} + P_{\text{CO}_2} = 1$) at -1.1 V vs RHE in 0.1 M KHCO₃.

However, Figure 3a shows that having CO added to CO₂ at -1.1 V, rather than dilution of CO₂ with He, is only beneficial in the P_{CO} range of 0.8 to 1.0 atm, i.e. at relatively low partial pressure of CO₂. On the contrary, below a P_{CO} of ~ 0.7 , dilution of CO₂ with CO rather than He (somewhat) negatively affects the FE towards ethylene.

The positive effect of CO at high relative pressures, may be explained by the higher coverage of adsorbed CO which is then achieved on the Cu surface. As

previously stated, a high CO surface coverage enhances the CO dimerization rate, and, due to the low solubility of CO, the P_{CO} needs to be relatively high for the CO feed to contribute to the optimized balance between surface CO and $H^{48, 74}$. Apparently at relatively low P_{CO} (and thus high P_{CO_2}), the coverage of the surface with CO_2 -derived CO is already sufficient, and having additional CO leads to sub-optimal deviation of the optimized CO / H surface ratio.

A negative effect of CO on the conversion of CO_2 to methane is apparent over the entire range of partial pressures, but most prominently apparent at a P_{CO} of ~ 0.8 . This is contrary to observations in ref.⁷⁹, where CO reduction was determined to lead to the highest rate, rather than reduction of CO_2 . We discovered that this discrepancy could be attributed to the effect of the pH of the electrolyte on methane formation. The formation of methane is highly dependent on availability of protons or hydrogen⁸⁰. The mentioned study⁷¹ was conducted in 0.1 M K_2HPO_4/KH_2PO_4 electrolyte (pH = 6.9), while we used the more basic 0.1 M $KHCO_3$ (pH=8.4). Consequently, in our study the alkalinity of the electrolyte likely suppressed methane formation in the reduction of CO. This effect will be discussed in more detail in section 3.3.

The effect of electrolyte anion on CORR

Since not only the P_{CO} , but also the local pH is likely to affect the surface coverage of CO, we studied the effect of the anion composition of the electrolyte on the performance of the oxide derived copper surface. To assess the effect of anionic species associated with potassium on the CO reduction activity, the Faradaic efficiencies and partial current densities (See Figures S4 and S5) of the reduction products were measured at the potential range of -0.4 to -1.4 V in various electrolytes. Anionic species such as ClO_4^- , HCO_3^- and $H_2PO_4^-$ greatly affect the selectivity of the CORR products due to their different buffering strengths⁸⁰. Phosphate buffers and 0.1 M KOH were employed to minimize the changes of local pH due to the generated OH^- at the electrode surface during the CORR from

hydrogen and hydrocarbon formation. In the presence of a buffering anion, the released OH^- is instantly neutralized by the following reactions:

On the other hand, the low buffer capacity of 0.1 M KHCO_3 and non-buffering capacity of KClO_4 solutions, would result in significant enhancement of the pH near the electrode surface during the CORR.

Table 1 shows the bulk pH and resistance of the 0.1 M electrolyte solutions prior to electrochemical reactions.

Table 1. pH and resistance of various 0.1 M electrolyte electrolytes.

electrolyte	KH_2PO_4	$\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$	KClO_4	KHCO_3	KOH
pH	4.6	5.9	5.9	8.4	13
Resistance (Ω)	86	78	64	78	34

Despite minimizing the pH changes at the electrode, phosphate which is a strongly adsorbing anion could act as hydrogen donor. As a result, it can negatively affect CORR and promote the hydrogen evolution reaction, based on the following reaction⁸⁰:

Turning now to the experimental evidence, Figure 4 compares the product distribution of CORR in various electrolytes. We begin by examining and explaining ethylene formation.

Figure 4. Faradaic efficiencies of ethylene, ethane and methane as a function of applied potential in (a, b and c) RHE and (d, e and f) SHE scale in various electrolytes. Potentials were converted to the Standard Hydrogen Electrode (SHE) scale by $V_{\text{vs. SHE}} = V_{\text{measured vs. Ag/AgCl}} + 0.197$.

Ethylene: In Figure 4a, we can see a significant difference in the position (potential) at which the ethylene optimizes. This is related to the way the data have been plotted, i.e. *versus* potential on the RHE scale. Figure 4d represents ethylene Faradaic efficiencies on the SHE scale. Comparing Figures 4a and d, it can be seen that ethylene formation is pH dependent on the RHE scale but (roughly) pH independent on SHE scale. These results reflect previous analyses of similar data by the groups of Hori and Koper⁸¹⁻⁸³. Figure 4(d) shows that the ethylene FE is strongly anion dependent. The highest Faradaic Efficiency was observed for KOH (43.2%), followed by KClO₄ (36.7%) and KHCO₃ (28.7%), while the phosphate containing solutions hardly resulted in the formation of ethylene. In Figure 5 the values for the FE are plotted against the pH of the solution, showing an increasing trendline as a function of increasing pH. Clearly the data for KClO₄ do not follow the trendline,

suggesting that for this anion, the local pH near the surface of the electrode is significantly higher than measured in solution, as indicated by the extrapolation (blue dotted arrows) in Figure 5.

Figure 5. The electrolyte resistance (Ω), red line, and the highest ethylene faradaic efficiency (%), blue line, vs. the bulk pH of various electrolytes. Please note that the pH near the electrode surface of the KClO_4 is likely significantly higher than measured, around 10.8, as indicated by the blue arrows. Furthermore, extrapolation of the resistance value to the trend-line, suggests the pH is around 9.8.

The trendline in Figure 5 shows once more how strongly dependent the ethylene formation in Cu-catalyzed reduction is on alkalinity. In addition to electrolyte pH and buffering capacity, it is necessary to address conductivity as another aspect of the electrolyte. The conductivity may have a significant effect on the total current density⁸⁴. Please note that also the resistance of the solution appears pH dependent, ranging from 85 to 30 Ohm, as shown in Figure 5. What stands out in this graph is that KClO_4 did not conform to the overall trend in conductivity, again suggesting that the actual pH on the electrode surface is higher than the bulk value. Based on

the relationship between pH, resistance and ethylene efficiency, the actual pH value can be estimated to be ~9.5-11.

Hori et al. has suggested that ethylene can be formed by two mechanisms⁸³. The first one involves the dimerization of two adsorbed CH₂ intermediate species, and in the second one, a Fischer–Tropsch like combination of adsorbed CH₂ and CO plays a role. Recent theoretical and experimental studies have provided strong evidence that ethylene is formed through hydrogenation of surface adsorbed CO to form the CHO intermediate, also a common intermediate in the route towards methane⁸⁵⁻⁸⁶. In addition, previous research has established that a CO dimer is the first intermediate towards ethylene formation⁸⁷⁻⁸⁸. Formation of the *C₂O₂ dimer consists of CO coupling, mediated by electron transfer. The overall reaction to form ethylene is:

In conclusion, the effect of the anion can be correlated to the (local) pH; when this is highest, the activity of C₂ products is most abundant, consistent with other reports that demonstrate that OH⁻ promotes C-C coupling⁸².

Ethane: To date, a few studies have investigated ethane formation which is only observed on very rough copper surfaces. Surface defects associated with roughness most likely favor the reaction of adsorbed hydrogen species crucial for ethane formation⁸³. Ethane can be formed through two proposed mechanisms. One pathway involves dimerization of CO followed by hydrogenation of the ethylene intermediate^{43, 89}, while the second pathway suggests dimerization of CH₃ species⁹⁰ which is also a proposed intermediate for methane formation⁸⁸.

Figure 4b compares ethane formation in various electrolytes. From this figure we can see that production of ethane is suppressed in highly alkaline as well as very acidic electrolytes. The highest faradaic efficiency is observed in 0.1 M KHCO₃ (pH=8.4) followed by 0.1 M KClO₄ (solution pH=5.9). It should be noted that the

local pH of the latter is likely higher and is possibly moderately basic, supported by experimental evidence of this study. Besides, comparing Figs. 4a,b also revealed a smaller overpotential for the ethane production as opposed to maximum ethylene selectivity, similar to a previous study⁹⁰.

Formation of ethane is highly dependent on adsorbed hydrogen species. High concentrations of adsorbed hydrogen are expected at lower pH. On the other hand, ethane formation also requires dimerization of CO (or CH₃), which is enhanced at high pH. As a result, ethane was not significantly formed at the lower pH range and was inhibited at very high pH.

Turning to Fig 4e, it is apparent that formation of ethane is pH dependent on the RHE scale but pH independent on SHE scale, similar to ethylene. It is therefore likely that a shared mechanism exists between ethane and ethylene. However, further studies need to be undertaken to further analyze the formation of ethane, the hydrogenation of ethylene.

Methane: During CORR at low pH, the copper surface is enriched with adsorbed hydrogen species. The availability of protons or hydrogen species favors the formation of methane. As a result, methane formation and hydrogen evolution are major reactions in acidic electrolytes. The hydrogen evolution reaction and formation of adsorbed hydrogen proceeds as follows ⁹¹⁻⁹²:

The methane formation route proceeds through protonation of adsorbed CO to form CHO or COH intermediates^{83, 93-94}. Previous research has established that breaking of the C-O band occurs after protonation of CO to produce CHO or COH^{83, 88}.

Formation of methane was fully suppressed in basic electrolytes with the exception of 0.1 M KHCO_3 where a minor amount of methane was formed (see Figure 4c). Methane formation is correlated with the concentration of adsorbed hydrogen species on the electrode surface. Hence, at lower pH, the enrichment of electrode surface with adsorbed hydrogen makes methane the dominant product. The large amount of methane and small amount of ethylene produced at low pH values demonstrates that the protonation of CO is favored over the CO dimerization.

Interestingly, solutions of 0.1 M KClO_4 and 0.1 M $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ buffer have similar pH of 5.9, yet the local pH close to the electrode surface of these two differs significantly. As a results, formation of methane was not observed in KClO_4 , providing further evidence for a rise of local pH at the electrode surface.

A comparison of the figures 4c and f reveals that the onset potential for formation of methane takes place on the same potential on the RHE and SHE scale. However, since we did not carry out further experiments at more negative potentials, the peak of methane formation was not observed and hence we could not derive any conclusions.

In-situ ATR-SEIRAS to study CO adsorption

To further understand effect of electrolyte anion on the CORR mechanism, ATR-SEIRAS was used to investigate CO adsorption on the Cu electrode. Figure 6 represents in-situ ATR-SEIRA spectra during CVs from -0.7 to -1.5 V vs. Ag/AgCl in 0.1 M solutions of KH_2PO_4 , KClO_4 , KHCO_3 and KOH. Due to the pH dependence of the RHE, the potentials in this section are reported vs. the Ag/AgCl reference electrode. The reference spectra were taken at -0.8 V. Figure 7 shows the corresponding integrated areas of CO_{atop} bands taken from Figure 6.

Figure 6. In-situ ATR-SEIRA spectra of CO_{atop} and CO_{b} as a function of applied potential in CO-saturated 0.1 M KH_2PO_4 , KClO_4 , KHCO_3 and KOH in H_2O . The reference spectrum was recorded at -0.8 V.

Figure 7. Integrated band area of CO_{atop} as a function of applied potential in CO-saturated 0.1 M KH_2PO_4 , KClO_4 , KHCO_3 and KOH in H_2O , respectively.

As shown in Figure 6, the band corresponding to linearly bound CO at an atop site (CO_{atop}) appears at ~ -1 V and then gradually increases until the highest value at -1.4 V. The CO_{atop} band consists of two bands at 2040 and 2075 cm^{-1} attributed to the low frequency band (LFB) and high frequency band (HFB), respectively⁹⁵. The sharp HFB is assigned to CO adsorbed on weakly coordinated defect sites, while the more narrow LFB is attributed to CO adsorption on highly coordinated sites. In KClO_4 and KHCO_3 , bridge-bonded CO (CO_b) can also be observed at 1900 and 1940 cm^{-1} . Based on previous studies, CO_b is unreactive and predominantly appears under alkaline conditions⁹⁶⁻⁹⁷. Analysis of figure 6 further reveals that the onset potential of CO adsorption is not dependent on anion identity, again consistent with literature⁹⁸. In addition, a significant difference between the adsorption intensity of the CO bands is observed as a function of anion.

In the previous section we illustrated the effect of electrolyte anion on catalytic performance and showed that an increasing ethylene FE was achieved in the order of $\text{KH}_2\text{PO}_4 < \text{KHCO}_3 < \text{KClO}_4 < \text{KOH}$. Turning to the spectroscopic evidence from Figure 7, it can be seen that the integrated band areas are also strongly dependent on anion identity and increase in the order of $\text{KH}_2\text{PO}_4 < \text{KClO}_4 < \text{KHCO}_3 < \text{KOH}$. It is now well established from a variety of studies that the integrated band area of CO is proportional to CO coverage⁹⁹⁻¹⁰¹. Based on this, observing the lowest CO_{atop} band area (and consequently the CO coverage) for KH_2PO_4 is consistent with the low formation of C_2 products and relatively high methane production. At low CO coverage and high coverage of adsorbed hydrogen (associated with the low pH), protonation of CO is favored over CO dimerization. On the other hand, the highest CO coverage in KOH can explain the high ethylene FE of 43.2%, since a high CO coverage on the surface, kinetically favors C-C coupling and ethylene formation¹⁰². Interestingly, KClO_4 showed a relatively low CO coverage compared to KHCO_3 despite having higher ethylene FE. This discrepancy has been proposed to be related to competitive adsorption of the perchlorate anion⁹⁸, but given the high FE towards

ethylene, this appears not very likely. Alternatively, the combination of a low surface coverage with CO and a superior production of ethylene, could be explained by an enhanced stimulated rate of CO dimerization in perchlorate environment, although the origin of this phenomenon is not yet known¹⁰³.

4.4 Conclusions

In summary, we have shown that a high FE towards ethylene in the electrochemical reduction of CO is depending on a delicate balance of the ratio of CO and H on the surface of the copper electrodes. This ration can be manipulated by the applied potential, partial pressure of CO in inert gas, or CO₂, and the anion determined (local) pH near the electrode surface. An optimized FE towards ethylene was obtained using an applied potential of -1.25 V *vs* SHE, a partial pressure of 1.0 atm of CO, and using KOH as electrolyte. When CO₂ is present, a ratio of 0.4 atm of CO in 0.6 atm of CO₂ appears optimal, at an applied potential of -1.1 V *vs* RHE.

Further experiments on electrolyte anions confirmed that the concentration of adsorbed hydrogen is associated with the formation of the dominant hydrocarbon. At lower pH where adsorbed hydrogen is abundant, methane formation is prevalent. At higher pH where less adsorbed hydrogen is available and C-C coupling is enhanced, ethylene formation is predominant over ethane formation. Moreover, in-situ ATR-SEIRAS studies revealed that anions play an important role in determining the CO surface coverage. It was revealed that with increase in pH, CO coverage was significantly increased, favoring the CO dimerization pathway towards ethylene. Taken together, these results highlight the significant role of CO(CO₂) partial pressure and electrolyte anions in the selective production of hydrocarbons.

4.5 Appendix

Figure S1. Faradaic efficiency vs. E (V vs. RHE) of a) ethylene, b) ethane and c) methane under varying applied potentials in 0.1M KHCO₃.

Figure S2. Comparison of Faradaic efficiency of ethylene vs. P_{CO} (for CO/He and CO/CO₂ mixtures) or P_{He} (for CO₂/He mixtures) at various potentials.

Figure S3. Comparison of Faradaic efficiency of methane vs. P_{CO} (for CO/He and CO/CO_2 mixtures) or P_{He} (for CO_2/He mixtures) at various potentials.

Figure S4. (a, b and c) partial current densities of ethylene, ethane and methane as a function of applied potential in various electrolytes.

Figure S5. (a) Sum of hydrocarbons partial current densities and (b) total current densities as a function of applied potential in various electrolytes

Chapter 5.

Infrared analysis of interfacial phenomena during electrochemical reduction of CO₂ over polycrystalline copper electrodes

Abstract

Using ATR infrared spectroscopy and ~10 nm thick, sputtered Cu-films on single bounce Si-ATR-crystals, we have analyzed the electrochemical conversion of CO₂ in NaOH/D₂O solutions. By using cyclic voltammetry, transitions in selectivity of surface-adsorbed species could be identified. At highly negative potential (more negative than -1.2 V (vs. RHE)) the formation of OD⁻ and D₂ is dominant, resulting in a relatively high concentration of carbonate in solution near the interface, with a maximum in IR intensity at ~1410 cm⁻¹. When the potential is less negative than -

1.2 V, spectroscopically resolved interconversion of carbonate (CO_3^{2-}) to bicarbonate (HCO_3^-) is evident, explained by a decrease in local pH. Furthermore, in a potential range of -1.2 to -0.5 V (vs RHE), using D_2O , the recently proposed CO_2 -Dimer-Radical-Anion was observed on polycrystalline copper films. We also assign a previously unresolved band at $\sim 1610\text{ cm}^{-1}$ to this species. The dimer disproportionates to CO and CO_3^{2-} , the latter being converted to bi-carbonate. Adsorbed CO is sensitive to a Stark shift. i.e. a shift as function of applied potential. Eventually, CO disappears, and the infrared signature of (dissolved) formate at $\sim 1590\text{ cm}^{-1}$ appears at $\sim -0.5\text{ V}$. We discuss the spectra and chemistry in detail, based on reference spectra of carbonate, bicarbonate and formate, and using $^{13}\text{CO}_2$ to substantiate the formation of the dimer. The results are discussed and compared to recent literature on infrared analysis of electrochemical reduction of CO_2 .

5.1 Introduction

Surface enhanced infrared absorption spectroscopy (SEIRAS) combined with attenuated total reflection (ATR) FTIR, is a very sensitive method for investigation of electrocatalytically active surfaces¹⁰⁴. One of the applications of this technique is the *operando* study of the electrochemical reduction of CO_2 (ER- CO_2)^{99, 105-112}. The mechanism of ER- CO_2 on Cu is quite complex, and includes various, voltage-dependent reaction intermediates and products^{23, 52, 113}. In addition, the electrochemical potential is known to induce significant changes in interfacial pH values, as well as spectroscopic shifts due to the so-called Stark effect, which predicts that spectral lines of molecules shift due to the presence of an external electric field. SEIRAS is responsive to these changes, and surface-adsorbed molecules relevant to ER- CO_2 such as CO, HCO_3^- , CO_3^{2-} and HCOO^- , can be distinguished, since these exhibit different, highly IR active vibrational modes¹¹⁴. It should, however, be mentioned that all previous studies applying SEIRAS predominantly identified final products in various concentrations as a function of electrolyte, CO_2 partial pressure, and applied voltage, while (short-lived)

intermediates have not been clearly identified. Furthermore, while spectral assignments have been made, these are often ambiguous as a result of overlap of the O-H bending mode of water with vibrations of products and intermediates in the critical wavenumber region between 1700-1550 cm^{-1} ¹¹⁵. Besides, extreme care must be taken not to mistake commonly occurring (local pH dependent) bicarbonate bands for developing adsorbed intermediates. Fortunately, several assignments have been corroborated by isotopic labeling using $^{13}\text{CO}_2$ ^{108, 116-117}.

In this study, further clarity in spectral development has been achieved by using D_2O solutions. Combination of ATR-SEIRAS, isotopic labeling of CO_2 ($^{13}\text{CO}_2$) and use of D_2O enabled a thorough investigation of voltage dependent dynamic chemical changes at the electrode-electrolyte interface in alkaline conditions. We will demonstrate that both, surface adsorbed species and species present at the interface in solution, can be monitored. This study makes several original contributions to a more detailed interpretation of spectra, in comparison to the existing literature. Most importantly, the present research explores the presence of the CO_2 dimer-radical-anion on roughened copper surfaces in protic conditions. This dimer is commonly advocated in the literature for reduction of CO_2 in aprotic conditions, and was only previously proposed in protic (aqueous) conditions to explain the behavior of Cu nanoparticles in visible light sensitized ER- CO_2 ¹¹⁷. In addition, we identify (qualitatively) local pH changes in the boundary layer near the electrode surface, by analysis of the interconversion of carbonate to bicarbonate, and formic acid to formate. Finally, we show that at relatively small negative potentials, formation of formate is accompanied by formation of adsorbed carbonate species.

5.2 Experimental Section

Thin film preparation and characterization

Cu thin-film electrodes were prepared by magnetron sputtering from a copper source, directly onto the reflecting plane of a 45° silicon ATR crystal. The sputtering was carried out using an argon flow of 25 ml/min, and applying a power of 30 W. These relatively mild conditions result in a sputtering rate of 0.044 nm/s. Since the time of sputtering was set at 270 s, a film thickness of 12 nm was produced after 270 s. The resistance of each film tested across a 1.5 cm length of the layer was around 8 Ω . Surface characterization of the copper film was carried out using atomic force microscopy (AFM). The working mode of the applied AFM system (Cypher, Oxford Instruments), was amplitude modulation, with a NSC36 double side probe coated cantilever, and the measurements were carried out in air.

Electrochemical Measurements

All electrochemical experiments were performed in a custom-made three-electrode cell, with the Cu film being used as the working electrode. A graphite rod, rather than a Pt wire, was used as counter electrode to eliminate any possible Pt contaminations on the working electrode, while a Ag/AgCl electrode (3 M NaCl, BASi) was used as reference electrode. A VersaSTAT 3 potentiostat was used to perform electrochemical measurements. The experiments were conducted in a Bruker Vertex 70 spectrometer equipped with a liquid nitrogen-cooled MCT detector and a Veemax III ATR accessory. The electrolyte consisted of 0.1 M NaOH in D₂O (Sigma, 99.9 atom % D) and prior to each experiment, CO₂ (or ¹³CO₂) was bubbled through for 15 minutes to saturate the solution. The Cu films were activated by three cycles between 0.6 and -0.6 V in the 0.1 M NaOH in D₂O electrolyte, in order to improve the signal. During these cycles the development of large peaks ranging from 1500 to 1553 cm⁻¹ (the position was dependent on potential) was observed, together with a peak at around 1230 cm⁻¹. These peaks can be assigned to adsorbed carbonate, as will be discussed in the following section. These species thus

already existed on the electrode surface before the (spectroscopically monitored) cyclic voltammetry (CV) was carried out. A reference spectrum was recorded and spectra were taken with 4 cm^{-1} resolution during a CV with a typical scan rate of 3 mV/sec , under continuous purge of CO_2 (or $^{13}\text{CO}_2$).

The reason for choosing NaOH over bicarbonate, was to allow experiments in a $^{13}\text{CO}_2$ atmosphere. In bicarbonate solutions, rapid scrambling of $^{13}\text{CO}_2$ with $\text{H}^{12}\text{CO}_3^-$ can be expected, which reduces the spectral intensity of ^{13}C -labeled products and intermediates, complicating interpretation. The spectra are shown in (reflectance) absorbance units, where positive bands represent the formation, and negative bands the decomposition of interfacial species. All the potentials were converted to the Reversible Hydrogen Electrode (RHE) scale by $V_{\text{vs. RHE}} = V_{\text{measured vs. Ag/AgCl}} + 0.198 + 0.059 * (\text{pH of solution})$.

5.3 Results and Discussion

Surface characterization of copper films

In order to estimate the thickness and to study the morphology of the sputtered copper films on ATR crystals, Atomic Force Microscopy (AFM) was used. Figures 1 and S1 illustrate some main characteristics of the film. As can be seen in Figure 1a, a rough landscape of metallic copper was formed during the sputtering process. AFM images also reveal a diameter of elevated areas of approximately $\sim 30\text{ nm}$ and a film thickness of $\sim 12\text{ nm}$. This rough structure provides strong surface IR enhancement effects, crucial for SEIRAS studies, and allowed us to probe chemical changes during cyclic voltammetry of the ER- CO_2 with high sensitivity. The observed film thickness of $\sim 12\text{ nm}$, is in good agreement with the theoretically calculated film thickness on the basis of the rate and time of the sputtering procedure.

Figure 1. 200 nm $\times$ 200 nm AFM images of the Cu film sputtered on the applied Si crystal in (a) three-dimensional and (b) two-dimensional view.

Cathodic scans (to more negative potential)

The potential dependent spectra of species interacting with the Cu surface in CO_2 -saturated 0.1 M NaOH from -0.24 (at which potential the background was recorded) to -1.18 V can be seen in Figure 2. While scanning towards more negative potentials, various bands can be identified in the range of 2200-1200 cm^{-1} . Initially, a negative band develops around 1517 cm^{-1} , accompanied by formation of a positive peak around 1592 cm^{-1} . In the fourth spectrum and-up, several bands appear in the 2100 cm^{-1} to 1800 cm^{-1} region, accompanied by a negative shoulder on the 1592 cm^{-1} band (1610 cm^{-1}), and formation of two dominant bands at 1627 cm^{-1} and 1366 cm^{-1} . The latter peak position is likely affected by a few negative contributions. The bands in the 2100 cm^{-1} to 1800 cm^{-1} region maximize and disappear, while the 1627 cm^{-1} and 1366 cm^{-1} show continuous growth. Several minor changes in the spectra can also be observed, but these are better resolved in anodic scans (to more positive potential), and will be addressed accordingly. In the following we will interpret the observations during negative scans based on decreasing wavenumber.

Figure 2. ATR spectra of the Cu thin film during a negative scan in CO₂ saturated in 0.1 M NaOH-containing D₂O solution. The applied reference spectrum was recorded at -0.24 V. The potential interval between spectra is ~0.07 mV.

2200-1800 cm⁻¹: Formation of CO

In the higher range of wavenumbers a shouldered band apparent in a relatively large range of potentials, can be assigned to various configurations of adsorbed CO. A sharp band maximizing at 2070 cm⁻¹ developed next to a shoulder at around 2040 cm⁻¹. These peaks have been interpreted as the low frequency band (LFB) and the high frequency band (HFB) of atop-bound CO, respectively⁹⁵. Figure 3 shows an overview of the development in intensity (height), as well as peak position of these two bands as a function of applied potential. From this graph it is evident that the HFB position, which was initially observed at 2070 cm⁻¹, red-shifts to lower

wavenumber, when the potential is swept negatively, consistent with previous findings^{108, 118-119}. This shift is related to the so-called Stark effect, which predicts that spectral lines of molecules shift due to the presence of an external electric field. An oscillating dipole will have different resonant frequencies when immersed in different electric fields, here obvious by a decreasing wavenumber if the potential becomes increasingly more negative. In addition, a broad band at 1935 cm^{-1} simultaneously develops. This band can be attributed to bridge-bound CO, as previously reported for copper to show vibrations in the $1800\text{--}2000\text{ cm}^{-1}$ region^{96, 120-121}. The broadness, and much lower intensity of this band, makes the correlation between applied potential and position in the spectrum, less evident.

Figure 3. Peak intensity (height) of the shifting maximum of the HFB of CO. The LFB position is difficult to determine, due to the low intensity of this band (not shown).

1700-1300 cm^{-1} : Carbonate and bicarbonate

Turning to lower wavenumbers, the two simultaneously rising bands at 1627 and 1363 cm^{-1} formed from -0.7 V and developing at more negative potentials, are

assigned to bicarbonate. This agrees with reference spectra recorded for D₂O and NaHCO₃ in D₂O on a bare Si crystal surface (Figures S2 and S3). After saturation with CO₂, the 0.1 M NaOH electrolyte has converted significantly to bicarbonate (See Figure S4). The negative band with minima in the range of 1517-1508 cm⁻¹ (depending on potential) was previously assigned to desorption of surface-adsorbed carbonate anions. A brief overview of the bicarbonate and carbonate band assignments in recent literature^{108, 119, 122-123}, is summarized in Table 1. The peak is rather asymmetric, and the (negative) intensity increases at more negative potentials, likely due to increasing electric repulsions, inducing carbonate desorption¹⁰⁸.

Table 1. Vibrational assignments of bicarbonate and carbonate anions

Surface		Method	Band center(cm ⁻¹)	Species	Assignment
Pt(111) and Pt(110) ¹²²		IR	1530	Adsorbed CO ₃ ²⁻	
			1410	Solution CO ₃ ²⁻	
Au (111) ¹²³		IRAS	1397	Solution CO ₃ ²⁻	V _a (CO ₂)
			1450-1511	Adsorbed CO ₃ ²⁻	
			1629	HCO ₃ ⁻	V _a (CO ₂)
			1362	HCO ₃ ⁻	V _s (CO ₂)
Cu(100) and polycrystalline Cu ¹¹⁹		FTIR	1545	Adsorbed CO ₃ ²⁻	
Cu ¹⁰⁸		ATR-	1544-1517	Adsorbed CO ₃ ²⁻	
		SEIRAS	1394	Solution CO ₃ ²⁻	
NaCO ₃ and NaHCO ₃ as a reference for this study		ATR	1626	HCO ₃ ⁻	V _a (CO ₂)
			1365	HCO ₃ ⁻	V _s (CO ₂)
			1410	Solution CO ₃ ²⁻	V _a (CO ₂)

Further examination of Figure 2 reveals a clear shift in wavenumber from 1517 to 1508 cm^{-1} , a trend which was also observed in previous studies^{103, 108}. To further probe this behavior, the starting position of the band as a function of initially applied potential was studied and the obtained frequency (wavenumber) at which the peak minimizes at 0.04 mV more negative potential (spectra not shown) is presented in Figure 4. Upon increasing the starting potential of the negative scan, the (negative) band position dramatically shifts to higher wavenumbers. A possible explanation for this red-shift might again be found in the Stark tuning effect^{118, 124}. Interestingly, there is a significant difference in the slope of the curves in the potentials more negative and more positive than 0 V, which suggests a significant change in electrical field when the voltage turns positive. It should also be mentioned that changes in local pH as a function of potential, might affect the peak position of adsorbed carbonate. Protonation or deprotonation (upon increasing basicity) of surface adsorbed carbonate is likely, and the degree of protonation will determine the peak position. Finally, the nature of the adsorbed state (monodentate or bidentate) of carbonate might also be potential dependent and determine the observed wavenumber.

Figure 4. Band position of adsorbed carbonate as a function of potential. The peak position was determined on the basis of changes in peak intensity as follows. First a reference spectrum was recorded at the potential, which is indicated on the x-axis. Then the potential was swept in the direction of (more negative) values at 3 mV/sec, resulting typically in negative contributions in intensity of the adsorbed carbonate. The position of the peak intensity was determined at 0.04 mV more negative than the potential used for recording of the background (and indicated on the x-axis).

In addition to the bicarbonate-carbonate bands, complicated transients in negative intensity of the band around 1592 cm^{-1} (adjacent to the positive band at 1627 cm^{-1}) are apparent in Figure 2. The spectral changes are better resolved in Figure S5, showing spectra in a negative scan direction starting at 0 V. It is apparent from this figure that the position of the band seems potential dependent and also red-shifts if the potential becomes more negative. This band (moving from 1610 to 1584 cm^{-1} in Figure S5) is likely related to formate, and should not be mistaken for the O-H bending mode of water, since we performed experiments in D_2O . Besides, based on reference spectra taken for H_2O (Figure S2), the bending mode of water is expected around 1640 cm^{-1} . The peak eventually disappears at -0.63 V , concurrently with

formation of bicarbonate (bands at 1627 and 1365 cm^{-1}), in agreement with a shift in selectivity of copper electrodes from formate to CO. The assignment to a vibrational mode of (adsorbed) formate is not straight forward. It cannot be the asymmetric mode of bidentate adsorbed formate, because it is forbidden by the surface selection rule. Assignment to the C=O stretching vibration of monodentate adsorbed formate is also unlikely since, (i) this mode has never been observed even in solutions containing large concentrations of formate/formic acid, (ii) formate (anion) adsorption at negative potentials appears unlikely, and (iii) the C=O stretching mode of monodentate adsorbed formate would be close to the same mode of formic acid (1710 cm^{-1}). It is more likely that this band corresponds to the asymmetric O-C-O stretching of formate in solution (see Fig S8), and the apparent shift is related to changes in intensity of adjacent spectral features, e.g. due to formation and adsorption of (bi)carbonate.

In the next section, ATR spectra obtained during a positive scan are revealing similar, but more detailed dynamic changes (Figure 5).

Positive (anodic) scans:

We will now further identify the potential ranges in which the various species appear and disappear in a reverse scan, again in the order of appearance in the spectra. The background (reference) spectrum was recorded at the starting, negative value of the potential.

2200-1800 cm^{-1} : Formation of CO

Figure 5 shows a series of spectra recorded during a scan towards more positive potentials (an anodic scan), for which the reference spectrum was taken at -1.2 V. At the initial potential of the scan (-1.2 V), adsorbed CO was not present, in agreement with Figure 2. The atop-bound CO band grows in as the potential is swept towards more positive values, and then disappears again. The broad peak from ~1900 to 2000 cm^{-1} representing the bridge-bound CO is also observed, which did

not disappear until the end of the scan at 0 V. A strong Stark shift is now also apparent.

1700-1300 cm⁻¹: Carbonate and bicarbonate

In the most interesting region, the pair of bands at 1627 and 1363 cm⁻¹ attributed to bicarbonate develops, while a band at 1410 cm⁻¹ grows in negatively. According to the ATR-IR spectra of Na₂CO₃ (Figure S6) and NaHCO₃ (Figure S3), as well as the assignments proposed in a number of earlier reports summarized in Table 1, the band at 1410 cm⁻¹ is assigned to solution-based carbonate anions. This is also in agreement with the absence of a stark shift as a function of increasing (less negative) potential. A possible explanation for the negative growth of this band is a change in the equilibrium composition of CO₂, HCO₃⁻ and CO₃²⁻ at the interface (solution boundary layer), which shifts towards bicarbonate if less OH⁻ is formed, induced by reduction in rate of water consuming reductive processes occurring on the surface at more positive potentials (the exact opposite of what was observed in Figure 2)¹²⁵. Previous studies also indicate that carbonate in solution only exists at very negative potentials when the local pH is high¹²². Starting at -1.2 V and during the sweep to more positive potentials, carbonate converts to bicarbonate and CO₂. The band at 2342 cm⁻¹ was previously assigned to CO₂ dissolved in the electrolyte. The increase in CO₂ concentration during the scan is apparent in Figure 5, and is observed due to mass transfer limitations¹²⁵. To further elucidate the interchange of carbonate and bicarbonate, necessary to facilitate the interpretation of the dynamic changes shown in Figure 5, the potential was initiated at -1.7 V, and scanned towards -0.9 V.

Figure 5. ATR spectra of the Cu thin film during anodic scan in CO₂ saturated 0.1 M NaOH in D₂O solution with reference spectrum taken at -1.2 V.

Interfacial phenomena at potentials ranging from -1.7 to -0.9 V:

At the potential of -1.7 V, chemistry is dominated by hydrogen (D₂) evolution, and conversion of CO₂ is limited. Starting at this potential, and scanning more positively, allowed us to evaluate changes in local pH by monitoring the carbonate/bicarbonate equilibrium. The results of the positive scan from -1.7 to -0.9 V followed by a negative scan back to -1.7 V are presented in Figure 6. At -1.7 V the local pH is very basic. Since solution-based carbonate is the dominant species, this suggests that the pH is at least 11. Evaluation of the intensity changes of the bicarbonate band at 1627 cm⁻¹ reveals a decrease in pH (pK=10.32) at potentials more positive than -1.7 V, suggesting that transport is not fast enough to cancel any pH decrease. At potentials more positive than -1.45 V, the interfacial pH and the interfacial concentration of bicarbonate will gradually approach that in the bulk,

which is what Figure 7 is showing. Additionally, the ration in intensity of bicarbonate-carbonate is again changing during a reverse, negative sweep, resulting in a baseline spectrum at -1.55 V, where hydrogen evolution (D_2 in this case) is again dominant. During the negative scan, the concentration of bicarbonate will decrease, and that of carbonate will increase, showing pH changes are close to reversible (see Figure 6b). These results confirm the change in equilibrium composition of bicarbonate and carbonate anions in the potential range where ER- CO_2 takes place¹⁰⁸.

Figure 6. (a) ATR studies of bicarbonate and carbonate during scan from -1.7 V to -0.9 V and back to -1.7 V in CO_2 saturated 0.1 M NaOH in D_2O solution with the reference spectrum taken at -1.7 V and (b) 1627 cm^{-1} band intensity during the CV. The potential interval between spectra is $\sim 0.11\text{ mV}$. Please note that the frequency of the maxima of the various peaks does not shift as a function of applied potential.

Formate and other intermediates

Revisiting Figure 5 and returning to the lower wavenumber region at more positive potentials (~ -0.52 V), three additional bands need further interpretation, located at 1597 cm^{-1} , $1520\text{--}1533\text{ cm}^{-1}$, and 1335 cm^{-1} . The band at 1597 cm^{-1} can be assigned to the C=O stretching vibration of formate (see Figure S7). The other features of formate at 1351 and 1383 cm^{-1} , assigned to the $\nu_{\text{s(OCO)}}$ and $\delta_{\text{(CH)}}$, respectively, cannot not be easily resolved, due to overlap with the (negative) carbonate band at 1410 cm^{-1} and overlap with the 1363 cm^{-1} band of bicarbonate. Table 2 provides an overview of formate band assignments from previous studies¹²⁶⁻¹³². In addition, Figures S8 show dynamic changes in formic acid/formate peak positions when a potential is applied. These data are also included in Table 2. The band at $1520\text{--}1533\text{ cm}^{-1}$ has been extensively discussed (see Figure 4) and can be assigned to (protonated) surface adsorbed carbonate, now appearing as a positive band due the potential at which the background was recorded. The band at 1335 cm^{-1} is the most difficult to assign. To demonstrate this band is related to reduction of CO_2 , we will now discuss spectra obtained by isotopic labeling.

Isotopic labeling

The spectra shown in Figure 7 were obtained by purging $^{13}\text{CO}_2$ gas in the electrolyte for 30 minutes, to ensure saturation, and carrying out a scan in the positive direction starting from -1.2 V to 0 V. Comparing the spectra obtained in $^{13}\text{CO}_2$ (Figure 7) to the spectra shown in Figure 5, reveals several band shifts. The adsorbed ^{13}CO band is located at 2023 cm^{-1} . The interchange of solution based carbonate to bicarbonate is clearly evident by the negative band at 1376 cm^{-1} , accompanied by the positive bicarbonate bands at 1575 cm^{-1} and 1333 cm^{-1} . The surface carbonate band at $1520\text{--}1533\text{ cm}^{-1}$ is evident at $1468\text{--}1488\text{ cm}^{-1}$ using $^{13}\text{CO}_2$. Most likely, the unknown band at 1335 cm^{-1} has shifted to 1294 cm^{-1} , demonstrating this is CO_2 related. In particular for carbonate species on oxide surfaces, various modes of interaction have been proposed, including monodentate and bidentate interaction. Table 3 provides additional assignments of IR bands to various

carbonate species^{79, 132-134}, indicating that the 1335 (1294 for $^{13}\text{CO}_2$), might be related to bidentate carbonate, as proposed for Ag-based catalysts³⁸. Indeed there appears a similarity in growth-rate of the 1533 and 1335 cm^{-1} band in Figure 5. In the following we discuss potential additional contributions to the CO_2 -associated features in the spectra.

Figure 7. ATR spectra of the Cu thin film during positive scan in $^{13}\text{CO}_2$ saturated 0.1 M NaOH in D_2O solution with reference spectrum taken at -1.2 V. The potential interval between spectra is ~ 0.08 mV.

Table 2. Vibrational assignments of the formate ion

Surface	method	Band center(cm^{-1})	Assignment
Ni(110) ¹²⁶	IRAS	1365	$\text{V}_{\text{s}}(\text{OCO})$
		2854	Combination of $\delta_{(\text{CH})}$ and $\text{V}_{\text{a}}(\text{OCO})$
		2943	$\text{V}_{(\text{CH})}$
Cu(100) ¹²⁷	IRAS	1348-1358	$\text{V}_{\text{s}}(\text{OCO})$
		2958	Combination of $\delta_{(\text{CH})}$ and $\text{V}_{\text{a}}(\text{OCO})$
		2900	$\text{V}_{(\text{CH})}$
Cu(100) ¹²⁸	HREELS	2910, 2840	$\text{V}_{(\text{CH})}$
		1330	$\text{V}_{\text{s}}(\text{OCO})$
		1460	$\text{V}_{\text{a}}(\text{OCO})$
Pt ¹²⁹	SEIRAS	1325	$\text{V}_{\text{s}}(\text{OCO})$
		1590(not observed)	$\text{V}_{\text{a}}(\text{OCO})$
Pt ¹³⁰	SEIRAS	1730	C=O formic acid
		1325	$\text{V}_{\text{s}}(\text{OCO})$
		missing	$\text{V}_{\text{a}}(\text{OCO})$
Sodium formate salt ¹³¹	IR	2841	$\text{V}_{(\text{CH})}$
		1366	$\text{V}_{\text{s}}(\text{OCO})$
		1567	$\text{V}_{\text{a}}(\text{OCO})$
		1377	$\delta_{(\text{CH})}$
Y ₂ O ₃ ¹³²		1595	$\text{V}_{\text{a}}(\text{OCO})$

			1381	$\nu_s(\text{OCO})$
			2856	$\nu(\text{CH})$
Aq. Soln. of K salt ¹³¹	IR		2803	$\nu(\text{CH})$
			1351	$\nu_s(\text{OCO})$
			1585	$\nu_a(\text{OCO})$
			1383	$\delta(\text{CH})$
Potassium formate soln. as a reference for this study	ATR		2930, 2960	Combination of $\delta(\text{CH})$ and $\nu_a(\text{OCO})$
			2814	$\nu(\text{CH})$
			1351	$\nu_s(\text{OCO})$
			1383	$\delta(\text{CH})$
			1587	$\nu_a(\text{OCO})$

Table 3. Vibrational assignments of carbonate species

surface	method	Band center(cm^{-1})	assignment
Tin(IV) Oxide ¹³³	IR	1630-1590	Bidentate
		1270-1260	
		1530-1470	Monodentate
		1370-1300	
Cu(111) ⁷⁹	DFT	1533	ν_s bidentate
Cu(100)	DFT	1540	
	ATR-SEIRAS	1495	
Ag/MgO ¹³⁵	FTIR	1530	ν_{as} monodentate
		1390	ν_s monodentate
Ag/Ga ₂ O ₃		1590	ν_{as} bidentate

		1320	ν_s bidentate
$Y_2O_3^{132}$	FTIR	1585	ν_{as} bridged
		1334	ν_s bridged
KMG30* ¹³⁴	IR	1570	ν_{as} bidentate
		1335	ν_s bidentate

*potassium-promoted hydrotalcite

Additional spectral contributions: the Dimer

Very recently, rapid scan ATR FTIR spectroscopic studies have provided indications for a CO₂ dimer radical anion intermediate at an aqueous interface of Cu nanoparticles¹¹⁷. To verify the formation of the dimer on roughened copper surfaces in our study using ATR-SEIRAS, an anodic scan with a rate of 2 mV/sec from a significantly negative potential of -1.3 V (used as reference spectrum) was performed. The potential was selected based on the potential dependent appearance of observed species in this study. The absence of previously discussed bands except for bicarbonate and carbonate anions, allowed for precise deconvolution and spectral analysis as shown in Figure 8.

Development of the 1363 cm⁻¹ band while scanning towards more positive potentials is illustrated in Figure 8a. Further analysis by deconvolution of the bands reveals maxima at 1369, 1361 and 1351 cm⁻¹. Analysis of the time-dependent intensity of these bands reveals noticeable discrepancy in the growth kinetics of the 1369, compared to the 1361 and 1351 cm⁻¹ bands (Figure 8c). The potential (time) dependent relative intensity of the 1361 and 1351 cm⁻¹ bands was measured to be fixed at a value of 2 ± 0.05 , suggesting they belong to a single species. In order to ensure that this set of bands originated from carbon-containing species, the experiment was also carried out using ¹³CO₂. The results (figure 8b) reveal potential (time) dependent development of a set of bands at 1335, 1324 and 1315 cm⁻¹. Similar to ¹²CO₂ studies, the relative intensity of 1324 and 1315 cm⁻¹ bands was measured

to be a fixed value of 2.15 ± 0.05 , suggesting they belong to a single species. Based on a previous report of Frei and coworkers¹¹⁷, the pair of bands at 1361 and 1351 cm^{-1} (1324 and 1315 cm^{-1} for $^{13}\text{CO}_2$) together with a potential dependent asymmetric stretch at 1627 cm^{-1} (1575 cm^{-1} for $^{13}\text{CO}_2$, see Figure 7) could be assigned to the C_2O_4^- radical anion, which is then apparently a relatively stable intermediate.

C_2O_4^- is the product of coupling of CO_2 and the CO_2^- radical by forming a C-O bond (see structure in Figure 9), the CO_2^- being the first and most frequently cited intermediate for hydrocarbons and C1 products^{14, 136}. In the pathway towards CO, adsorbed CO_2^- is believed to react with physisorbed CO_2 and form the more stable CO_2 dimer radical anion¹³⁷⁻¹³⁸. While this dimer has been predominantly proposed for reduction of CO_2 in aprotic conditions, it is recently also believed to play a mechanistic role in ER- CO_2 in aqueous solutions¹³⁹⁻¹⁴⁰. Generally the dimer is proposed to disproportionate into CO and CO_3^{2-} :

If this intermediate would play a major role, a decreasing intensity of the spectral features of the dimer, should be accompanied by increasing intensity of the bands due to (surface adsorbed) CO and carbonate. However, this correlation is affected by other processes which simultaneously occur, such as protonation of the carbonate, and reaction of CO to form ethylene. In protic conditions, generally proton assisted formation of products is proposed, such as the following reactions leading to formate ((4), (5)), while also the formation of CO can be explained by proton assisted reduction of CO_2 , yielding water (6):

The formation of formate is evident from several spectra in this study, as previously discussed. The relative contribution of reaction (6) as compared to reaction (3) will determine spectral dynamics, and this is likely potential dependent. An accurate overview of the results discussed so far on the formation of CO, revealed that the CO peak was observed at potentials as negative as -1.24 V. At more negative potentials the CO peak disappears, which can be due to competitive binding of hydrogen, in addition to accelerated CO dimerization to form hydrocarbons. As previously discussed extensively, the dynamics of the carbonate bands as a function of applied potential, besides being the consequence of reaction (3), can also be largely affected by changes in local (surface) pH, orientation of the molecule (mono- vs bidentate) on the surface, and/or desorption of adsorbed carbonate, which influences the so-called collective vibrations in the adlayer.

Figure 8. Spectral deconvolution of bands during positive scans from -1.3 V to -1.15 V with a scan rate of 2 mV/sec in (a) CO_2 and (b) $^{13}\text{CO}_2$, saturated in 0.1 M NaOH in D_2O solution, with the reference spectrum taken at -1.3 V. (c) Growth kinetics of the 1369, 1361 and 1350 cm^{-1} bands and (d) 1335, 1324 and 1315 cm^{-1} bands during a positive scan. The potential interval between spectra is ~ 0.05 mV.

Figure 9. Structure of the carbon dioxide dimer radical anion ($\text{C}_2\text{O}_4^{\bullet-}$).

5.4 Conclusions

This study set out to probe possible reaction intermediates and products of ER-CO₂ on Cu by employing *in situ* ATR-SEIRAS and isotopic labeling. The following observations have been made and can be interpreted as follows. At relatively small negative applied potential, formate is formed in the presence of adsorbed carbonate, likely in the bidentate form. At more negative potential, the selectivity shifts towards CO and (solution-based) bicarbonate. Local pH changes largely influence the ratio of bicarbonate *vs* adsorbed, and solution-based carbonate¹⁰⁷⁻¹⁰⁸. One of the more significant findings to emerge from this study was detection of the CO₂ dimer radical anion, which we propose to contribute to the formation of CO by disproportionation. To the best of our knowledge, this is the first observation of this dimer using ATR-SEIRAS on Cu electrodes and in aqueous conditions¹¹⁷. At potentials more negative than -1.4 V, CO is no longer adsorbed, the dimer concentration is low, and the spectra only reveal solution-based carbonate with residual bi-carbonate. Intermediates for ethylene formation have not been revealed, likely due to their short lifetimes. Transient ultrafast IR spectroscopy (microsecond timescales) will be attempted in order to elucidate mechanistic pathways towards ethylene in ER-CO₂.

5.5 Appendix

Figure S1. $2\ \mu\text{m} \times 2\ \mu\text{m}$ AFM images of the Cu film sputtered on Si crystal in (a) three-dimensional and (b) two-dimensional view.

Reference spectra:

Figure S2. Infrared spectrum of H_2O and D_2O .

Figure S3. Infrared spectrum of 0.5 M sodium bicarbonate in D₂O.

Figure S4. Development of bicarbonate peaks after purging 0.1 M NaOH solution (in H₂O) with CO₂.

Figure S5. ATR spectra of the Cu thin film during negative scan in CO₂ saturated 0.1 M NaOH in D₂O solution in 1700-1300 cm⁻¹ region with reference spectrum taken at 0 V.

Figure S6. Infrared spectrum of 0.5 M sodium carbonate in D₂O.

Figure S7. Infrared spectrum of Potassium formate (1 M) in D₂O. The C-H stretch vibration is present at 2815 cm⁻¹, while the CO₍₂₎ stretch vibration is present at 1587 cm⁻¹.

Figure S8. Infrared spectra of 0.1 M NaOH in D₂O, in contact with a Cu film. Formic acid was added at -0.2 V (with applied potential on). The background spectrum taken at 0 V prior to addition of formic acid. The peak at 1710 cm⁻¹ is attributed to C=O stretch vibrations of formic acid. The C-H stretch vibrations at 2946 and 2848 cm⁻¹ are relatively weak. In the potential range of -0.3 to -0.7 V the height of the 1710 cm⁻¹ band decreases, while the increasing bands at 2848, 1591, 1383 and 1353 cm⁻¹ are associated with formate.

Chapter 6.

Correlating the surface structure and composition of copper to high selectivity towards ethylene in reduction of CO₂

Abstract

Development of a selective Cu-based electrocatalyst for electrochemical reduction of CO₂ for production of C₂₊ hydrocarbons requires understanding of the effect of the electrode structure on i) the nature of surface adsorbed intermediates and ii) the final composition of the product-gas. In this study, the electrode structure of electropolished Cu was manipulated by addition of variable concentration of 0.1-1 mM of CuSO₄ to 0.1 M or 0.5 M of KHCO₃ electrolyte. The faradaic efficiency (FE) of electropolished Cu towards ethylene increased from ~30 to ~40% by the

incorporation of 0.1 mM of CuSO_4 in 0.1 M KHCO_3 solution, while larger quantities up to 1 mM lead to lower FE and favor H_2 formation, in particular at 0.5 M KHCO_3 concentration. Based on the study of the surface morphology, the added CuSO_4 causes in-situ electrodeposition of Cu microstructures, enhancing the roughness of the electrode, the highest for the 1 mM CuSO_4 concentration as determined by capacitance measurements. The key result of this study is the demonstration using SERS, that addition of 0.1-1 mM CuSO_4 significantly enhances the surface coverage of CO in 0.1 M KHCO_3 , as well as the potential range at which adsorbed CO is present, facilitating CO dimerization and selective formation of ethylene. In addition, SERS reveals a lower intensity and stability of surface Cu-OH bands by addition of CuSO_4 , suggesting too high coverage with Cu-OH might be detrimental for ethylene selectivity. These observations are significantly less pronounced in 0.5 M KHCO_3 and discussed and compared to recently postulated hypotheses on the surface composition during CO_2 reduction.

6.1 Introduction

The electrochemical reduction of CO_2 is a technology presently under development to mitigate high CO_2 concentrations in the atmosphere, and to produce renewable fuels and feedstock. Cu uniquely converts CO_2 to a wide range of hydrocarbons²³. The surface morphology and roughness of Cu electrodes have previously been proven to greatly influence the activity and product selectivity during CO_2RR . The selectivity towards ethylene can be significantly enhanced by the use of foam like structures¹⁴¹, nanowires^{106, 142-143}, mesocrystals¹⁴⁴, nanocubes¹⁴⁵, nanoparticles²⁸, thick deposited Cu oxide films^{28, 43, 146} and sputtering²⁸. All these methods lead to enhanced roughness and an enhanced active surface area of the electrodes. A possible explanation for the observed enhanced ethylene selectivity is that the higher current densities obtained on roughened electrodes lead to higher local pH values, favoring formation of ethylene^{57, 147-148}. Another explanation is that surface roughening introduces surface defects such as steps, edges, terraces and

vacancies. Higher density of such surface adsorption sites of low-coordination favors adsorption properties of the catalyst^{28, 63, 83}. Abundance of these active surface sites resolves the preference towards C₁ or C₂ reaction pathways as compared to the production of hydrogen. In addition to ex-situ methods to enhance the roughness, few studies exist which discuss in-situ electrodeposition of Cu¹⁴⁹⁻¹⁵⁰ and in-situ deposition of nickel¹⁵¹. In such an approach, in addition to the electrolyte composition, i.e. the alkali (bi)carbonate concentration, Cu cations are added, which influence the electrode performance^{45, 147, 152}.

To identify the catalytically active sites under operating conditions, in-situ spectroscopic techniques have gained attention in recent years. Under cathodic conditions, copper oxides are quickly reduced and as a result, it is difficult to employ ex-situ methods to identify the oxidation state of Cu during CO₂RR. Consequently, in-situ SERS has been used to monitor the oxidation state of the catalyst surface^{106, 153-156}. In addition, SERS is a powerful tool for examining adsorbed intermediates.

In this report, in-situ electrodeposition was employed to effectively obtain highly active sites showing high electrocatalytic selectivity towards ethylene. Surface characterization of the electrodeposited Cu reveals significant enhancement in roughness. We also try to unravel the oxidation state of Cu in action, and to identify adsorbed species at highly negative potentials where CO₂RR is dominant, using the in-situ SERS technique. We show that increasing surface roughness significantly increases surface coverage of CO, a key intermediate in the formation of ethylene, while the surface coverage is also dependent on the concentration of the applied KHCO₃ solution. The resulting enhanced probability for CO dimerization explains the highly selective formation of ethylene. This work also reveals that Cu-OH species are present during CO₂RR, even at negative potential, and decrease in relative intensity by the presence of Cu²⁺-ions in solution. Based on these results, we establish a deeper understanding of how the electrode morphology can lead to selective ethylene formation pathways.

6.2 Experimental section

Materials and Film Deposition

Cu foils used as working electrode were prepared by mechanical polishing, followed by electropolishing in 85% phosphoric acid, potentiostatically at 3 V vs. a graphite foil counter electrode. Finally the electrodes were cleaned ultrasonically in ethanol and water.

The electrolyte solutions of KHCO_3 (Sigma Aldrich, 99.99% metals basis), NaHCO_3 (Sigma Aldrich, 99.7%), Li_2CO_3 (Sigma Aldrich, 99%), CsHCO_3 (Alfa Aesar, 99.99%), KCl (Sigma Aldrich, 99%), $\text{Cu}(\text{CH}_3\text{COO})_2$ (Sigma Aldrich, 99.99%), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Sigma Aldrich, 99%) and CuSO_4 (Sigma Aldrich, 99%) were prepared using deionized water (Millipore MilliQ, 18.2 $\text{M}\Omega \text{ cm}$). For preparation of 0.1 M LiHCO_3 , 0.05 M Li_2CO_3 was purged overnight with a flow of 20 ml/min. of 100% CO_2 .

The morphology of the surface of the electrode was examined using scanning electron microscopy (JEOL JSM-6010LA).

Electrochemical Measurements

All electrochemical measurements were carried out using a Bio-Logic VSP Potentiostat. A home-made, two-compartment electrochemical cell using a three electrode assembly was used to carry out the CO_2 electrochemical reduction. Various concentrations (0.1-1 mM) of Cu salts were added to 0.1 M KHCO_3 as electrolyte. Glassy carbon (SIGRADUR® G) was used as the counter electrode and was separated from the working electrode using an anion exchange membrane (Selemion AMV, AGC, Inc.). Ag/AgCl in 3 M NaCl was used as a reference electrode and potentials were converted to the Reversible Hydrogen Electrode (RHE) scale by $V_{\text{vs. RHE}} = V_{\text{measured vs. Ag/AgCl}} + 0.198 + 0.059 \cdot (\text{pH of solution})$.

The CO_2 gas was continuously purged through a glass frit at a rate of 20 ml min^{-1} for 30 minutes before each experiment, using a mass flow controller. The flow rate

was then decreased to 5 ml min^{-1} during the electrochemical reduction. The reactor effluent was vented directly into the gas sampling loop of a micro-gas chromatograph (micro-GC) equipped with a pulsed discharge detector (PDD) every 4 minutes. The micro-GC was equipped with two different columns (Molsieve plot and Rt-Q Bond) for separation of H_2 , CO, CO_2 and hydrocarbons. The data were averaged from four individual injections after 1 hour of electrochemical reduction to ensure steady state conditions. During chronoamperometry (CA) measurements, the current continuously increased and the current densities are reported according to the selected GC injections.

Raman spectroscopy was carried out using an Avantes AvaRaman spectrometer with an Intertec laser as excitation source at $\lambda = 785 \text{ nm}$. In-situ experiments were performed in a homemade flow cell with Pt mesh as counter electrode and Ag/AgCl in 3 M NaCl as a reference electrode. The electrolyte was continuously purged with CO_2 throughout the experiment. The Raman probe was separated from the electrolyte by a quartz window. An acquisition time of 10 seconds was selected to record each spectrum.

Electrochemical surface area measurements

The relative surface roughness factors of the electrodes after CO_2RR in 0.1 M $\text{KHCO}_3 + x \text{ mM CuSO}_4$ ($x=0, 0.1, 0.5$ and 1) were calculated by measuring the double layer capacitance values in 0.1 M KCl. Pt mesh was used as a counter electrode and Ag/AgCl was used as reference electrode. Cyclic voltammetry (CV) was performed with different scan rates (5, 20, 40, 60, 80, 100 mVs^{-1}) in the potential range in which no Faradaic processes occur. The slope of the current density (the absolute values of the forward and backward scans were quite comparable) vs. scan rate gave the capacitance value which was normalized to smoothened copper, to obtain relative surface roughness factors.

6.3 Results and discussion

Surface characterization of in-situ electrodeposited Cu

To explore whether addition of CuSO_4 to the electrolyte affects the morphology of the electrode, the surface morphology of the Cu deposits during the electroreduction in 0.1 M KHCO_3 +0.1 mM CuSO_4 was investigated by scanning electron microscopy (SEM) (See Figure 1 and Figure S1). To evaluate development of the electrode morphology, samples were studied after 5 min, 30 min and 1 hr of electrodeposition. Electropolished Cu foil (Figure 1a) shows an almost uniform flat surface with no significant features. As can be seen from Figure 1b, after 5 minutes of electroreduction, dandelion-like structures with an average diameter of 20 microns were formed. After 30 minutes, a more complex microstructure was revealed. The dandelions slightly grew in size and newly formed, smaller and horizontally oriented dendrite structures with the length of a few microns are visible, as well as nanoparticles. After 1 hour of electrolysis, the complex dandelion + surface dendrite morphology was retained and only slightly further developed, still leaving significant areas of the electrode void of dandelion structures. Figure S2 provides different magnifications from significant features of the surface structure after 1 hour of electroreduction. These images confirm that the average size of the dandelion-like microstructures was around 30 microns and dendrites consist of central backbones with the length of few microns and sharp secondary branches. Increasing the concentration of the added CuSO_4 to 1 mM resulted in highly porous integrated, three-dimensional dendritic microstructures (See Figure S2). Contrary to the 0.1 mM concentration in which dandelion coverage appears to consist of highly crystalline structures, the continuous integrated network of dendrites is less crystalline and structures reveal similar morphology as the few dendrites in the 0.1 mM solution.

Figure 1. SEM images showing development of microstructures electrodeposited on electropolished Cu after (a) 0 min, (b) 5 min, (c) 30 min and (d) 1 hour of reduction at -1.1 V vs RHE in 0.1 M KHCO_3 + 0.1 mM CuSO_4 .

In the next section, the significant impact of these morphological characteristics on the resulting CO_2RR product distribution will be discussed.

Effect of Cu salt additive on selectivity and activity

To assess the effect of Cu salt and its concentration, appropriate amounts of copper sulfate, acetate and chloride were incorporated into a 0.1 M KHCO_3 solution to adjust the concentration from 0 to 1 mM. The performance in electrochemical reduction of CO_2 was subsequently assessed (See Figures 2 (using sulfate as anion) and S3 (using acetate and chloride as anion)). Increasing the added salt up to a concentration of 0.1 mM leads to a rise in FE of ethylene from 29 to 42%, consistent with significant loss in methane FE from 18 to 6% and suppression of hydrogen evolution. Higher concentrations of salt did not favor ethylene formation and instead, favored hydrogen evolution to the expense of ethylene and methane. The methane

FE was slightly decreased as more salt was incorporated. The formation of CO was nearly unaffected by salt concentration. The anion composition of the copper salt did not significantly affect the results, with CuSO_4 leading to slightly higher FEs towards ethylene. Interestingly, the highest FE of ethylene and lowest methane and H_2 formation were observed at an optimum value of salt concentration of 0.1 mM.

Figure 2. Faradaic efficiency of C_2H_4 , CH_4 , CO and H_2 vs. added CuSO_4 concentration to 0.1 M KHCO_3 at -1.1 V vs. RHE.

Table 1. The capacitance values and surface roughness factors of the electrodes as a function of added CuSO_4 concentration to 0.1 M KHCO_3 electrolyte after 1 hour of electrochemical CO_2 reduction at -1.1 V vs. RHE.

Catalyst (added CuSO_4 concentration)	Capacitance (mF)	Roughness factor
Electropolished Cu	0.192	1
+0.1 mM	1.007	5.25
+0.5 mM	2.079	10.82
+1mM	3.454	17.99

On the basis of the above experimental evidence and morphological observations, the selectivity might be altered towards formation of ethylene and suppression of formation of methane and H_2 as the result of the improved surface roughness, and associated higher reactivity and local pH. To quantify the roughness, the roughness factors of post-reduction Cu electrodes were estimated by the double layer capacitance method, and the results are represented in Table 1 (see Figure S4 for the CVs at different scan rates). The results indicate that an increase in additive concentration leads to higher surface roughness factors, while the highest selectivity towards ethylene is obtained at an optimum roughness factor value of ~ 5 times higher than of electropolished copper. To offer an explanation for this optimum value, we need to examine other effects of improved roughness.

There are two likely causes for the enhanced catalytic performance of the roughened surface. Firstly, roughened surfaces have significantly greater density of low-coordinated sites such as steps, edges and terraces, particularly given the dendritic shape of the copper structures. Compared to terraces, steps are known to facilitate high coverage of CO, and therefore a shift in selectivity towards C_{2+} hydrocarbons can be expected^{39, 63}. On the other hand, edges promote the coverage of $*CHO$ and $*CH_2O$. At highly elevated surface roughness (>5 times of electropolished copper), a very large population of low-coordinate sites strongly bind H atoms and favor the hydrogen evolution reaction compared to CO_2RR ⁴⁰. Interestingly, this is in agreement with the results presented in Figure 2, showing elevated values of H_2 formation at the highest $CuSO_4$ concentration (correlated with highest roughness factor). It is worth noting that a smooth surface mostly made of low index crystal facets, such as Cu(100) and Cu(111) is more selective towards methane and hydrogen.

Secondly, the higher active surface area of the roughened electrode leads to higher current densities and consequently, an increase in local pH, which is known to alter the reaction pathway towards formation of ethylene^{70, 80, 147-148}. The rise of local pH

at high current densities occurs due to fast proton consumption at the surface. To assess the influence of roughness on current density of Cu electrodes, I-t curves were examined.

Figure 3. (a) CO₂RR activity (chronoamperometry) of electropolished Cu foil in CO₂-saturated 0.1 M KHCO₃+ 0, 0.1, 0.5 and 1 mM CuSO₄ electrolytes at -1.1 V vs. RHE and (b) partial current density of products as a function of CuSO₄ concentration.

The current density at rough Cu electrode (in 0.1 M KHCO₃+0.1 mM CuSO₄) increased gradually from 12.2 to 20 mA.cm⁻² during 1 hr of electroreduction (Fig. 3). The current density was improved more significantly as the concentration of CuSO₄ was increased. In contrast, the electropolished Cu electrodes experienced a slight decrease in current density over time under identical conditions in the absence of CuSO₄, as shown in Fig 3a. Hence, the activity of the rough electrode is superior to that of the smooth surface. Moreover, the rate of ethylene formation was notably increased as the concentration of CuSO₄ in the electrolyte was increased (Fig. 3b), consistent with the effect of local pH.

Taken together, the above discussion and our observations suggest that both, changes in surface orientation and site coordination, and the increased local pH at the rough electrode surface dictate the selectivity towards ethylene. This finding

supports the work of other studies demonstrating that the highest ethylene selectivity was achieved at an optimum surface roughness factor^{40, 43} or a balanced ratio of edge sites to plane sites in cube-shaped nanoparticles¹⁵⁷. To establish whether addition of CuSO₄ is generally enhancing performance, this was tested at variable bicarbonate concentration and electrolyte anion.

Effect of bicarbonate concentration

The effect of KHCO₃ concentration on product distribution using different KHCO₃ electrolytes (0.05, 0.1, 0.2, 0.3, 0.5M) in the presence of 0.1 mM CuSO₄ at -1.1 V vs RHE was investigated. Figure 4 provides an overview of the FE of the main products as a function of KHCO₃ concentration, determined after 1 h of operation. As can be seen, product distribution is greatly affected by electrolyte concentration, of which the trend is generally in agreement with trends reported by others in the absence of CuSO₄ in solution^{52, 147, 158}. However, at the concentration of 0.5 M KHCO₃, formation of ethylene was significantly suppressed, and the increasing trend in methane FE interrupted. Apparently, at 0.5 M KHCO₃, formation of hydrocarbons is significantly inhibited by the addition of CuSO₄. It seems likely that this result is due to deactivation of the Cu electrode against CO₂ reduction. In a previous study by Kas et al., it was established that the oxide derived Cu electrode was deactivated in 0.5 M KHCO₃ electrolyte at significantly higher rates as compared to in 0.1 M electrolyte¹⁴⁷. To gain more insight, in the final section we employ in-situ SERS to investigate the interfacial phenomena at 0.5 M KHCO₃.

Figure 4. Faradaic efficiency of C₂H₄, CH₄, CO and H₂ vs. KHCO₃ concentration with 0.1 mM CuSO₄ at -1.1 V vs. RHE.

Effect of electrolyte cation

The effect of alkali-metal cations on product distribution in the presence of 0.1 mM CuSO₄ was studied at -1.1 V vs RHE as shown in Figure 5. Increasing the alkali-metal cation size in the order of Li⁺ < Na⁺ < K⁺ < Cs⁺ significantly enhances ethylene formation, consistent with the literature^{46, 152, 159-161}, and the presence of CuSO₄ does not seem to affect the trend. Quantitatively the ethylene partial current density is somewhat larger in the presence of CuSO₄, particularly for the K⁺ and Na⁺ electrolytes. DFT calculations by Gao et al. attributed the promoting effect of K⁺ and Cs⁺ on ethylene production to formation of intermediates (CO*, OCCO*, OCCOH*) favoring the C₂+ pathway¹⁵⁹. Furthermore, Frumkin proposed that larger cations influence surface reactions by stabilizing anion intermediates on the cathode surface, enabling higher current densities¹⁶², in accordance with the present results. Smaller cations on the other hand, have large hydrating shells and hence lower propensity for adsorption on the electrode surface. This causes increase of Cu-H coverage and

favors hydrogen evolution¹⁶¹. Methane formation was most predominant in the Na⁺ electrolyte.

Figure 5. Partial current density of C₂H₄, CH₄, CO and H₂ in CO₂-saturated 0.1 M MHCO₃ (M = Li, Na, K, Cs) +0.1 mM CuSO₄ electrolyte at -1.1 V vs. RHE.

In situ Raman spectroscopy of Cu²⁺-mediated reduction of CO₂

SERS was performed on a Cu electrode in CO₂-saturated 0.1 M KHCO₃ electrolyte in the absence or presence of a flowing solution of 1 mM CuSO₄, at a constant potential of -1.1 V vs. RHE. The time dependent in-situ Raman spectra of the Cu electrode at -1.1 V are presented in Figure 6 (each spectrum, bottom to top, was recorded after 10 consecutive minutes). The first measurement was collected at open circuit potentials and clearly revealed the characteristics of Cu₂O at 150, 400, 525 and 620 cm⁻¹ ¹⁶³. After applying the -1.1 V vs. RHE, Cu₂O peaks rapidly disappear, and major peaks at 310, 380 and 518 cm⁻¹ develop. These peaks can be assigned to surface oxide/hydroxides (Cu(O)_x/(OH)_y) ¹⁶⁴. Based on our previous study¹⁶⁵, we assign the peaks at 310 and 380 cm⁻¹ to CuO and the one at 518 cm⁻¹ to Cu-OH. Initially, the 380 and 518 cm⁻¹ bands dominate, while the 380 cm⁻¹ decreases, the 310 cm⁻¹ peak appears, and the 518 cm⁻¹ band increases and broadens as a function of time, suggesting compositional changes in the CuO/OH deposit.

Nevertheless, the persistence of these bands suggest that the surface of the copper electrode is not fully reduced, and oxide/hydroxide species cover the surface when at potentials where CO_2 is reduced to ethylene. In accordance with the present results, a number of previous studies have confirmed the presence of Cu^+ at negative potentials with the help of in-situ techniques¹⁶⁶⁻¹⁷⁰. Generally this has been proposed as being favorable for the ethylene FE, but in the following we will demonstrate that in fact the intensity of Cu^+ (identified by Cu-OH) inversely correlates with the surface coverage of CO, which positively correlates with the FE towards ethylene.

Figure 6. In-situ SERS of a Cu surface in CO_2 saturated 0.1 M KHCO_3 +1 mM CuSO_4 during 1 hr of CA at -1.1 V.

Figure 7. In-situ SERS of Cu surface in CO₂ saturated (a) 0.1 M KHCO₃ and (b) 0.1 M KHCO₃+1 mM CuSO₄ (already subjected to 1 hr of CA in the same electrolyte). Spectra were collected during a CV with the rate of 10 mV/sec and the potential interval between spectra is 0.2 V.

First we show in Figure 7 the spectra of the electropolished and rough Cu electrodes during the CV in CO₂ saturated 0.1 M KHCO₃ and 0.1 M KHCO₃+1 mM CuSO₄ electrolyte, respectively. During a negative scan, on electropolished Cu, adsorbed CO starts to develop at the potential of -0.4 V, identified by the Raman intensity at ~2080 cm⁻¹. Also the peak at 280 cm⁻¹ can be assigned to adsorbed CO, while adsorbed CO is most clearly revealed by the growth of peak at 360 cm⁻¹, showing similar dynamics, but more clearly resolved, as observed for the ~2080 cm⁻¹ band. As the potential was swept more negatively, these peaks disappeared, while these re-appeared (but less intensively) during the positive scan in a similar potential range (Figure 7a). If we now turn to the spectra in the presence of CuSO₄ (Fig. 7b), the same set of bands not only do not disappear at highly negative potentials, but are also generally more pronounced, indicative of a larger concentration of adsorbed CO¹⁷¹⁻¹⁷⁴. These peaks correspond to libration, frustrated translation, and the

stretching vibration of the adsorbed CO molecule, respectively. To validate this assignment and correlation between these peaks, in-situ SERS of Cu electrode in CO₂ saturated 0.1 M KHCO₃+1 mM CuSO₄ during 1 hr of CA at -0.8 V was carried out (See Figure S7). This potential was chosen to assure CO is formed, as is confirmed by the presence of the 2080 cm⁻¹ band. The simultaneous development of these peaks validates their assignment to a single species (CO). It has been suggested that a high surface coverage of CO is a key factor in selectivity towards ethylene^{74, 76, 101-102, 159}. Building on our earlier discussions, we hypothesize that on roughened Cu electrodes by Cu deposition, the abundance of low-coordinated sites induces a high CO coverage. The increased CO coverage enhances CO dimerization and shifts the selectivity towards formation of ethylene. This finding broadly supports the work of other studies demonstrating that a CO coupling mechanism was enhanced at a high local pH^{85, 147-148}. On the other hand, on the electropolished electrode with lower CO coverage, hydrogenation of adsorbed CO forms *COH and promotes reaction pathways toward C₁ products.

Turning back to Figure 7, at the potential of -0.6 V, a peak was developed at 518 cm⁻¹ which can be assigned to Cu-OH, indicative of Cu⁺. What is striking about this peak is that it coexists with the series of bands assigned to CO and is present at highly negative potentials where hydrocarbons are dominant products. However, by comparing Figs. 7a and b, it can be seen that in Fig 7b the peak at 518 cm⁻¹ is significantly suppressed. This was consistent through all the swept potentials and suggests that the surface hydroxide is less abundant, and indeed inversely correlates with the surface coverage of CO.

Figure 8. Comparison of in-situ SER spectra of Cu surface in CO₂ saturated 0.1 M KHCO₃, 0.1 M KHCO₃+1 mM CuSO₄, 0.5 M KHCO₃ and 0.5 M KHCO₃+1 mM CuSO₄ at -1 V.

To support the inverse correlation, SERS was performed on Cu electrodes in CO₂-saturated 0.5 M KHCO₃ and 0.5 M KHCO₃ +1 mM CuSO₄ electrolytes during CVs from +0.4 to -1.4 V (See figures S8 and S9). To compare the results with the results of 0.1 M KHCO₃ experiments (Fig. 7), spectra taken at -1 V are presented in Figure 8.

What is striking about this figure is that when using 0.1 M KHCO₃ electrolyte, all three peaks of CO at 275, 360 and 2090 cm⁻¹ (blue spectra) show significantly higher intensities compared to 0.5 M KHCO₃ conditions (red spectra). In addition, at 0.1 M KHCO₃, the intensities of the Cu-OH peaks at 520 cm⁻¹ were much lower than the peaks at 360 cm⁻¹ (representing CO). This indicates that in 0.1 M KHCO₃ electrolytes, the surface coverage of CO is higher and the surface composition contains less hydroxide (hence more metallic Cu) compared to 0.5 M KHCO₃. These

observations accords well with the results of product distribution, showing correlations between CO coverage and formation of ethylene.

Another important finding was revealed by comparing the spectra in 0.5 M KHCO_3 and 0.5 M KHCO_3 +1 mM CuSO_4 electrolytes. In the latter, the intensity of CO band is extremely low and the carbonate band at 1070 cm^{-1} indicates that the electrode surface is still partially occupied by this species even at highly negative potentials (See figure S9). It can thus be suggested that the adsorbed carbonate has limited the formation of CO intermediate, in agreement with the suppression of ethylene formation on the same surface as shown in figure 4. It is interesting to note that in both KHCO_3 concentrations with CuSO_4 present in the electrolyte, the same CO band position was observed at 2090 cm^{-1} which suggests that similar linearly bonded CO adsorption sites were occupied.

The results of this study indicate that a combination of both high CO coverage and relatively small intensity of Cu-OH band is crucial to high selectivity towards ethylene.

Several studies have employed in-situ techniques to reveal the catalytically active sites in CO_2RR . The majority has demonstrated that metallic Cu sites are responsible for CO_2 activation while others attributed the activity to Cu^+ species or the Cu^+/Cu^0 interface. In accordance with the present results, previous mechanistic studies revealed that CO dimerization is stabilized at the interface between surface of metallic Cu and Cu^+ ¹⁷⁵⁻¹⁷⁶. They concluded that the synergy between Cu^0 and Cu^+ promoted both CO_2 activation and CO dimerization, while blocking C_1 pathways. Therefore, we conclude that the presence of both Cu^0 and Cu^+ assist C-C bond formation and is responsible for ethylene production.

Another key results is the correlation between the set of peaks at $360\text{-}320\text{ cm}^{-1}$ and $1550\text{-}1510\text{ cm}^{-1}$ which appear at potentials from +0.2 to -0.4 V on the negative scan and from +0.2 to +0.6 V on the positive scan. The correlation can be easily

noticed by looking at crossed arrows in figure 8b. Several reports have assigned the 1540 cm^{-1} band to adsorbed carbonate^{73, 99, 110, 165, 177}. Based on these reports on peak position and observed potentials range, we assign this set of peaks to adsorbed carbonate.

Together these spectroscopic evidence showed that increased roughness promotes selectivity towards ethylene. The shift of reaction pathway due to high density of non-coordinated sites stabilizing CO adsorbed species was confirmed by in-situ SERS spectroscopy. Besides, we concluded that both metallic Cu and oxide/hydroxides are stable at CO₂RR potentials and are key for controlling selectivity. Our study has demonstrated that both morphological effect and local pH effect are crucial for activating ethylene pathways on Cu electrodes.

6.4 Conclusion

In this work, we report the highly selective and stable electroreduction of CO₂ to ethylene. In situ electrodeposition process was used to modify the surface of electropolished Cu foils to generate microstructured morphology. The in-situ formation of this electrocatalyst resulted in highly roughened surface areas and higher availability of active sites. An optimized population of surface defects in addition to local pH effects were found to be determining factors for the enhanced selectivity towards ethylene. Based on our in-situ SERS measurements, we showed that high CO coverage on rough electrodes is responsible for selectivity towards formation of ethylene. We also provided direct evidence that Cu oxide/hydroxide species are stable at highly negative potentials during CO₂RR and likely diminish selectivity. This work provides a strategy for in situ modification of surface morphology on Cu electrodes to improve the selectivity towards ethylene.

6.5 Appendix

Figure S2. SEM images showing the morphology of the film after 1 hour of reduction at -1.1 V vs RHE in 0.1 M KHCO_3 + 1 mM CuSO_4 at different magnifications.

Figure S3. Faradaic efficiency of C_2H_4 , CH_4 , CO and H_2 vs. added (a) copper acetate and (b) CuCl_2 concentration to 0.1 M KHCO_3 at -1.1 V vs. RHE.

Figure S4. (a) Cyclic voltammograms of the Cu electrode in 0.1 M KHCO_3 +0.1 mM CuSO_4 subjected to 1 hr electrochemical reduction, followed by various scan rates in a potential window where only double-layer charging and discharging is relevant, (b) Double layer capacitance values of a smooth Cu electrode and the rough electrodes after 1 hr of electroreduction in 0.1 m KHCO_3 + 0.1, 0.5 and 1 mM CuSO_4 . The slopes have been calculated by linear fitting in Origin Pro.

Figure S5. Cyclic voltammograms of Cu electrodes in 0.1 M KHCO_3 electrolyte with scan rate of 10 mV/sec .

Figure S6. Cyclic voltammograms of Cu electrodes in 0.1 M KHCO_3 , 0.1 M KHCO_3 +1 mM CuSO_4 and after 1 hr of CA in the same electrolyte with scan rate of 50 mV/sec.

Figure S7. In-situ SERS of Cu surface in CO_2 saturated 0.1 M KHCO_3 +1 mM CuSO_4 during 1 hr of CA at -0.8 V.

Figure S8. In-situ SERS of Cu surface in CO_2 saturated 0.5 M KHCO_3 . Spectra were collected during a CV with the rate of 10 mV/sec and the potential interval between spectra is 0.2 V.

Figure S9. In-situ SERS of Cu surface in CO_2 saturated 0.5 M KHCO_3 +1 mM CuSO_4 (already subjected to 1 hr of CA in the same electrolyte). Spectra were collected during a CV with the rate of 10 mV/sec and the potential interval between spectra is 0.2 V.

Chapter 7.

In situ Raman study of potential dependent surface adsorbed carbonate, CO, OH and C-species on Cu-electrodes during electrochemical reduction of CO₂

Abstract

Using In-situ Surface-enhanced Raman spectroscopy (SERS) to study Cu-catalyzed electrochemical reduction of CO₂ in carbonate solution, and ¹³C/¹²C and D₂O/H₂O isotopic labeling for assignment, we show reduction of Cu(I)oxide is accompanied by adsorption of predominantly monodentate carbonate starting at ~1067 cm⁻¹ in the potential range from [+0.2 V → -0.2 V]. While the presence of a band at ~1540 cm⁻¹ has been previously assigned to adsorbed carboxylate (*CO₂⁻), we alternatively assign this to bidentate carbonate, with a strong Stark tuning effect with a rate of ~60 cm⁻¹/V. As expected, appearance of surface CO was observed in

the range of $[-0.4 \text{ V} \rightarrow -1.0 \text{ V}]$, clearly identified by the Cu-CO vibration at 360 cm^{-1} . At the more negative end of this potential range, we identified the formation of copper hydroxide, and for the first time a surface-carbon species, showing Raman bands at $\sim 525 \text{ cm}^{-1}$ (Cu-OH) and ~ 500 (Cu-C), respectively. In the potential range of $[-1.0 \text{ V} \rightarrow -1.4 \text{ V}]$, surface CO disappeared, but the Cu-OH and Cu-C species were persistent. Interestingly positive polarization at $> 0.1 \text{ V}$ converts these species and restores surface Cu(I)oxide, rendering the surface processes completely repeatable.

7.1 Introduction

The reduction of CO_2 to value-added chemicals such as hydrocarbons and alcohols has received a great deal of attention in the scientific literature. Copper is the most promising electrocatalyst for this reaction^{23,80}. However, tuning the catalyst to achieve high energy efficiency and product selectivity, is still a significant challenge. To this purpose, understanding of the nature of the catalytically active site(s), rate determining steps, and interfacial phenomena is critical. Despite major scientific advances, these are still not fully resolved.

In general, it is well established that native, crystalline Cu oxides (Cu_2O , CuO) are reduced to crystalline metallic Cu at the negative potentials required for CO_2RR . However, residual (hydr)oxide, either subsurface or surface-adsorbed, as well as carbonates, have also been proposed to play a major role in controlling reaction selectivity. In oxide-derived copper electrocatalysts, existence of subsurface oxygen is believed to play a role in selectivity towards multicarbon products¹⁷⁸. Alternatively, Cu^+ sites remaining on the catalyst surface during the reaction have also been considered as active sites¹⁷⁹⁻¹⁸⁰.

Electrochemical surface-enhanced vibrational spectroscopy has already established itself as a powerful tool to examine the presence of adsorbed species and related surface phenomena. For instance, in our recent study, we explored surface

adsorbed products and intermediates of CO₂RR on Cu using in-situ surface-enhanced infrared absorption spectroscopy (SEIRAS), and demonstrated the presence of a variety of species, including adsorbed carbonates, adsorbed CO, and possibly a carbon dioxide dimer radical anion⁷³. However, due to limitations in the spectral range of the SEIRAS technique, the presence of surface (hydro)oxides during CO₂RR is difficult to identify.

Compared to SEIRAS, which does not provide sufficient throughput in the low-wavenumber region, Surface Enhanced Raman Spectroscopy (SERS) lowers the accessible range well below 1000 cm⁻¹, where metal-oxide/hydroxide vibrations can be observed. In addition, while SEIRAS spectra are dependent on reference spectra, sometimes leading to complicated band patterns in *in situ* measurements, SERS spectra show absolute, real-time intensities. Based on this, besides detection of adsorbed species¹⁸¹⁻¹⁸², in-situ SERS is used to monitor the oxidation state of catalyst surface^{106, 154, 156, 163, 174}. Surprisingly, to the best of our knowledge, the number of studies that employed in-situ techniques to demonstrate the presence of surface Cu⁺ species during CO₂R is quite limited¹⁶⁶⁻¹⁷⁰.

Herein, we report an in situ SERS investigation of electrochemical reduction of CO₂ on electropolished, polycrystalline Cu at a wide range of potentials. We consistently used 0.1 M KHCO₃ as electrolyte, which we previously demonstrated to lead to locally high pH values, which promote formation of ethylene³. Although highly SERS-active substrates normally suffer from instability, causing poor reversibility¹⁸³, our electrodes showed excellent activity and reversibility in the potential region chosen for this study. In other words, compared to previous studies, we could obtain spectra with high intensity of adsorbed species even at highly negative potentials and during the anodic scan. We observed potential-dependent features associated with carbonates, bicarbonates, CO, and most importantly hydroxide species and a stable C-containing species on Cu using a combination of SERS and ¹³C/¹²C and D/H isotopic labeling. Most importantly, we provide evidence

that not only Cu-OH, but also a Cu-C species remain persistent on the surface of the copper electrode, when active in the formation of CO, ethylene and methane, likely deactivating the surface.

7.2 Experimental Section

Materials and electrode preparation

Polycrystalline Cu electrodes were prepared by mechanical polishing, followed by anodic treatment (in 85% phosphoric acid, potentiostatically at 3 V vs. a graphite foil counter electrode), and cleaning ultrasonically in ethanol and water.

The electrolyte solutions of KHCO_3 (Sigma Aldrich, 99.99% metals basis) and $\text{KH}^{13}\text{CO}_3$ (Sigma Aldrich, 99 atom % ^{13}C) were prepared using deionized water (Millipore MilliQ, 18.2 $\text{M}\Omega\text{ cm}$). Solution of 0.1 M KDCO_3 was prepared by purging CO_2 in 0.05 M K_2CO_3 (Sigma Aldrich, ACS reagent, $\geq 99\%$) in D_2O (Sigma Aldrich, 99.9 atom % D).

Electrochemical Measurements

All in-situ electrochemical experiments were performed in a custom-made three-electrode cell, with the Cu film being used as the working electrode. A Pt mesh was used as counter electrode, while a Ag/AgCl electrode (3 M NaCl, BASi) was used as reference electrode. A Bio-Logic VSP potentiostat was used to perform the electrochemical measurements. The reversibility and reproducibility of the spectra when applying multiple oxidation-reduction cycles, demonstrates Pt contamination of the Cu electrode is negligible.

The Cu films were activated by three oxidation-reduction cycles between 0.6 and -0.6 V in the 0.1 M KHCO_3 in H_2O electrolyte, in order to achieve a desirable level of Raman signal enhancement. In other words, electrochemical roughening of the Cu electrode was achieved through dissolution and redeposition reactions. The electrolyte was continuously purged with CO_2 or $^{13}\text{CO}_2$ throughout the experiment with flow rates of 20 and 0.5 ml/min, respectively.

Raman spectroscopy was carried out using an Avantes AvaRaman spectrometer, equipped with an Intertec $\lambda = 785$ nm laser as excitation source. The Raman probe was focused on the electrode/electrolyte through a quartz window. An acquisition time of 10 seconds was selected to record each spectrum.

All reported potentials were converted to the Reversible Hydrogen Electrode (RHE) scale by using the equation:

$$V_{\text{vs. RHE}} = V_{\text{measured vs. Ag/AgCl}} + 0.198 + 0.059 * (\text{pH of solution}).$$

7.3 Results

The potential dependent results of in-situ SERS of the Cu surface in CO₂ saturated 0.1 M KHCO₃ from 0.4 to -1.4 V can be seen in Figure 1. In this Figure, characteristic spectral features strongly depend on the applied potential, confirming that the Cu film is SERS active. Besides, during an anodic scan (from -1.4 to +0.4 V), strong SERS signals were also recorded (See Figure S1 and S2-3 for reproducibility) and cycling of the potentials lead to stable and reproducible SERS spectra. We will address the most likely surface composition at each potential, with variable concentration of carbonate, bicarbonate, adsorbed CO, Cu(OH)_x, Cu-C, and water, and discuss spectra of isotopically labeled conditions subsequently to corroborate the assignments.

Figure 1. In-situ SERS of a Cu surface in CO₂ saturated 0.1 M KHCO₃ and (b) development of the bands at 502 and 524 cm⁻¹ during a cathodic scan. Spectra were collected using a CV rate of 10 mV/sec. The potential interval between spectra is 0.2 V. Spectra were vertically shifted to facilitate comparison.

The first spectra at +0.4 V and +0.2 V clearly reveal the characteristics of (native), surface Cu₂O at 150, 400, 525 and 620 cm⁻¹ ¹⁶³. This set of bands was also observed when reaching positive potentials in the anodic scan, explained by surface oxidation of Cu to Cu₂O (Figure S1). Very little spectral features are visible at higher wavenumbers at these potentials. Consequent to applying a more negative potential, Cu₂O was reduced, and as the potential was swept more negatively, new features in the range of 200-600 cm⁻¹ appeared. Particularly interesting is the pair of bands located at 524 and 502 cm⁻¹ (Figure 1b), which are likely related to Cu-hydroxide and Cu-carbon species (see also Figure S1b). Definitive assignment of these peaks is complicated, as the spectral overlap was not reported in recent publications, nor accounted for in theoretical predictions for copper oxide/hydroxide species. Therefore, we employed ¹³C/¹²C and D/H isotope exchange to identify the origin of

these bands more precisely. The results are presented in detail in the “oxide/hydroxide” section. We will first address the development of carbonate and bicarbonate features, and the dynamics of CO.

Figure 2. In-situ SERS of the Cu surface in CO₂ saturated 0.1 M KDCO₃ in D₂O showing potential-dependent development of the adsorbed and in solution carbonate during (a) a positive and (b) a negative potential scan. Spectra were collected during a CV with a rate of 10 mV/sec and the potential interval between spectra is 0.1 V.

Carbonate and bicarbonate bands

As shown in Figures 1 and 2, a dominant feature in the *in situ* spectra is a strong band at 1072-1067 cm⁻¹, showing a Stark tuning effect with a rate of ~7 cm⁻¹/V. The band rises and then falls, and is visible up to a potential of approximately -0.8 V. To assign this band, a reference spectrum of formate as a possible reaction product at

low overpotentials was recorded (Figure S4). Clearly, the dominant band of formate is located at 1359 cm^{-1} and not at $\sim 1070\text{ cm}^{-1}$, so this assignment can be discarded. On the basis of evidence from other studies^{175, 182, 184-185}, this band can be attributed to the C–O symmetric stretching mode of (weakly adsorbed) monodentate carbonate. In principle this assignment can be corroborated by changing ^{12}C for ^{13}C in the carbonate, which should lead to a shift in band position.

Figure 3. In-situ SERS of Cu surface in CO_2 saturated 0.1 M KHCO_3 in H_2O , $^{13}\text{CO}_2$ saturated $0.1\text{ M KH}^{13}\text{CO}_3$ in H_2O and CO_2 saturated $0.05\text{ M K}_2\text{CO}_3$ in D_2O at 0 V vs. RHE showing the effect of isotope exchange on adsorbed species.

However, as shown in Figure 3, the position of the 1070 cm^{-1} peak is very little affected by $^{13}\text{C}/^{12}\text{C}$ or D/H isotope exchange. This is consistent with recent findings in the literature, also reporting a negligible shift upon $^{13}\text{C}/^{12}\text{C}$ exchange, which is explained by the centrosymmetric movements of the oxygen atoms with respect to the central carbon atom^{182, 186}. To further confirm this assignment to carbonate, CO_2 -

free solutions were used to ensure elimination of $\text{CO}_2/\text{HCO}_3^-$ -derived carbonaceous adsorbates. In agreement with literature, comparison of the spectra measured in CO_2 -saturated and N_2 -saturated 0.1 M KClO_4 (See figure S5) reveals the absence of the 1070 cm^{-1} band in CO_2 -free conditions.

An additional observation regarding the peak position is the following. As indicated previously, the peak position is dependent on the applied potential, and therefore likely due to an adsorbed carbonate species. Principally the electrolyte was prepared by dissolution of bicarbonate, which is apparently deprotonated to a large extent at reductive potentials, due to the basicity of the interfacial region near the electrode. Two different configurations can be proposed for adsorbed carbonate, namely bidentate and monodentate. Here we follow the previously, well supported and discussed assignment of the $\sim 1070\text{ cm}^{-1}$ band to monodentate carbonate, in agreement with the centrosymmetric movements of the oxygen atoms.^{11,15}

As shown in Figure 2, in the potential range of +0.2 to -0.3 V, when performing a negative scan (and from -0.1 to +0.4 V when performing a positive scan), two bands at 1547 and 350 cm^{-1} concurrently appear or disappear. The similarity in Stark shift of this pair of bands (Figure S6) furthermore indicates that these belong to the same chemisorbed species on the catalyst surface.

To assign this pair to a vibrational mode, it is useful to track the existing literature. Based on experimental evidence, the 1540 cm^{-1} band has been assigned to the vibration of adsorbed carbonate^{108, 119, 122, 177} or more precisely, the asymmetric C–O stretching mode of strongly adsorbed bidentate carbonate¹⁸⁴. This assignment is also consistent with our previous findings measuring similar electrodes using SEIRAS⁷³, showing a strong resemblance in peak position as a function of applied potential. To further examine this assignment, the results of isotopic labeling experiments can be considered, as shown in Figures S7-9 (using $\text{KH}^{13}\text{CO}_3$ and $^{13}\text{CO}_2$) and S10 (in D_2O). The red-shift of the band from 1547 to 1524 cm^{-1} due to $^{13}\text{C}/^{12}\text{C}$ isotope exchange,

and immunity to D/H isotope exchange as shown in figures S7 and S10, further confirms this assignment.

It should be mentioned, however, that in a recent study¹⁸² this assignment was discarded and the pair of peaks at 1540 and 350 cm^{-1} were attributed to carboxylate, as the first intermediate in CO_2RR . Looking back to Figure 2a, it is evident that during the anodic scan, the pair of bands persists in the potential range of -0.1 to +0.4 V, which is associated with a positive current (see Fig. 5). As a result, it is highly unlikely that these bands are associated with CO_2RR . Based on this assumption, we discard the assignment to carboxylate, and confidently assign this pair to adsorbed carbonate species, in the bidentate form.

Next, as shown in Figure 1 in the potential range of +0.4 to -0.2 V, another feature at 1345 cm^{-1} (1344 cm^{-1} in Figure 3) is revealed, albeit significantly smaller in intensity than the ~1070 cm^{-1} band. Isotopic labeling experiments were employed and revealed that the band originally at 1344 cm^{-1} shifted to 1332, or 1360 cm^{-1} due to $^{13}\text{C}/^{12}\text{C}$ or D/H isotope exchange, respectively (See figure 3). This implies that the vibratory chemical bonds are associated with both H and C atoms. According to the above analysis, and in agreement with the literature^{181, 187}, we assign this band to bicarbonate vibrational modes. The isotopic labeling results are also in good agreement with band assignments from a recent study¹¹⁷.

Interestingly, we also detected a weak band at 1678 cm^{-1} between ~+0.4 and -0.2 V. While this band was unaffected by $\text{D}_2\text{O}/\text{H}_2\text{O}$ isotope exchange, it shifted to 1629 cm^{-1} as a result of $^{13}\text{C}/^{12}\text{C}$ isotope exchange. This band has recently been attributed to the asymmetric stretch of the carbonyl group associated with a $^*\text{COOH}$ intermediate¹⁸⁸. However, there is no convincing evidence to prove this assignment. Therefore, as suggested by another study¹⁸², further research should be undertaken to identify the origin of this band.

Adsorbed CO

Starting from higher frequencies, the band corresponding to adsorption of CO on atop sites (linearly adsorbed, CO_{atop}) appeared at 2070 cm⁻¹ at -0.4 V and shifted to 2050 cm⁻¹ at more negative potentials, which is consistent with the literature^{73, 108}. This shift with potential is again due to the Stark effect, and is indicative of chemisorbed species. Besides this band, two low-frequency metal-adsorbate bands at 360 and 275 cm⁻¹ also appeared simultaneously and thus in the same potential range. In agreement with previous Raman spectroscopic studies^{95, 153, 171-173, 175, 189}, these are also assigned to adsorbed CO on Cu.

At 1617 cm⁻¹, a broad band was developed at highly negative potentials. This peak could be assigned to the bending mode of H-O-H vibrations of interfacial water^{177, 188, 190}. Consistent with this assignment, this band was unaffected by ¹³C/¹²C isotope exchange in carbonate, and was observed at 1200-1187 cm⁻¹ when D₂O was used as solvent (See Figure S6). The observation of interfacial water at negative potentials is in agreement with previous studies^{79, 164, 191}.

Cu(OH_x/O_y/C)

To shine more light on the identity of the bands at 200-600 cm⁻¹ and gain insight into the chemical state of the active Cu species during CO₂RR, ¹³C/¹²C and D/H isotope exchange experiments were carried out and the results are presented in Figure 4. We will now demonstrate that the pair of bands located at 524 and 502 cm⁻¹ (Figure 1b, (see also Figure S1b)), are related to hydroxide and a copper-carbon species. In KHCO₃ (Figure 4, left) at -0.5 V and more negative potentials, a band centered at 522 cm⁻¹ with an apparent shoulder at 502 cm⁻¹ was developed (see also Figure 1b, and Figure S1b).

Figure 4. In-situ SERS of the Cu surface in CO_2 saturated 0.1 M KHCO_3 in H_2O , CO_2 saturated 0.05 M K_2CO_3 in D_2O and $^{13}\text{CO}_2$ saturated 0.1 M $\text{KH}^{13}\text{CO}_3$ in H_2O showing development of bands in the region of 250-600 cm^{-1} during a cathodic scan. Spectra were collected during a CV with the rate of 10 mV/sec. The black dotted lines at 320 and 380 cm^{-1} , while the green dashed lines at 275 and 365 cm^{-1} represent adsorbed CO.

By substituting D for H, features associated with surface CuO_y should not exhibit a frequency shift, while spectral features correlated to adsorbed $\text{Cu}(\text{OH})_x$ should display a downshift. Turning to the spectral evidence in KDCO_3 , a single band at 495-510 cm^{-1} was observed. We identified this peak as a deuterium monoxide (OD) associated vibration. Apparently, by replacing H with D, SERS bands are shifted towards lower frequencies from 522 to 495 cm^{-1} , with the frequency ratio of ~ 0.96 from Cu-OD versus Cu-OH vibrations being in close accordance with earlier studies¹⁹²⁻¹⁹³. Interestingly, due to the absence of a band at $\sim 470 - 480 \text{ cm}^{-1}$, the band at 502 cm^{-1} did not exhibit any shifts as the result of D/H isotope exchange, and is likely located underneath the dominant O-D band at 495-510 cm^{-1} . If we now turn to results of $^{13}\text{C}/^{12}\text{C}$ isotope exchange in $\text{KH}^{13}\text{CO}_3$, we observe a significant

difference compared to KHCO_3 . While the band at 522 cm^{-1} , assigned to adsorbed hydroxide species based on the above discussion, remained unchanged, the shoulder originally at 502 cm^{-1} is now shifted to $\sim 480\text{ cm}^{-1}$. This ^{13}C isotopic shift, reveals the C-containing origin of this band. To the best of our knowledge, this is the first report on finding such species. Due to the complexity of possible species that could bond to the Cu surface, a more accurate assignment than “Cu-C” of this band is challenging and remains to be elucidated.

Another minor feature in the spectra, is the band at 460 cm^{-1} , which only displays sensitivity to H/D exchange and shifted to 445 cm^{-1} in KDCO_3 , while this contributes to the spectrum in ^{13}C -labeled carbonate as a *non*-shifted shoulder on the band at 480 cm^{-1} . We assign this band to Cu hydroxide species. The previous assignments of hydroxide species are in accordance with the two different states of adsorbed OH^- ions, OH-Cu-OH and $\text{Cu}(\text{OH})_2$ at 450 and $488\text{-}520\text{ cm}^{-1}$ reported in the literature ^{164, 192-195}.

Turning now to the wavenumbers below 400 cm^{-1} in Figure 4, the bands at 275 and 360 cm^{-1} attributed to Cu-CO are marked with green dashed lines. At highly negative potentials at which Cu-CO bands are suppressed, two bands at 320 and 380 cm^{-1} , marked with black dotted lines concurrently appeared. This pair is also present during the anodic scan, until eventually disappearing at -0.4V (See Figure S1). These two bands are tentatively assigned to features of surface CuO, in good agreement with calculated frequencies of CuO and previously observed positions at ~ 300 and $\sim 350\text{ cm}^{-1}$ ¹⁹⁶.

Based on the above discussions, three types of surface species were resolved in our SER spectra: oxides at 320 and 380 cm^{-1} , hydroxides at 460 and 520 cm^{-1} , and a C-containing compound at 502 cm^{-1} . Thus, counter-intuitively, Cu^+ species exist at relatively deep negative potentials, and are potentially inhibiting CO_2RR .

7.4 Discussion

To gain further insights into the dynamics of the adsorbed species, we analyzed the adsorption/desorption intensities as a function of potential, including carbonates, CO and hydroxide on the Cu electrode, and compare these to the electrochemical response in a cyclic voltammogram in Figure 5. To produce Figure 5a, specific band intensities were derived from figure S3, and were plotted against applied potential. An illustration of the cycle, with the adsorbed species present in several potential ranges can be found in Figure 6.

Figure 5. (a) Effect of electrode potential on intensities of Cu(OH)_x , CO, and adsorbed CO_3^{2-} bands and (b) Cyclic voltammograms of the Cu electrode in CO_2 -saturated 0.1 M KHCO_3 with a scan rate of 10 mV/sec. Clearly, between 0.4 V $\rightarrow$ 0.0 V two reductive waves are apparent, likely due to reduction of (surface) Cu(I)oxide to Cu(m).

Figure 6. Simplified scheme of the adsorbed species present at different potentials in a cyclic voltammogram. A., B., and C. indicate different stages at -0.4 V, -1.0 V, and -1.4 V. The products indicated to be formed from the surface are known from multiple previous studies on electrochemical reduction of CO₂. Desorption of CO₃²⁻ is assumed to explain the large change in intensity between stages A. and B., while formate production is in agreement with the reductive current observed below ~-0.5 V in Figure 5 (b).

As shown in figure 5 (a), at a potential of +0.2 V, adsorption of both configurations of carbonate, i.e. monodentate and bidentate takes place. At 0 V, the adsorption of the carbonate band at 1540 cm⁻¹ is the highest, and as the potential is swept more negatively, it desorbs until finally disappearing at ~-0.4 V. Then, the intensity of the monodentate carbonate band reaches a maximum. Next, what is striking is that this potential also coincides with the appearance of a CO band on the electrode surface. As evident from Figure 5a, CO adsorption is accompanied by dramatic desorption of specifically adsorbed anions^{95, 197}. It is noteworthy that desorption of pre-adsorbed anions has significant activation barriers, and can be overcome by applying negative potentials¹⁹⁸, consistent with our findings. Finally,

as CO is adsorbed on the surface and displaces the adsorbed anions, a sharp increase in cathodic current is observed (Figure 5b), which besides to the reductive formation of CO, might be associated with the production of formate, as indicated in the cycle displayed in Figure 6.

Further increase in CO population on the surface of the electrode is achieved until CO reaches its highest intensity at ~ -0.9 V upon complete removal of monodentate carbonate in accordance with literature^{73, 95, 108}. At more cathodic potentials, desorption of CO from the electrode surface is probably due to the displacement of adsorbed CO by adsorbed hydrogen atoms, and is accompanied by the formation of hydrocarbons (Figure 6)¹⁰⁷.

As the potential is scanned even more negatively, approximately at -0.6 V, the hydroxide band emerges at 520 cm^{-1} . This band continues to grow in intensity as the potential is swept more negatively. It is obvious that Cu^+ species (specifically hydroxide in this case) persists even below the potentials at which adsorbed CO and carbonates are present. As illustrated in Figure 6, the presence of hydroxide is accompanied by the presence of a Cu-C species, of which the exact origin remains to be elucidated. Figure 6 implies the reversibility of the process, although the adsorbed carbonate and CO bands are less intense in an anodic scan, than observed in a cathodic scan. When the potential reaches $+0.4$ V vs RHE, the Cu-OH and Cu-C species disappear, and the surface is oxidized to create the surface oxide Cu_2O .

7.5 Conclusions

In summary, we investigated the CO_2RR process on a Cu electrode by the powerful in-situ SERS technique. Employing isotopic labeling enabled us to reveal the identity of detected species and verify the assignments. Several novel observations have been made. First, this study identified two configurations of adsorbed carbonates, i.e. bidentate and monodentate, and disproves a previous assignment of the 1540 and 360 cm^{-1} bands to carboxylate. Then, another major

finding is the direct observation of displacement of electrolyte anions by CO, a crucial intermediate towards hydrocarbons. Most importantly, Raman spectroscopy resolved the presence of surface species including oxides and hydroxides during CO₂RR at highly negative potentials, which were surprisingly stable against reduction. In addition, another Cu-related compound containing carbon was observed for the first time. On the basis of these results, we propose that Cu-OH and/or Cu-C species might constitute the active site in CO₂RR towards ethylene and methane. To comprehend the role of Cu⁺ species as catalytically active sites for CO₂RR, more experimental and theoretical work is crucial.

7.6 Appendix

Figure S1. In-situ SERS of the Cu surface in CO_2 saturated 0.1 M KHCO_3 , increasing the potential from -1.4 V to +0.6 V. Spectra were collected using a scan-rate of 10 mV/sec, and the potential interval between spectra is 0.2 V. The zoomed area shows the development of bands at 504 and 524 cm^{-1} during an anodic scan and represents the spectra recorded at -1.4, -1.2, -1.0, -0.8, -0.6, and -0.4 V (bottom to top), respectively. A band at 750 cm^{-1} is observed only during the anodic scan at positive current densities, suggesting that it does not belong to any reactive species for CO_2RR . To this date, no research has addressed this band and its origin remains to be elucidated. Furthermore, it is evident that the intensity of adsorbed species in the anodic scan is weaker compared to cathodic scan. This is most possibly due to the fact that at highly negative potential of -1.4 V, significant amount of gaseous products are released from the electrode surface, blocking the Raman probe. Some bubbles remain on the electrode surface and negatively influence the intensity of the spectra during the rest of scan.

Figure S2. In-situ SERS of the Cu surface in CO_2 saturated 0.1 M KHCO_3 , in CV from 0.3 to -1.4 to 0.6 V. Spectra were collected using a scan-rate of 10 mV/sec, and the potential interval between spectra is 0.2 V.

Figure S3. In-situ SERS of the Cu surface in CO_2 saturated 0.1 M KHCO_3 , during cathodic scan from +0.2 to -1.4 V. Spectra were collected using a scan-rate of 10 mV/sec, and the potential interval between spectra is 0.1 V.

Figure S4. Raman Spectrum of 1 M Potassium formate in H₂O.

Figure S5. In-situ SERS of the Cu surface in (a) CO₂ saturated and (b) N₂ saturated 0.1 M KClO₄ showing potential-dependent development of a carbonate band in (a) during a negative scan. The peaks at 460 and 934 cm⁻¹ are indicative of the ClO₄⁻ anion. Spectra were collected during a CV with a scan-rate of 10 mV/sec.

Figure S6. In-situ SERS of Cu surface in CO_2 saturated 0.1 M KHCO_3 showing potential-dependent development of the pair of adsorbed carbonate bands during scan from -0.3 V to +0.2 V and back to -0.4 V. Spectra were collected during a CV with the rate of 10 mV/sec and the potential interval between spectra is 0.1 V.

Figure S7. In-situ SERS of Cu surface in $^{13}\text{CO}_2$ saturated 0.1 M $\text{KH}^{13}\text{CO}_3$ showing potential-dependent development of the adsorbed and in solution carbonate during a negative scan. Spectra were collected during a CV with a scan-rate of 10 mV/sec and the potential interval between spectra is 0.1 V, ranging from +0.3 V to -0.4 V.

Figure S8 and S9. Broad range spectra of *in-situ* SERS of the Cu surface in $^{13}\text{CO}_2$ saturated 0.1 M $\text{KH}^{13}\text{CO}_3$. Spectra were collected during a CV with a scan-rate of 10 mV/sec. On this electrode the adsorbed CO features are less obvious.

Figure S10. In-situ SERS of the Cu surface in CO₂ saturated 0.1 M KDCO₃ in D₂O. Spectra were collected during a CV with a scan-rate of 10 mV/sec.

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Summary

In this thesis, the selective formation of ethylene on Cu electrodes by electrochemical reduction of CO₂/CO was investigated. I propose strategies to more selectively form ethylene on rough Cu electrodes. Fundamental spectroscopic studies were also employed to help understand the formation mechanism of hydrocarbons on Cu electrodes. **Chapter 1** provides motivation and background information on utilization of CO₂. Electrochemical reduction of CO₂ into hydrocarbons could be a promising way to close the carbon cycle.

In **chapter 2**, various experimental setups used in this thesis to evaluate the performance of Cu electrodes in the reduction of CO₂ are described. We also provide brief theoretical background on the main characterization techniques used in this thesis: gas chromatography, ATR-FTIR and Raman spectroscopy.

In **chapter 3**, the influence of the CO₂ partial pressure on the catalytic performance of the oxide-derived copper electrodes in electrochemical reduction reaction is discussed. We observed that the faradaic efficiency of ethylene increased from ~37% to 45% as a result of decreasing the CO₂ partial pressure from 1 to 0.4 atm. We hypothesized that this is due to the rise in local pH, and to test this theory we investigated the effects of potential, buffer concentration and surface roughness on the product distribution. Based on the observations, we confirmed the significant role of local pH conditions on the selectivity of rough Cu electrodes.

In **chapter 4**, we studied electrochemical reduction of various CO/CO₂ mixtures on rough Cu electrodes. We discovered that the highest ethylene faradaic efficiency was obtained at a CO₂ partial pressure of ~0.6 atm (CO partial pressure of 0.4 atm). Besides, we studied the effect of CO partial pressure on electrochemical CO reduction and concluded that ethylene faradaic efficiency was linearly dependent on the CO partial pressure. Next, we investigated the effect of anion composition of the electrolyte on the product distribution of electrochemical CO reduction. Highest

ethylene and lowest methane formation were observed in KOH with the pH of 13, while in phosphate buffer at pH of 4.6 the opposite was found. Finally, in-situ ATR-SEIRAS was employed to help understand the effect of electrolyte anion on the distribution of surface adsorbed species on electrochemically activated Cu surfaces. The results suggest that the CO coverage is enhanced as the pH is increased, and the proton concentration is decreased. At high CO coverage on the surface, C-C coupling is favored and ethylene formation is significantly improved.

In **chapter 5**, we employed ATR-FTIR spectroscopy to investigate electrochemical conversion of CO₂ on a rough Cu electrode fabricated via sputtering. We aimed to obtain insights in the key intermediates and used isotopic labeling to identify the observed peaks. For this purpose, we used 0.1 M NaOH in D₂O solution saturated with CO₂ (¹³CO₂). We observed surface-adsorbed species of formate, carbonate, CO and bicarbonate, respectively, when increasingly more negative potentials were applied. Besides, we hypothesize we were able to detect the CO₂ dimer radical anion, the first and most frequently cited intermediate in CO₂RR in non-aqueous conditions, which we propose to contribute to the formation of CO by disproportionation in aqueous conditions. We were not able to identify any other intermediates, possibly due their short lifetimes.

In **chapter 6**, we investigated the origin of ethylene selectivity on rough Cu electrodes. We employed in-situ electrodeposition to form rough Cu structures and observed enhanced ethylene formation while formation of methane and hydrogen were suppressed. We attributed this to enhanced number of low coordinated sites, as a result of improved roughness. To obtain more insights in the key intermediates that determine the selectivity of CO₂ reduction to ethylene, we compared electrochemical reduction of CO₂ on smooth and roughened Cu electrodes. We concluded that on rough Cu electrodes, a significantly increased CO coverage leads to high rate of CO coupling, and consequently shifted the selectivity toward ethylene. Moreover, we

believe that a high content of Cu hydroxide on the smooth electrode surface plays a role in inhibiting ethylene formation.

Finally, in **chapter 7**, we employed Raman spectroscopy and isotopic labeling to identify surface composition including the oxidation state of Cu. For this purpose, we developed highly SERS active electrodes that showed excellent activity and reversibility in the potential region chosen for this study. We were able to identify carbonates, bicarbonates and CO and their potential dependence. One of the more significant findings to emerge from this study was the presence of Cu oxides and hydroxides at highly negative potentials. Future experimental and theoretical work is needed to comprehend the role of such Cu^+ species as catalytically active sites for CO_2RR .

Samenvatting

In dit proefschrift wordt beschreven hoe procesvariabelen de selectieve vorming van ethyleen in de elektrochemische reductie van CO₂ en/of CO over Cu elektroden beïnvloeden. Het effect van de aangelegde potentiaal, de partiële druk, en de concentratie en chemische samenstelling van het elektrolyt is onderzocht door middel van gedetailleerde gas analyse, aangevuld met inzichten in de chemie die plaats vindt op het oppervlak van koper elektroden, verkregen door middel van Raman en Infrarood spectroscopie.

Hoofdstuk 1 geeft achtergrondinformatie voor de noodzaak om de emissies van CO₂ in de atmosfeer terug te dringen. Elektrochemische reductie van CO₂ naar koolwaterstoffen zou een veelbelovende manier kunnen zijn om de uitstoot daarvan te beperken en de koolstofcyclus te sluiten, en daardoor opwarming van de aarde tegen te gaan.

In **hoofdstuk 2** worden de verschillende toegepaste elektrochemische opstellingen beschreven voor de uitvoering van de reductie van CO₂. Ook worden de belangrijkste analyse technieken behandeld, namelijk gas chromatografie, ATR-FTIR (en speciale manier om Infrarood spectra op te nemen) en Raman spectroscopie.

In **hoofdstuk 3** wordt de invloed van de partiële druk van CO₂ op de katalytische activiteit van koper elektroden onderzocht in KHCO₃ elektrolyt. De efficiëntie naar de vorming van ethyleen verbetert van 37% naar 45% ten gevolge van het verlagen van de partiële druk van CO₂ van 1 naar 0.4 Bar. Een verhoging van de pH op het grensvlak tussen het metaal en het elektrolyt zou een verklaring voor deze observatie kunnen zijn. Om deze hypothese te testen is het effect van potentiaal (en daarmee correlerende stroomdichtheid), de bufferconcentratie en oppervlakteruwheid op de productverdeling onderzocht en gemodelleerd. Op basis van observaties uit deze experimenten wordt bevestigd dat de lokale pH een significante rol speelt in de product selectiviteit op ruwe koperen elektroden.

In **hoofdstuk 4** is de elektrochemische reductie van verschillende CO/CO₂ mengsels op ruwe koperen elektroden bestudeerd. De hoogste faradische efficiëntie van ethyleen wordt verkregen met een partiële druk van CO₂ van 0.6 atm (en samenhangende partiële druk van CO van 0.4 atm). Daarnaast is ook het effect van de partiële druk van CO op de elektrochemische reductie van CO onderzocht. De productiviteit naar ethyleen vertoont een oplopend verband met de partiële druk van CO. Vervolgens is het effect van de anion samenstelling van het elektrolyt op de productverdeling tijdens de elektrochemische reductie van CO onderzocht. In een KOH oplossing met een pH van 13 werd de hoogste productie van ethyleen en de laagste productie van methaan waargenomen, terwijl in de aanwezigheid van een fosfaat buffer met pH 4.6, de vorming van koolwaterstoffen beperkt is. Tot slot, is gebruik gemaakt van in-situ ATR-SEIRAS om het effect van het elektrolyt anion op product selectiviteit te begrijpen. De resultaten doen vermoeden dat de bedekking van de elektrode met CO verhoogd wordt bij toenemende lokale pH, waardoor de vorming van ethyleen wordt bevorderd.

In **hoofdstuk 5** wordt gebruik gemaakt van ATR-FTIR spectroscopie om de elektrochemische reductie van CO₂ op ruwe koperen elektroden nader te onderzoeken. Deze ruwe koperen oppervlakten zijn gefabriceerd middels een sputtertechniek en aangebracht op een Si kristal. Er is gebruik gemaakt van verschillende isotopen van water (D₂O) en CO₂ (¹³CO₂) om verschillende pieken te identificeren. Een 0.1 M NaOH in D₂O oplossing verzadigd met CO₂ (¹³CO₂) is gebruikt voor deze experimenten. Bij toenemende negatieve potentialen kan achtereenvolgens geadsorbeerd formiaat, carbonaat, CO en bicarbonaat waar worden genomen. Daarnaast zijn sterke aanwijzingen verkregen voor de vorming van het CO₂ dimeer radicaal anion, een mogelijk tussenproduct in de elektrochemische reductie van CO₂. Verdere reductie van dit dimeer radicaal anion leidt tot de vorming van CO en carbonaat anionen (CO₃²⁻).

In **hoofdstuk 6** wordt de het effect van de morfologie van ruwe koperen elektroden op de selectiviteit naar ethyleen nader onderzocht. In-situ elektrodepositie door toevoeging van koperzouten aan het elektrolyt, werd toegepast om ruwe Cu-structuren te vormen. Dit leidt tot verbeterde ethyleenvorming terwijl de vorming van methaan en waterstof wordt onderdrukt. We hebben dit toegeschreven aan een groter aantal laag gecoördineerde sites als gevolg van verbeterde ruwheid. Raman spectroscopie laat zien dat de oppervlakte concentratie van CO aanzienlijk hoger is op ruwe Cu-elektroden, wat leidt tot een hoge mate van CO-koppeling, en daardoor hoge selectiviteit naar ethyleen. Verder is de vorming van een hydroxide verbinding bij negatieve potentiaal waargenomen, waarvan de aanwezigheid een negatieve correlatie vertoont met de productiviteit van de elektrode in de vorming van koolwaterstoffen.

In **hoofdstuk 7** hebben we Raman-spectroscopie en verschillende isotopen van water (D_2O) en CO_2 ($^{13}CO_2$) gebruikt om de belangrijkste tussenproducten en de oxidatietoestand van Cu tijdens de reactie te identificeren. Voor dit doel hebben we zeer actieve SERS elektroden ontwikkeld die uitstekende activiteit en reproduceerbaarheid vertoonden in het toegepaste bereik van de elektrochemische potentiaal. De potentiaal afhankelijkheid van geadsorbeerde carbonaten, bicarbonaten en CO zijn geïdentificeerd. Een belangrijke bevinding was de aanwezigheid van Cu-oxiden en -hydroxiden, en een mogelijke Cu-C verbinding bij zeer negatieve elektrochemische potentialen. Toekomstig experimenteel en theoretisch werk is nodig om de rol van dergelijke Cu-OH en Cu-C verbindingen in de katalytische conversie van CO_2 beter te begrijpen. Zoals beschreven in hoofdstuk 6, bestaat het vermoeden dat de aanwezigheid van deze verbindingen de activiteit en de stabiliteit van de elektrode negatief beïnvloeden.

List of Publications

1. **Moradzaman, M.**, Sánchez-Martínez, C. and Mul, G. "Effect of partial pressure on product selectivity in Cu-catalyzed electrochemical reduction of CO₂." *Sustainable Energy & Fuels* 4 (2020): 5195-5202
2. **Moradzaman, M.** and Mul, G. "Infrared analysis of interfacial phenomena during electrochemical reduction of CO₂ over polycrystalline copper electrodes." *ACS Catalysis* 10 (2020): 8049–8057.
3. **Moradzaman, M.** and Mul, G. "In situ Raman study of potential dependent surface adsorbed carbonate, CO, OH and C-species on Cu-electrodes during electrochemical reduction of CO₂." *ChemElectroChem* (2021).
4. **Moradzaman, M.** and Mul, G. "Optimizing CO coverage on rough copper electrodes: effect of the partial pressure of CO and electrolyte anions (pH) on selectivity toward ethylene". *The Journal of Physical Chemistry C* (2021).
5. **Moradzaman, M.** and Mul, G. " Correlating the surface structure and composition of copper to high selectivity towards ethylene in reduction of CO₂ ". In preparation.

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