



Controlling the selectivity of CO₂ electroreduction on copper: The effect of the electrolyte concentration and the importance of the local pH



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ABSTRACT

In the present study we demonstrate that the activity and selectivity of copper during the CO₂ electrochemical reduction can be tuned by changing the concentration of the bicarbonate electrolyte. Comparing the absolute formation rate and Faradaic selectivity of H₂, CH₄, CO, and C₂H₄ as a function of the applied electrode potential, we show that variations in the bulk buffer capacities of the electrolyte have substantial impact on absolute product formation rates and relative faradic selectivity. We find that high concentrations of bicarbonate improve the overall Faradaic CO₂ electroreduction activity, largely due to higher absolute formation rates of H₂ and CH₄. In lower-concentrated bicarbonate electrolytes with their lower overall activity, the selectivity toward ethylene was drastically enhanced. Following earlier theoretical work, we hypothesize the pH near the copper electrode interface to largely account for the observed effects: diluted KHCO₃ solutions allow for more alkaline local pH values during CO₂ electroreduction. Our study highlights the controlling role of the interfacial pH on the product distribution during CO₂ reduction over a wide electrode potential range.

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1. Introduction

In recent years the electrochemical CO₂ reduction has attracted attention as an alternative method to produce synthetic fuels from CO₂ and water [1–3]. Such methods would involve the utilization of waste CO₂ to make hydrocarbons, or CO-rich feeds of high interest for industry. Ideally, electricity from renewable sources would be the driving force for this reaction, making this process CO₂ neutral. Furthermore, the CO₂ reduction reaction (CO₂RR) would allow storing the excess of electricity from renewable sources into carbon based chemicals that can be used as fuels within the existing technologies [4].

Copper is the most studied material as catalyst for this process, given its unique capability of making hydrocarbons in considerable amounts [5–10]. Nevertheless, CO₂RR on copper is not highly selective to one particular product and results in a mixture in which the main products are H₂, CO, CH₄ and C₂H₄ [11–13]. In addition, the reaction takes place at high overpotentials, which implies important energy losses. Given these challenges, the technological

viability of this process relies on the development of more efficient and selective catalysts. In order to achieve this goal it is crucial to gain fundamental understanding of the different factors that control catalytic activity of copper.

It has been established that the selectivity of the CO₂RR depends on many factors such as the working potential, the pretreatment of copper surface and the nature of the electrolyte [9,11,14,15]. The local pH, however, is a kinetic parameter, the effect of which on rate and selectivity has often been overlooked.

Hori et al. [16] were among the first to show that the formation of CH₄ depends on proton concentration, while that of ethylene is not affected by the pH. Consistently with this observation, ethylene has been the predominant hydrocarbon product in basic electrolytes, while in acidic or neutral solutions CH₄ formation was preferred.

Recently, Schouten et al. [17–19] studied the CO reduction on Cu single crystals in different pHs. In accordance with Hori's studies, they observed that the onset potential for CH₄ is dependent on pH, the same was found for ethylene formation in Cu (1 1 1) facet. On the contrary, the onset potential for ethylene on Cu (1 0 0) was independent of pH, suggesting a mechanism for ethylene formation on Cu (1 0 0) in which proton transfer is not the rate determining step [20].

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In contrast with common electrocatalytic reactions, CO₂ reduction is usually carried out at close to neutral pH. Under such conditions small changes in proton concentration can have a dramatic effect on the pH. During the electrochemical CO₂ reduction, the pH near the electrode surface is expected to be higher than in the bulk due to proton consumption. Gupta et al. [5] presented a mathematical study to estimate the local pH during CO₂ electroreduction. According to their finding the local pH can be up to 6 units higher than in the bulk pH. How big this difference is, is determined by three main factors, the thickness of the diffusion layer, the current density and the electrolyte buffer capacity. Therefore, the effect that different electrolytes have on the selectivity can partially be attributed to a local pH effect. In electrolytes with low buffer capacities such as KClO₄ the local pH is expected to be high enhancing the selectivity of C₂ products. On the contrary, in buffered electrolytes like phosphate the production of methane is favored over ethylene due to a local pH close to neutral [11].

The importance of the buffer capacity becomes evident when working with different bicarbonate concentrations. This effect was first observed by Hori and co-workers who studied the CO₂ and CO reduction at one constant current in different KHCO₃ concentrations. They observed that methane was favored in high concentrations of bicarbonate which is attributed to a difference in buffer capacity of the electrolytes. Consistently, Mul and co-workers recently observed that the production of hydrocarbons on Cu nanoparticles at constant potentials was clearly affected by concentration of KHCO₃ [21]. Herein, we expand previous studies on the local pH by doing a potential dependence study of the CO₂RR on polycrystalline copper in different KHCO₃ concentrations. In accordance with previous results, high concentration of bicarbonate, in which the local pH is expected to be close to neutral, favored methane formation. On the contrary, a higher selectivity toward ethylene was observed on low bicarbonate concentrations. More importantly, we observed that the onset potential and the formation rate dependence on potential for methane are also determined by the electrolyte's buffer capacity. Interestingly, this is not the case for ethylene, for which the formation rate follows the same Tafel relation in all the studied KHCO₃ concentrations. These results indicate that methane formation is determined by the local pH while the ethylene formation is independent from the local pH.

2. Materials and methods

Electrochemical measurements were carried out in a costume-made H-cell, in which the working electrode was separated by a Nafion® membrane. The glassware was cleaned in a NOCHROMIX® bath followed by concentrated HNO₃. Afterwards, the cell was rinsed and sonicated with ultra-pure water several times, and dried at T=60 °C in a drying cabinet.

Each working compartment was filled with 125 mL of CO₂ (Air liquid 4.5) saturated electrolyte. For this study 3 different concentration of KHCO₃ (0.05 M, 0.1 M and 0.2 M) were used as electrolyte. The pH of the saturated solution was determined by SympHony SP70P pH-meter.

A platinum mesh 100 (Sigma–Aldrich 99.9%) was used as counter electrode (CE) and a leak-free Ag/AgCl electrode was used as reference electrode (Hugo Sachs Elektronik Harvard apparatus GmbH). The working electrode consisted of a Cu foil (Alfa Aesar 99.999%) contacted by a gold clamp. Prior to each experiment the Cu foil was polished mechanically using diamond pastes particle diameter down to 1 μm, after which the electrode was sonicated in ultra-pure water–acetone–water. The morphology of the polished copper electrode was investigated by scanning electron microscopy (SEM). SEM was measured in secondary electron mode with a Jeol 7401F field emission SEM operated at 10 kV.

Table 1

Bulk pH and Ohmic resistance values as a function of bicarbonate concentration in the CO₂ saturated electrolyte.

Bulk KHCO ₃ concentration (M)	Bulk pH	Ohmic resistance (Ω)
0.05	6.5	17.75
0.1	6.8	11.15
0.2	7.15	3.46

Every measurement was started with a linear voltammetric sweep, performed with a scan rate of 5 mV/s, between –0.1 V vs. NHE and the working potential, followed by a 10 min chronoamperometric measurement. All reported potentials are corrected for Ohmic drop determined by electrochemical impedance spectroscopy (EIS). EC-Lab software was used to automatically correct 75% of the Ohmic drop, the remaining 25% was corrected manually. For each measurement a freshly polished copper foil and new electrolyte were used to ensure that adsorbates from previous experiments did not influence the result. At the end of the amperometric step, the gas products were analyzed by gas chromatography (Shimadzu GC 2014) equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Argon (Air liquid 5.0) was employed as carrier gas.

The relative Faradaic selectivity FS of the gaseous products was determined by calculating the charge used in the production of each product divided by the sum of the charge of all products, as shown in Eq. (1):

$$FS_i = \frac{z_i X_i}{\sum z_i X_i} \cdot 100 \quad (1)$$

where z represents the number of electrons needed for the formation of each product and X : the product's formation rate.

In some cases the liquid products were analyzed by high performance liquid chromatograph (Agilent 1200 series) equipped with an organic acid resin from Ziemer chromatographie® column, a reflection index detector and a UV detector.

3. Results

We studied the activity and selectivity of copper toward the CO₂ electroreduction at various bulk electrolyte concentrations and overpotentials. Fig. 1 shows SEM images of the polished copper electrode before the electrochemical measurements. Previous studies suggested that a polished Cu surface should consist predominantly of low index facet such as (100) and (111) [14,22]. However, Fig. 1 shows slightly rough and structured surface with some grooves of different width. In such a surface an important amount of low coordinated defective sites is expected to be present.

The KHCO₃ concentration has a clear effect on the bulk pH and the Ohmic resistance of the electrolyte (see Table 1). As expected a lower concentration results in a higher resistance due to a lower conductivity. Lower concentrations also result in a lower bulk pH, given the equilibrium between HCO₃[–]/H₂CO₃:



In contrast, the local pH was predicted to follow an opposite trend [5,21]. The exact pH value at the interface, however, will also depend on the reduction current and therefore it would be different for each reaction point. For this reason we report our results on the NHE scale instead of on the commonly used RHE scale. The latter one would require determining the exact local pH at the interface which can be challenging.

The linear sweep voltammetry measurements in Fig. 2a represent the overall reaction rates of the catalytic processes occurring on the Cu surface. We observed that both the onset potential and the total currents are affected by the KHCO₃ concentration. At high

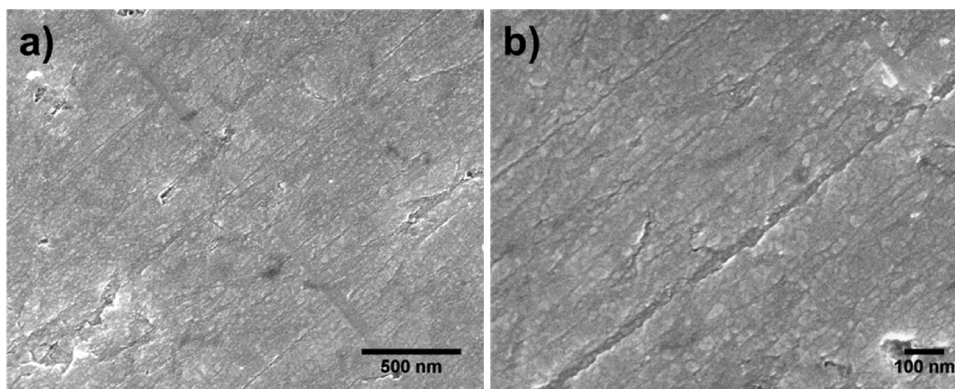


Fig. 1. SEM image of the as prepared Cu foil (after mechanically polishing), with two different magnifications: (a) 50,000 \times and (b) 100,000.

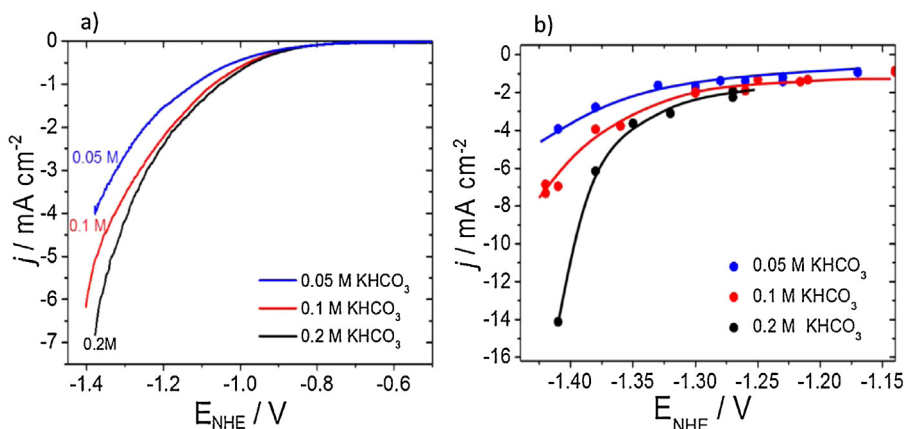
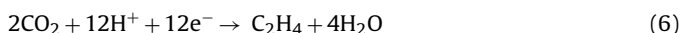
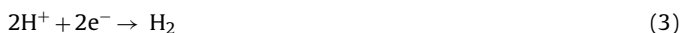


Fig. 2. Activity measurements for polycrystalline copper in CO_2 saturated 0.05 M KHCO_3 (blue), 0.1 M KHCO_3 (red) 0.2 M KHCO_3 (black). (a) Linear sweep voltammetry in CO_2 saturated electrolyte. (b) Geometric current density recorded during the chronoamperometric step. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

concentration, copper exhibits a larger catalytic reduction activity. The observed current is attributed to two simultaneous reactions: hydrogen evolution reaction (HER) and CO_2RR :



In order to distinguish between these processes it is necessary to quantify the formation rate of the various reaction products. For this purpose we performed bulk electrolysis at a constant electrode potential and analyzed the gas phase after 10 min. Fig. 2b shows the average current during the last minute of the chronoamperometric measurement. Consistently with Fig. 2a, Fig. 2b shows that copper has higher activity in higher concentrations of bicarbonate.

Fig. 3 shows the Faradaic selectivity of the gaseous products. The trend obtained in 0.1 M KHCO_3 is consistent with previous results on polycrystalline copper [11,12]. At low overpotentials, hydrogen is produced with a Faradaic selectivity close to 100%, however, while going to more cathodic potentials it decreases to around 20%. Ethylene formation starts at -1.20 V, while methane is produced at higher overpotentials. Interestingly, according to Fig. 3 the selectivity of copper is clearly affected by the bicarbonate concentration; in particular the hydrocarbon selectivity is dramatically influenced by the buffer capacity of the electrolyte. On one hand, methane is preferred at high bicarbonate concentrations; while ethylene selectivity is higher when the KHCO_3 concentration is low.

It is important to keep in mind, however, that the selectivity plots in Fig. 3, only provide information about the ratio between the amount of products formed and not about the formation rates themselves. This can be deceiving, especially, when working with different current densities as in the present study. Therefore we have include the formation rate in Fig. 4, which allow us to get a better understanding of which products are favored under different conditions. For instance, Fig. 3a suggests that hydrogen production is similar in all electrolytes. Nevertheless in Fig. 4a, which shows the H_2 formation rates, it is clear that hydrogen production is inhibited in 0.05 M bicarbonate. In addition, the H_2 production shows a plateau region similar to that observed by Mayrhofer and co-workers for HER on a Pt electrode, which can be attributed to a change in the interfacial pH [23]. Regarding hydrocarbon production (Fig. 4c and d), we observe that the rate for ethylene formation is similar in all electrolytes. In contrast, CH_4 formation rate is clearly dependent on bicarbonate concentration.

Figs. 3 and 4 correspond only to the analysis of the gas phase without considering liquid products. It is important to point out that these products do not account for the 100% of the reaction charge; some of it can be attributed to the formation of liquid products, mainly formate which according to the literature is up to 20% of Faradaic efficiency [11,12]. Our analysis of the liquid phased showed formate as only liquid product. Nevertheless, considering the total faradaic efficiency from gas and liquid product we do not reached a perfect 100% charge balance. We attribute this to an underestimation of the total amount of gas products. It is possible that, the reaction time was not enough to establish a complete

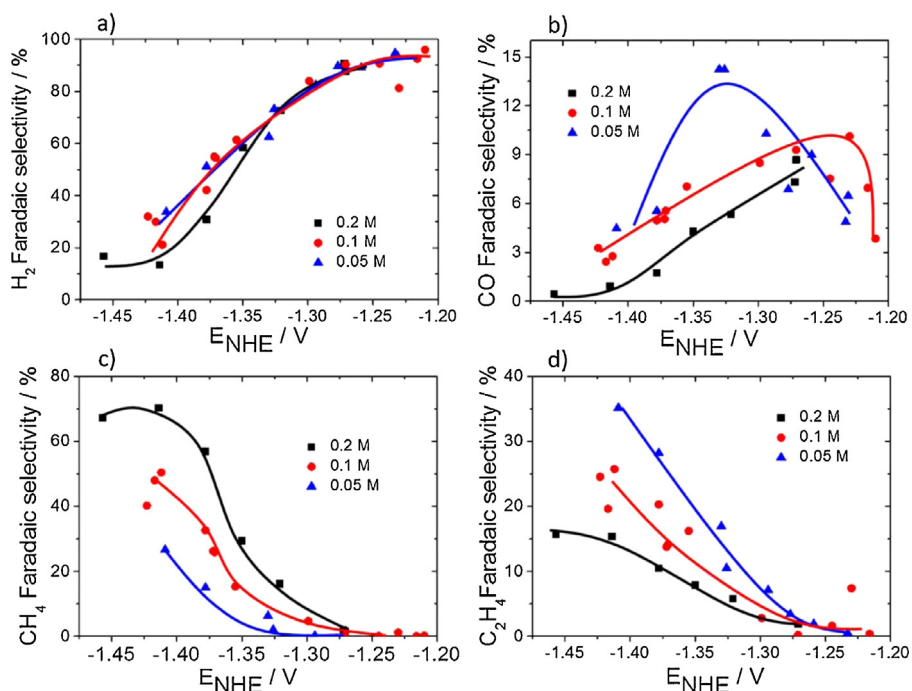


Fig. 3. Stationary Faradaic selectivities of gaseous products during CO₂ electroreduction as a function of electrode potentials in CO₂-saturated 0.05 M KHCO₃ (blue), 0.1 M KHCO₃ (red) 0.2 M KHCO₃ (black). (a) H₂, (b) CO, (c) CH₄, (d) C₂H₄. Lines to guide the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

stationary state in the products concentration in the head space. Despite not reaching a 100% balance we observe that the ratio between products in 0.1 M KHCO₃ (Figs. 3 and 4) is consistent with previous studies and therefore we are confident that the observed in trends in different electrolytes allow us to draw meaningful conclusions.

4. Discussion

Varying the bulk bicarbonate concentration of the electrolyte, a polycrystalline Cu catalyst has shown substantial variations in the overall Faradaic currents, individual product formation rates and Faradaic product selectivities. The experimental trends in

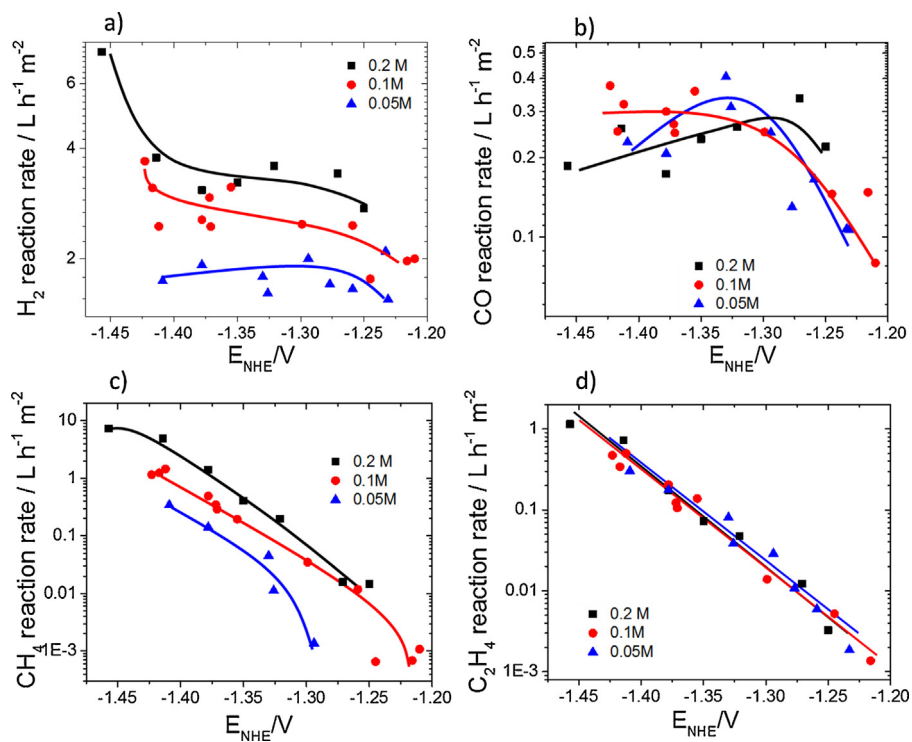


Fig. 4. Absolute product formation rates of gas products as a function of applied electrode potentials in CO₂ saturated 0.05 M KHCO₃ (blue), 0.1 M KHCO₃ (red) 0.2 M KHCO₃ (black). (a) H₂, (b) CO, (c) CH₄, (d) C₂H₄. Lines to guide the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

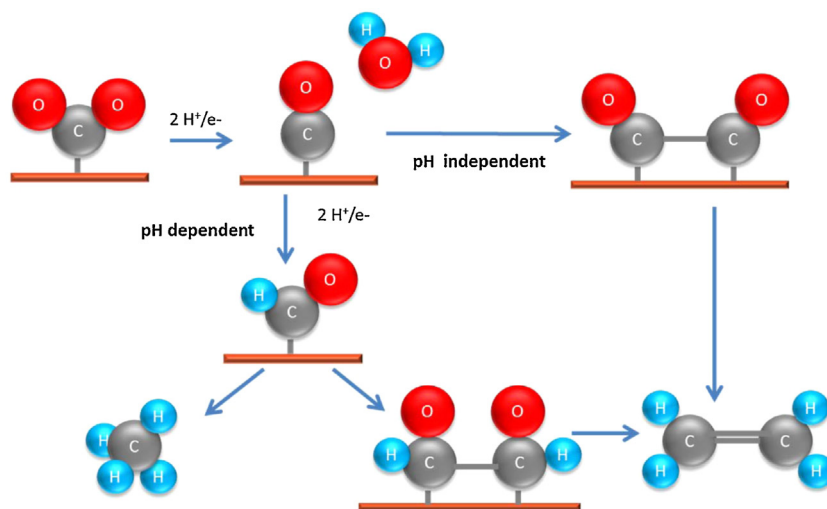


Fig. 5. CO₂ reduction mechanism scheme. Proton dependent mechanism according to Norskov and co-workers [25,26] and proton independent path according to Koper and co-workers [24].

product formation rates differed substantially from the observed trends in Faradaic product selectivities across the entire electrode potential range investigated. Following earlier reports, we attribute the dependence of the catalytic CO₂RR activity on the KHCO₃ concentration to a local interfacial pH effect. Consistently with the observation of Mayrhofer and co-workers, we attribute the observed plateau for hydrogen production to a drastic change in pH in the electrode surface [23]. According to their findings the height of the plateaus relates to the buffer capacity of the electrolyte, since it reflects the reaction rate required to achieve significant changes in local pH. In accordance, the different heights we observe for H₂ production plateaus confirm that the local pH in low KHCO₃ concentration is more sensitive to the reduction current than when working in high concentrations.

The pH is a critical value for the CO₂RR since it is known that the reaction rates of the HER and the CO₂RR to methane correlate with the proton concentration. Hori and co-workers showed that the partial current density for the reduction of CO to CH₄ is proportional to proton activity [16]. Based on this argument, one would expect higher H₂ and CH₄ formation rates at lower pH values. However, looking at the experimental bulk pH and the measured electrochemical product formation rates, we observed the opposite trend. This suggests that the bulk pH is actually not the critical parameter controlling the interfacial processes. The experimental observations can rather be explained by the correlation between electrolyte buffer capacity and local interfacial pH. Higher bulk bicarbonate concentrations may increase the bulk pH, yet their decisive characteristic is their higher buffer capacity and enhanced capability to suppress local pH increases during the catalytic consumption of interfacial protons. Thus, local pH increases are more dramatic in electrolytes with low buffer capacity such as diluted KHCO₃. Consequently, based on Gupta's study [5], we hypothesize that the interfacial pH near the copper surface, pH_{local} , increased during the CO₂RR according pH_{local} (0.2 M KHCO₃) < pH_{local} (0.1 M KHCO₃) < pH_{local} (0.05 M KHCO₃) explaining the observed activity trends in Fig. 2. Therefore, we attribute the low reduction activity in 0.05 M KHCO₃ to high values in pH_{local} associated with low local concentration of reactant protons. This trend in pH_{local} is also in agreement with the H₂ and CH₄ formation rates in Fig. 4: a low concentration of protons near the electrode surface in diluted KHCO₃ slows down the formation of hydrogen and methane, while the rates for CO and specially ethylene are not drastically affected. The lower methane and hydrogen formation rates result in lower overall catalytic reduction currents.

Interestingly, while the formation rate for CH₄ is dependent on pH_{local} , C₂H₄ appears to be less sensitive. Especially at low overpotentials, there is practically no difference in ethylene formation between different electrolyte concentrations (Fig. 4d). Furthermore, we observed that in the three studied electrolytes the formation ethylene as a function of potential follows a Tafel relationship independently from bulk or local pH, similar to the observation from Hori for CO reduction in different pH [16]. These similarities confirm that for neutral solutions the differences in local pH arising from the different buffer capacity of the electrolyte can be as dramatic as those of clearly different bulk pHs.

The different pH dependence on local and bulk pH for CH₄ and C₂H₄ is consistent with the mechanism proposed by Calle-Vallejo and Koper [24], in which a reductive CO dimerization, decoupled from proton transfer, was suggested to constitute the rate determining step in the ethylene formation pathway (Fig. 5). As this mechanism does not involve a coupled proton/electron transfer step, the formation rate is not dependent on pH. Our data indicate further that at high overpotentials the formation rate of ethylene increases with higher concentration in bicarbonate, suggesting that under these very cathodic conditions proton concentration takes on a more critical role in ethylene formation. This result is in accordance with the coexistence of two pathways for ethylene formation, as proposed by Koper and co-workers. One being the CO dimerization mechanism and a second one in which the rate determination step is CO protonation as for methane formation (Fig. 5) [20].

It is worth noticing that, even though our general observations are in accordance with recent work by Kas et al. our detailed results in 0.1 M KHCO₃ are drastically different. In their work, using Cu nanoparticles, C₂H₄ is clearly the predominant hydrocarbon with a Faradaic efficiency of more than 35% while the efficiency toward methane was lower than 5% [21]. In contrast, under similar conditions we observed CH₄ as the main hydrocarbon product. This can be attributed to the morphology of the copper surfaces. Polished copper is known to favor methane, while rough and oxide-derived Cu with its high degree of Cu grain boundaries generally showed ethylene as the main product [9,14,15,27–29].

The results of this study, however, indicate that the enhanced selectivity toward C₂ products on rough surfaces could also be at least partially attributed to local pH effect, instead than to a purely morphology phenomenon. As a general trend, on rough surfaces the geometric current densities are higher than on smooth surfaces. Consequently, we would expect a more dramatic reactive

depletion of interfacial proton concentration which is more difficult to be offset by planar diffusional transport of OH away from the interface. This will result in a high local pH that inhibits the H₂ and CH₄ formation causing the observed high ethylene selectivity.

Interestingly, Kas and co-workers shifted the selectivity of rough copper surfaces toward methane production by working with very high concentrations of bicarbonate. Under these conditions the pH remained close to 7 favoring the production of methane. In contrast to their conditions, in this work we demonstrate that smooth copper surfaces can become more selective toward ethylene by lowering the concentration of bicarbonate. Given the low buffer capacity of this solution the local pH would be alkaline making methane formation unfavorable. These results highlight the importance of taking into account the effect of local pH on the product distribution during CO₂RR. Herein, we showed that the local pH effect has a dramatic effect on the reaction selectivity, underestimating this effect could lead to incorrect conclusions. This is particularly important when working in electrolytes with a low buffer capacity or catalyst with high current densities, since under such conditions the changes in local pH are more pronounced. Therefore, in order to minimize the effect of local pH, it is possible to work in electrolyte with high buffer capacities or performed galvanostatic bulk electrolysis to ensure the same local pH on different catalyst.

5. Conclusion

We have demonstrated that the activity and product selectivity of a smooth copper surface can be controlled, even continuously tuned, by changing the buffer capacity of the electrolyte. Electrolytes with high buffer capacity such as concentrated KHCO₃ electrolytes favor coupled electron/proton transfer resulting in a higher yield of H₂ and CH₄ production. On the other hand, electrolytes with low buffer capacity such as diluted KHCO₃, make the formation these two products less favorable owing to a low concentration of protons near the electrode surface. At low overpotentials, ethylene formation is independent on the local pH supporting the idea of a non-proton/electron transfer rate determine step for ethylene formation [20,24].

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