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Electrocatalytic carbon dioxide reduction - A mechanistic study

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5 | Two pathways for the formation of ethylene in CO reduction on single crystal copper electrodes

Abstract

Carbon monoxide is a key intermediate in the electrochemical reduction of carbon dioxide to methane and ethylene on copper electrodes. We investigated the electrochemical reduction of CO on two single crystal copper electrodes and observed two different reaction mechanisms for ethylene formation: a first pathway that has a common intermediate with the formation of methane and that takes place preferentially at (111) facets or steps, and a second pathway at (100) facets in which CO is selectively reduced to ethylene at relatively low overpotentials. The (100) facets seems to be the dominant crystal facet in polycrystalline copper, opening up new routes to an affordable (photo-)electrochemical production of hydrocarbons from CO₂.

5.1 Introduction

The low-temperature reduction of carbon dioxide to hydrocarbons could be a very important step in a future sustainable carbon energy cycle.⁹⁸ Since the discovery by Hori *et al.* in 1985 it has been known that carbon dioxide can be electrochemically reduced to methane and ethylene, using copper electrodes.² The formation of methane and especially ethylene is surprising, and only takes place to a significant extent on copper electrodes. In spite of the extensive literature, the molecular mechanism is still unclear, in particular in relation to the carbon-carbon coupling step leading to the formation of ethylene. Understanding this C-C bond formation is important as it would open up routes to the production of high-energy fuels by the (photo-)electrochemical reduction of CO₂.

It is known that carbon monoxide is a key intermediate in the carbon dioxide reduction, and that from carbon monoxide, methane and ethylene are formed following different mechanisms.^{4,5,84,85} The central role of carbon monoxide as the intermediate in the formation of such highly non-trivial products as methane and ethylene follows from the fact that carbon monoxide is the only one-carbon molecule that gives the same product spectrum as carbon dioxide on a copper electrode, as documented in detail in the review by Hori.⁵ The formation of methane from CO depends on pH, in such a way that the rate determining step must involve the transfer of a proton and an electron.⁸⁴ Our own experiments presented in Chapter 3, as well as DFT calculations by Peterson *et al.*⁸⁶ suggested that the key intermediate to form methane is CHO_{ads}. The formation of ethylene from CO, on the other hand, does not depend on pH.⁸⁴ Therefore, a dimer of carbon monoxide, whose formation does not involve the transfer of an hydrogen atom but does depend on potential (*i.e.* involves electron transfer), has been suggested as the key intermediate in the C-C coupling.^{4,161}

Hori *et al.* showed that the extent of methane and ethylene formation sensitively depends on the surface orientation of the copper electrode.⁸⁷ On the (111) facet of the copper fcc crystal the formation of methane is favored, whereas on the (100) facet the formation of ethylene is dominant. Recent DFT calculations by Durand *et al.*⁸⁸ predicted that the limiting potential for the formation of the intermediates of the CO₂ reduction to CH₄ is lower on the Cu(211) surface compared with the Cu(111) and Cu(100) surface. No detailed DFT-based mechanism for the formation of ethylene

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was suggested, although these authors also consider CHO_{ads} as the intermediate in the formation of ethylene. Since the experiments by Hori *et al.* were carried out as long-term electrolysis experiments at a constant current, detailed information on the pathways of the carbon-carbon bond formation and its potential dependence is missing. Therefore, we report here on the reduction of carbon monoxide on two basal planes, Cu(111) and Cu(100), using online electrochemical mass spectrometry, to investigate the pathway to ethylene. This tip-based sampling technique allows to follow the formation of volatile reaction intermediates and products while changing the potential at the electrode surface, and is similar to the DEMS (Differential Electrochemical Mass Spectrometry) technique.^{108,162,163}

5.2 Experimental

All experiments were carried out in an electrochemical cell using a three-electrode assembly at room temperature. The cell and glassware were first cleaned by boiling in a mixture of 1:1 concentrated sulfuric and nitric acid and before each experiment by boiling in ultra clean water (Millipore MilliQ gradient A10 system, $18.2 \text{ M}\Omega \cdot \text{cm}$). A gold wire was used as counter electrode and a reversible hydrogen electrode (RHE) in the same electrolyte was used as reference electrode. All potentials in this paper are referred to this electrode. The potential was controlled using an Ivium A06075 potentiostat.

The experiments were carried out in $0.1 \text{ M K}_2\text{HPO}_4 + 0.1 \text{ M KH}_2\text{PO}_4$ (pH 7) or 0.1 M NaOH (pH 13) prepared from high purity reagents (Merck Suprapur, Sigma-Aldrich TraceSelect) and ultra clean water. Argon (Air Products, 5.0) bubbling was used to deaerate the electrolyte before saturation of the electrolyte with carbon monoxide (Linde, 4.7). The carbon monoxide was used without further purification. Bubbling CO through a concentrated hydroxide solution before entering the working solution did not affect our measurements, suggesting that the CO used is uncontaminated.

The single crystal copper electrodes used were bead-type electrodes cut and polished with an accuracy down to 0.5° (icryst). Prior to each experiment the electrode was electropolished in 66% H_3PO_4 at 3 V vs. a Cu counter electrode for 10 seconds.¹⁵⁴ Blank cyclic voltammograms (CV) in 5 mM H_2SO_4 were taken regularly to verify that our electrode surfaces main-

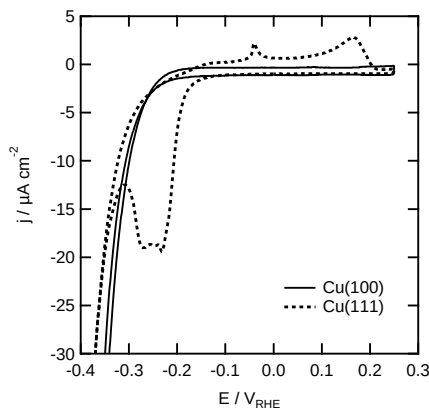


Figure 5.1 Cyclic voltammograms of Cu(100) and Cu(111) in 5 mM H_2SO_4 with a scan rate of 10 mV s^{-1} .

tain the right surface orientation. We used H_2SO_4 because the adsorption and desorption of sulphate on Cu(111) have characteristic features between the potentials of hydrogen evolution and copper dissolution, and therefore serve as a structural probe. On Cu(100), sulphate is not visible in the CV in this potential region. Examples of the CVs are shown in Fig. 5.1, and these voltammetric profiles agree well with the literature.¹⁴⁶

Online Electrochemical Mass Spectrometry (OLEMS) was used to detect the gaseous products formed during the reaction.¹⁰⁸ The reaction products at the electrode interface were collected with a small tip positioned close ($\sim 50 \text{ }\mu\text{m}$) to the electrode. The tip is a 0.5 mm diameter porous Teflon cylinder with an average pore size of 10–14 μm in a Kel-F holder. This tip is connected to a mass spectrometer with a PEEK capillary. The tip configurations were cleaned in a solution of 0.2 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 2 M H_2SO_4 and rinsed with ultra pure water before use. The products were measured while changing the potential of the electrode from 0.0 to -1.0 V and back with 1 mV s^{-1} . We only show $m/z = 2$ (H_2^+), 15 (CH_3^+) and 26 (C_2H_2^+) which correspond to respectively hydrogen, methane en ethylene, but also measured other mass fragments to distinguish, for example, ethylene from ethane. A secondary emission multiplier (SEM) voltage of 2400 V was used for all

mass fragments except hydrogen ($m/z = 2$) where a SEM voltage of 1200 V was used, because of the relatively high abundance of hydrogen gas caused by the reduction of water. We note that for most of the measurements to be described in this chapter, the Faradaic current is mainly determined by hydrogen evolution and does not give much specific information about the CO reduction.

Because the equilibration of the pressure in the system after introduction of the tip in the electrolyte takes a very long time, all mass fragments show a small decay during the measurement. We corrected for this background by fitting a double exponential function to the data in the potential regions where no change in activity is observed and subtracted this fit from the data. A mild smoothing function is applied to the data for the noise caused by gas bubble formation. All mass fragments shown in this chapter are background corrected in this way. Also note that between measurements, absolute values of the mass signals may vary as it is difficult to reproducibly place the OLEMS tip in relation to the single crystal electrode.

5.3 Results and discussion

Fig. 5.2 shows the reduction of carbon monoxide on Cu(111) in pH 7 (phosphate buffer, plotted with a dashed line with the current density and the mass signals on the left axis) and in pH 13 (NaOH, plotted with a solid line with the current density and the mass signals on the right axis). The potential is changed from 0 to -1 V and back with 1 mV per second. The recorded current is shown in the middle panel, and the volatile products measured during this potential scan are shown in the bottom panel. At -0.4 V the current increases due to the formation of hydrogen, both for pH 7 and 13 (although pH 13 appears to be more active for H_2 evolution). For all measurements performed, this current is mainly determined by hydrogen evolution and does not give any specific information about the CO reduction. The hydrogen evolution leads to the formation of gas bubbles trapped between the tip and the single crystal electrode and this explains the somewhat noisy character of the observed mass signals. At pH 13, hardly any hydrocarbons are observed, only very small amounts of methane (represented by $m/z = 15$, CH_3^+) and ethylene (represented by $m/z = 26$, $C_2H_2^+$) are formed at the most negative potentials, as well as a very small amount of ethylene but no methane) at -0.45 V. The latter is probably due to some (100) defects

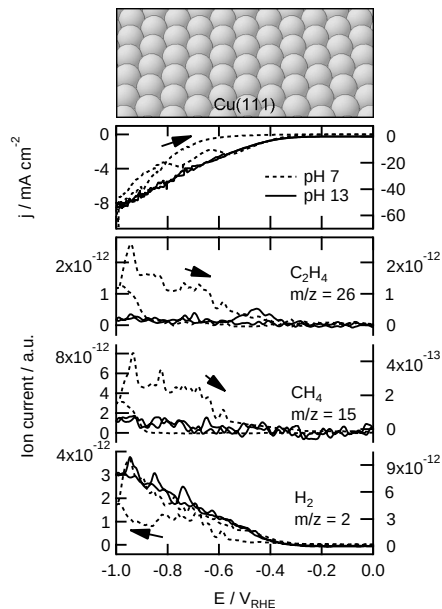


Figure 5.2 Top: (111) facet of the Cu fcc crystal. Middle: cyclic voltammograms on Cu(111) for the reduction CO saturated (~ 1 mM) in a phosphate buffer (pH 7) and NaOH (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for pH 7 is shown with a dashed line and plotted against the left axis, data for pH 13 is shown with a solid line and plotted against the right axis.

in the crystal, as can be concluded by comparing this to the results obtained on Cu(100) to be presented in Fig. 5.4. At pH 7, both methane and ethylene are formed, starting at -0.8 V, and both continue being formed in the positive-going scan until -0.4 V. Note that the potential dependence of the $m/z = 15$ curve is very similar to that of the $m/z = 26$ curve. One possible explanation for this similarity is that both masses are fragments of the same molecule. However, besides the mass fragments of methane and ethylene we did not find other mass fragments with the same potential dependence, which shows that $m/z = 15$ and 26 are fragments of different molecules. Therefore, we conclude that there must be a common (surface-adsorbed) in-

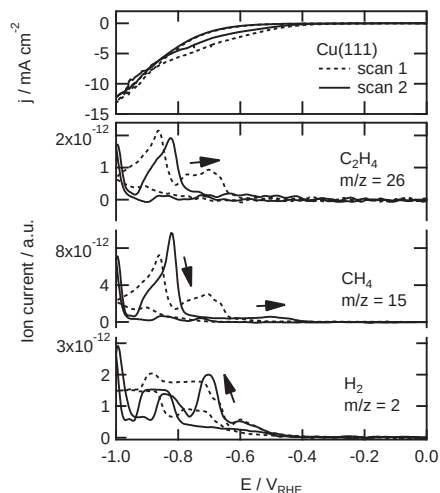


Figure 5.3 Hydrocarbon formation during consecutive scans of CO reduction on Cu(111). Top: cyclic voltammograms on Cu(111) for the reduction of a CO saturated (~ 1 mM) phosphate buffer (pH 7). Bottom: associated mass fragments of volatile products measured with OLEMS.

intermediate in the reduction of CO (and hence CO_2) to CH_4 and C_2H_4 , since methane and ethylene are formed with the same potential dependence on Cu(111). We suggest that the hydrogenation of CO, to form CHO_{ads} , is the key step in the formation of both methane and ethylene on Cu(111). This conclusion agrees well with the calculations by Peterson *et al.*, which indicated that for a stepped Cu(111) surface “the key step in the formation of the hydrocarbons CH_4 and C_2H_4 is the hydrogenation of the adsorbed CO to form CHO_{ads} ”.⁸⁶

When performing our potential-scanning experiments we did not observe the fast and complete deactivation of the Cu electrode as is reported in literature during long term electrolysis measurements at a constant current.¹⁰⁷ An example of two consecutive scans of CO reduction on Cu(111) at pH 7 is shown in Fig. 5.3. Comparable to the data shown in Fig. 5.2, the methane and ethylene traces are very similar, and their formation only starts at ~ 0.9 V, continuing until ~ 0.6 V in the positive going scan. If we ob-

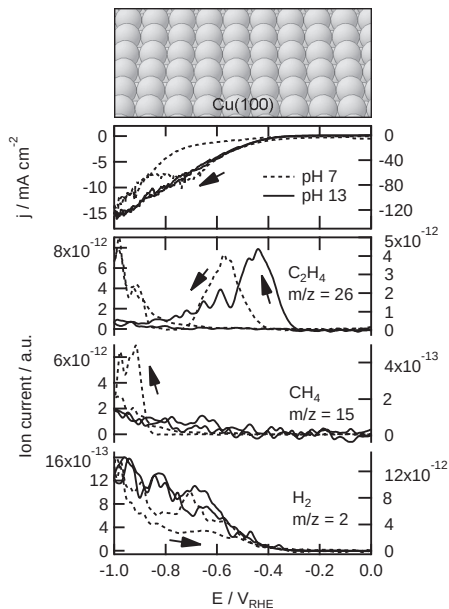


Figure 5.4 Top: (100) facet of the Cu fcc crystal. Middle: cyclic voltammograms on Cu(100) for the reduction CO saturated (~ 1 mM) in a phosphate buffer (pH 7) and NaOH (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for pH 7 is shown with a dashed line and plotted against the left axis, data for pH 13 is shown with a solid line and plotted against the right axis.

serve a decrease in hydrocarbon formation, it occurs especially between the first and second scan, but the potentials at which hydrocarbon formation takes place do not change, for neither of the electrodes we measured.

The reduction of CO was also performed on a Cu(100) electrode, the results of which are shown in Fig. 5.4. The magnitude of the observed Faradaic current on Cu(100) is about twice as large as the current on Cu(111), which primarily reflects the enhanced ability of Cu(100) to catalyze hydrogen evolution.¹⁴⁷ The observed hydrocarbon formation differs remarkably from that on Cu(111). Ethylene is formed already at -0.4 V in pH 7 and -0.3 V in pH 13. Ethylene formation exhibits a maximum at -0.45 and -0.6 V, respectively,

after which it decreases and eventually stops. The current and charge corresponding to this peak of ethylene formation is too high to be explained by the reduction of a surface-adsorbed species. No methane is observed at these potentials. At -0.8 V in pH 7, the formation of ethylene is again observed, now accompanied by the formation of methane, similar to the simultaneous formation of CH_4 and C_2H_4 on Cu(111) at these potentials. This simultaneous formation of CH_4 and C_2H_4 below -0.8 V is not observed at pH 13 on Cu(100), in agreement with Cu(111) at this pH.

These results strongly suggest that there are two separate pathways to form ethylene: one that shares an intermediate with the pathway to methane, as we observe on Cu(111) and below -0.8 V on Cu(100) at pH 7, and a second pathway that only occurs on Cu(100). For this second pathway we suggest that the formation of a CO dimer is the key intermediate to form ethylene. Such a surface dimer could explain the unique selectivity to ethylene (for detailed arguments, see Chapter 3), and is in agreement with the suggestion of Gatrell *et. al*, who proposed that this CO dimer would be more stable on Cu(100) surfaces.⁴

As can be seen in Fig. 5.4, we only observe ethylene formation at low overpotentials in the negative going scan, as ethylene is not formed at potentials positive of -0.8 V in the positive going scan. However, the ethylene formation is not permanently blocked. An example of repeated scans of CO reduction on Cu(100) at pH 7 is shown in Fig. 5.5, for clarity only scan 1 and 3 are shown. The first scan is plotted with a dashed line to the left axis and the third scan is plotted with a solid line to the right axis. By comparing the left and right axis it can be seen that the hydrocarbon formation has decreased by a factor of four between the first and third scan. Because also both the current and the hydrogen evolution decreased by a factor of two, deactivation cannot be the only explanation for the decreased hydrocarbon formation, since hydrogen evolution is promoted on deactivated copper surfaces.¹⁰⁷ If we stop the potential-scan at a potential where the hydrocarbon formation is relatively high, an example of the evolution of ethylene and hydrogen on Cu(100) at -0.4 V is shown in Fig. 5.6, the ethylene formation shows a fast decrease over time. On a freshly polished electrode (solid lines) the hydrogen formation increases when the ethylene formation decreases. On an electrode that has been cycled to negative potentials several times already (dotted lines) the initial ethylene production is lower compared with

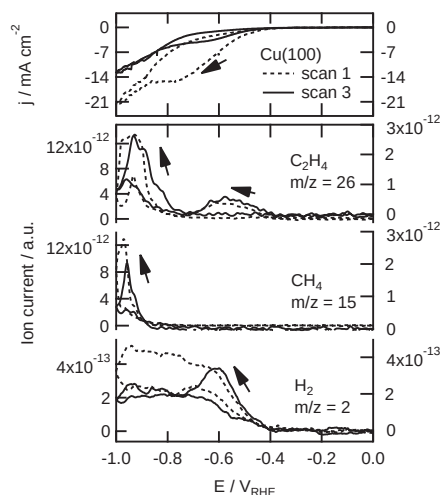


Figure 5.5 Hydrocarbon formation during multiple scans of CO reduction on Cu(100). Top: cyclic voltammograms on Cu(100) for the reduction of a CO saturated (~ 1 mM) phosphate buffer (pH 7). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for scan 1 is shown with a dashed line and plotted against the left axis, data for scan 3 is shown with a solid line and plotted against the right axis.

the freshly polished electrode, which is in agreement with the results shown in Fig. 5.5, and the hydrogen evolution does not increase anymore.

To investigate why ethylene is only formed on Cu(100) in the negative going scan at less cathodic potentials, we performed consecutive scans of CO reduction at pH 13 on Cu(100) and increased the negative vertex potential with each scan, the results of which are shown in Fig. 5.7. In the first scan (lightest gray) the ethylene formation increases when the potential was reversed at -0.38 V. In the second scan to -0.4 V the ethylene formation is similar for the positive and negative going scan. In the third scan the ethylene formation starts to decrease below -0.42 V, and the ethylene formation in the positive going scan is much lower than that in the negative going scan, and in the fourth scan the ethylene formation is already lower in the negative-going scan. The hydrogen formation shows the op-

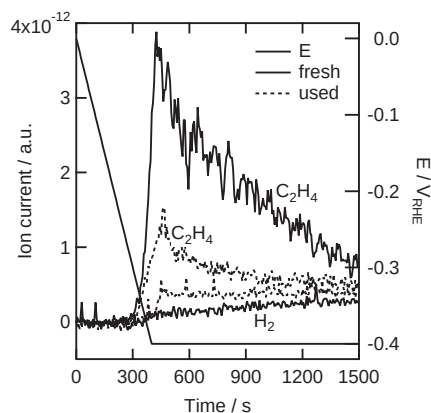


Figure 5.6 The formation of ethylene and hydrogen over time in a CO saturated NaOH solution, while scanning the Cu(100) electrode to -0.4 V and holding it at this potential. The data shown with solid lines is measured on a freshly polished electrode, the data with the dashed lines is measured on an electrode that has been cycled to negative potentials several times.

posite trend: there is no hydrogen formation in the first scan, only a minor hydrogen formation in the second scan, and the hydrogen formation in the fourth scan is significantly larger compared with the third scan. This is also reflected in the current, which increases from scan 1 to scan 4. These results clearly show that the deactivation is strongly potential dependent. A possible explanation for these observations is reconstruction of the electrode surface. On Cu(100) in acidic media a hydrogen induced reconstruction has been reported with a concomitant increase in the hydrogen evolution reaction rate.¹⁶⁴ Therefore, our observed increase in hydrogen formation and decrease in hydrocarbon formation could possibly be explained by such a reconstruction, but clearly, the details of this deactivation phenomenon remain to be understood. We also note that, according to Hori,¹⁰⁷ the deposition of metal impurities from the electrolyte is the most common reason for deactivation. Given the partial reversibility of the deactivation phenomenon shown in Fig. 5.7 we consider this explanation less likely, although we do not exclude that such effects may take place in our

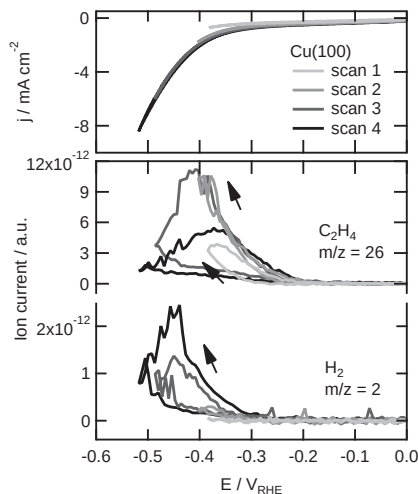


Figure 5.7 Consecutive scans of CO reduction with increasing cathodic potentials. Top: Cyclic voltammograms for the reduction of a saturated CO solution (~ 1 mM) on Cu(100) in NaOH (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS.

experiments on a longer time scale. One may also note that on Cu(111) the formation of methane and ethylene is enhanced on the positive-going back scan (see Fig. 5.2) suggesting a potential-driven activation of the (111) surface, in contrast to the potential-driven deactivation of ethylene formation on Cu(100).

Fig. 5.8 shows the results for CO reduction performed on a polycrystalline copper electrode. On this electrode, on which the various facets of the fcc crystal planes should be present, ethylene is formed at -0.5 V in pH 7 and -0.3 V in pH 13, similar to Cu(100) shown in Fig. 5.4. Also, the ethylene and especially methane formation below -0.8 V in pH 7 is very similar to that on Cu(100). Since the observed hydrocarbon formation on polycrystalline copper is similar to that on Cu(100), this suggests that the dominant crystal facet on polycrystalline copper is the (100) facet. Such a conclusion has been drawn previously, based on blank voltammetry at copper in alkaline media.¹⁵¹

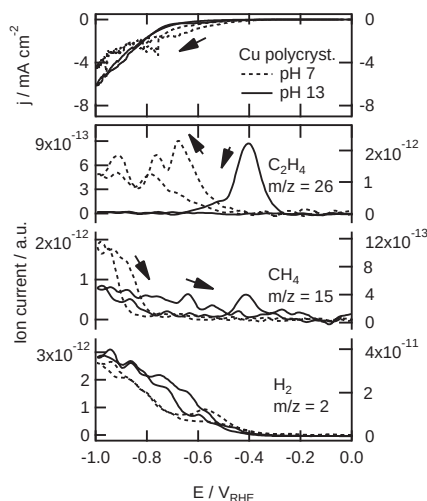


Figure 5.8 Top: Cyclic voltammograms for the reduction of a saturated CO solution (~ 1 mM) on polycrystalline copper in a phosphate buffer (pH 7) and NaOH (pH 13). Bottom: associated mass fragments of volatile products measured with OLEMS. Data for pH 7 is shown with a dashed line and plotted against the left axis, data for pH 13 is shown with a solid line and plotted against the right axis.

We note that our experiments at only two different pH values cannot accurately reflect the true pH dependence of the CO reduction. According to the results of Hori *et al.* the formation of methane should take place at the same potential on the RHE scale in both pH 7 and pH 13.⁸⁴ However, at pH 13, H_2 evolution is about an order of magnitude faster than at pH 7, presumably due to the absence of specifically adsorbing anions at pH 13,¹⁴⁷ and this may suppress CO reduction. Clearly, the influence of pH and electrolyte composition, such as the presence of strongly adsorbing anions, requires further scrutiny. For a more detailed investigation of the influence of pH and adsorbing anions we refer to Chapter 7. Furthermore, we note that because CO reduction currents are always low and also because hydrogen evolution close to the electrode leads to an effective stirring of the

electrolyte, it is difficult to estimate any mass transport effects in relation to CO reduction.

5.4 Conclusions

Summarizing, our experiments provide strong evidence for the idea that ethylene may be formed through two different mechanisms: a first pathway that has a common intermediate with the formation of methane and that takes place both at (111) and (100) surfaces, and a second pathway in which CO is selectively reduced to C_2H_4 at relatively low overpotentials, presumably through the formation of a surface adsorbed CO dimer.^{4,161} The latter pathway takes place preferentially at (100) facets. Moreover, the crystal plane at which this selective reduction to ethylene takes place, seems to be the dominant crystal facet in polycrystalline copper. These insights open up new routes to an affordable (photo-)electrochemical production of fuels from CO_2 , especially because the selective ethylene formation pathway from CO has a remarkably low overpotential.