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Leiden
The Netherlands

Influence of the electrode-electrolyte interface on electrochemical CO₂ reduction reaction and hydrogen evolution reaction

Ye, C.

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Chapter 5

Electrolyte Effect on the Electrochemical CO₂ Reduction on Copper Gas Diffusion Electrodes

Abstract: The electrochemical reduction of CO₂ (CO₂RR) to multicarbon products at high current density over long electrolysis times remains an important challenge for implementation of this technology. In addition to neutral and alkaline media, recent works has shown that CO₂RR to multicarbon products can also be achieved in highly acidic media (pH < 1). In this work, we investigate the influence of bulk electrolyte pH on CO₂RR product distribution by studying the CO₂RR product distribution on a copper gas diffusion electrode (Cu GDE) in a traditional bicarbonate electrolyte and a mildly acidic electrolyte in the presence of the same concentration of cations as in the bicarbonate electrolyte. We show that different CO₂RR product distributions were only observed at low total applied current densities. Our results indicate that the selectivity of CO₂RR on the copper GDE is independent of bulk pH and anions of the electrolyte at high total applied current densities. SEM images, along with EDX elemental mapping, indicate a less stable catalyst layer of the Cu GDE, resulting in electrode degradation over long electrolysis in acidic media compared to that in the bicarbonate electrolyte. Our work thereby confirms the importance of local environment on CO₂RR and offers a more comprehensive understanding of CO₂RR on Cu GDE in acidic media.

5.1 Introduction

The electrochemical carbon dioxide reduction reaction (CO₂RR) has gained substantial interest in the last few decades for the sustainable production of chemicals and fuels by utilizing an abundant carbon feedstock and renewable electricity. The CO₂RR can generate various products in aqueous media, including formic acid (HCOOH), carbon monoxide (CO), hydrocarbons, and alcohols, depending on the catalyst and the microenvironment.¹⁻⁴ Copper-based catalysts are the only catalysts which produce significant amounts of high-value multicarbon products such as ethylene and ethanol during CO₂RR.⁵ Despite extensive effort of the scientific community, reducing CO₂ toward multicarbon products with high activity and selectivity at low overpotentials remains challenging, which hinders the further industrial application of CO₂RR.⁶

In recent years, flow cells and gas diffusion electrodes (GDEs) have been employed to CO₂RR electrolyzers. The porous structure of the GDE allows continuous CO₂ supply to the catalyst-electrolyte interface and therefore greatly improves local CO₂ concentration near the electrode during CO₂RR, enabling high current densities even at ambient conditions.⁶⁻¹¹

In addition to the cell and GDE design, the nature of the catalysts as well as the electrolyte composition have been shown to play important roles in the CO₂RR. Highly alkaline potassium hydroxide electrolyte was found to improve the rate of C-C bond formation and facilitate production of C₂H₄.¹² However, rapid electrode degradation was observed in highly alkaline electrolyte,^{9, 13} with one of the degradation mechanisms being KHCO₃ precipitation resulting from the reaction between CO₂ and KOH.¹³⁻¹⁵ Other than the carbonate precipitation, such a reaction also leads to substantial CO₂ loss in the alkaline electrolyte and therefore greatly limits the carbon efficiency of the system.^{7, 9-11}

To overcome these shortcomings, recently acidic electrolytes have been employed in CO₂RR electrolyzers using flow cells and GDEs.^{7, 9-11} Previous work has shown a CO faradaic efficiency of 80-90% on a gold GDE in pH 3 and 4 sulfate electrolyte.⁷ In addition to a mildly acid electrolyte, strong acidic electrolyte (pH around 1) was employed with a Cu GDE

in flow cells.^{10-11, 16} Although less CO₂ loss is expected in acidic electrolyte, different product distributions have been observed on Cu GDE.^{10-11, 16} For example, FE of about 40% for hydrogen (H₂) and a total C₂₊ FE of 40% were observed on a Cu GDE modified with a cation-augmenting layer,¹⁰ CO and HCOOH were observed on Cu/C as main products at low overpotentials and FE with about 50% for H₂ at high overpotentials,¹¹ while a total FE of 83.7% for C₂₊ products was observed on electrochemically reduced porous Cu nanosheets.¹⁶ The observed different product distribution may result from various aspects, for example, gas electrode preparation method, electrode composition, CO₂ flow rate or cell configuration. Therefore, it is difficult to assign the stable electrolysis demonstrated in these works to the acidic electrolytes. To elucidate this, more systematic work is needed to exclude factors other than the pH of the electrolyte.

In this work, we investigate the influence of electrolytes with different bulk pH on both the CO₂RR product distribution and long-term electrode durability. We show the different product distributions at low total applied current densities, i.e. H₂ and HCOOH as main products in a CO₂ saturated 0.5 M KHCO₃ electrolyte and HCOOH and CO as main products in a CO₂ saturated pH 3 electrolyte with a presence of 0.25 M K₂SO₄ at the total applied current densities of 10 and 50 mA cm⁻², and similar product distributions at high current densities. In addition, we observed continuous decay after 5 hours electrolysis in both electrolytes. SEM images and EDX elemental mapping of Cu GDEs after long term electrolysis suggests that, in addition to the carbonate precipitation and Fe poisoning, the unstable catalyst layer in acidic media contributes to the electrode degradation during long term electrolysis.

5.2 Experimental Section

Materials and chemicals. KHCO₃ (99.5%), K₂SO₄(>99%) and H₂SO₄ (95% in water) were purchased from Acros Organics. Cu nanoparticles (25 nm), Nafion (5 wt % in lower aliphatic alcohols and water) and Chelex were purchased from Sigma-Aldrich. Milli-Q water (resistivity >18.2 MΩ·cm, TOC < 5 ppb) was used for all experiments in this work.

GDE preparation. The gas diffusion layer (GDL) was prepared using a previously reported method.⁷ The catalyst ink was prepared by suspending Cu nanoparticles in isopropanol and adding 380 μ l of Nafion solution (final 15 wt % of the catalysts). The mixture was then sonicated for 0.5 h to obtain a well dispersed suspension. Finally, the suspension was under continuous stirring to keep the suspension well dispersed. In the meantime, the suspension was airbrushed on a 17 cm^2 GDL. The final GDE was obtained after air drying. A catalyst loading of 1 mg/cm^2 was calculated from the weight difference before and after airbrushing.

Electrode characterization. Scanning electron microscopy (SEM) was performed on an Apreo SEM equipped with an energy-dispersive X-ray (EDX) analyzer to characterize the GDEs. SEM images were obtained with an acceleration voltage of 10 kV and an electron beam current of 0.8 nA. EDX (Instruments X-MaxN 150 Silicon Drift detector) was used for elemental analysis. The quantification was performed in automatic mode, without providing external standards. The data is displayed in atomic percentage for easier visualization.

Flow cell electrolysis. The bulk electrolysis experiments were carried out with a commercial two-compartment flow cell with 10 cm^2 GDE (ElectroCell, Micro Flow Cell). A reinforced Nafion membrane N234 was used to separate the anode and the cathode. 0.5M H_2SO_4 solution was used as anolyte and a dimensionally stable anode (DSA®, ElectroCell) was used as anode for all measurements. pH of the electrolyte was adjusted with H_2SO_4 and a pH meter when necessary. The catholyte was CO_2 saturated 0.5M KHCO_3 or pH 3 0.25M K_2SO_4 electrolyte. The electrolytes were circulated in the compartments at a flow rate of 30 mL/min with a peristaltic pump, CO_2 was fed through the GDE in the cathodic compartment at a flow rate of 30 mL/min . Before each experiment, CO_2 was purged through electrolyte for 1 h to obtain a stable electrolyte prior to each CO_2RR experiment. The cell was controlled by an Autolab PGSTAT100N potentiostat and each current density was applied for an hour. The gas product analysis was performed with a gas chromatograph (Varian 4900 micro GC) equipped with four modules: CO_x module, MS5 (mol. sieve) module, PPQ (poraplotQ) module and 52C WAX module. Gaseous samples were taken from gas outlet every 3 minutes. The current efficiencies shown throughout this work represent the average values obtained at 36, 48 and

60 mins during 1 h of electrolysis, with the corresponding standard deviation. Liquid products were analyzed with High Performance Liquid Chromatograph (HPLC) with an Aminex HPX-87H (BioRad) and a RID detector (Shimadzu). For stability performance, a total applied current density of 200 mA cm^{-2} was applied to the cell, with only gas products analyzed as an indicator of CO_2RR performance.

5.3 Results and Discussion

5.3.1 Results

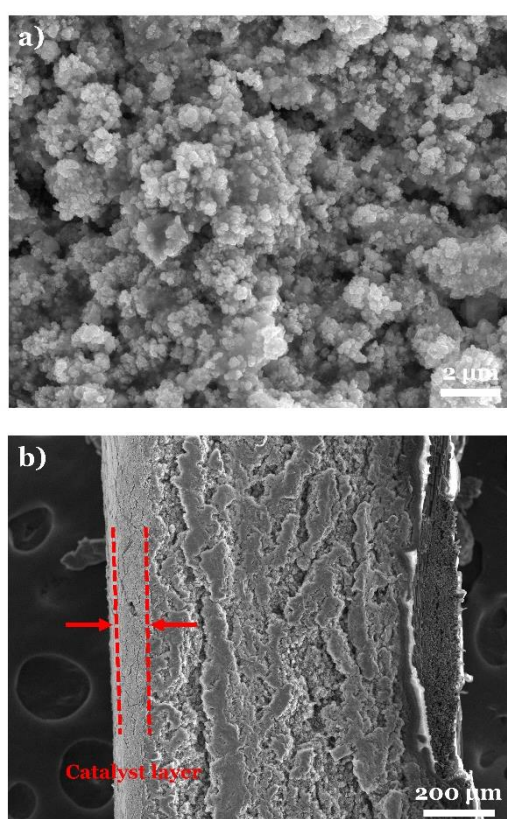


Figure 5.1 SEM images of a) the surface catalyst and b) cross section of the Cu GDE before CO_2RR experiments.

Scanning electron microscopy was used to characterize the morphology of the Cu GDEs. Figures 5.1a and 1b show SEM images of the surface catalyst and a cross section of the Cu GDEs, respectively, prior to CO_2RR experiments. The Cu nanocatalysts are well dispersed on the surface of the GDE with a layer thickness of about 100 μm (the thickness of the catalyst

layer was confirmed with elemental analysis).

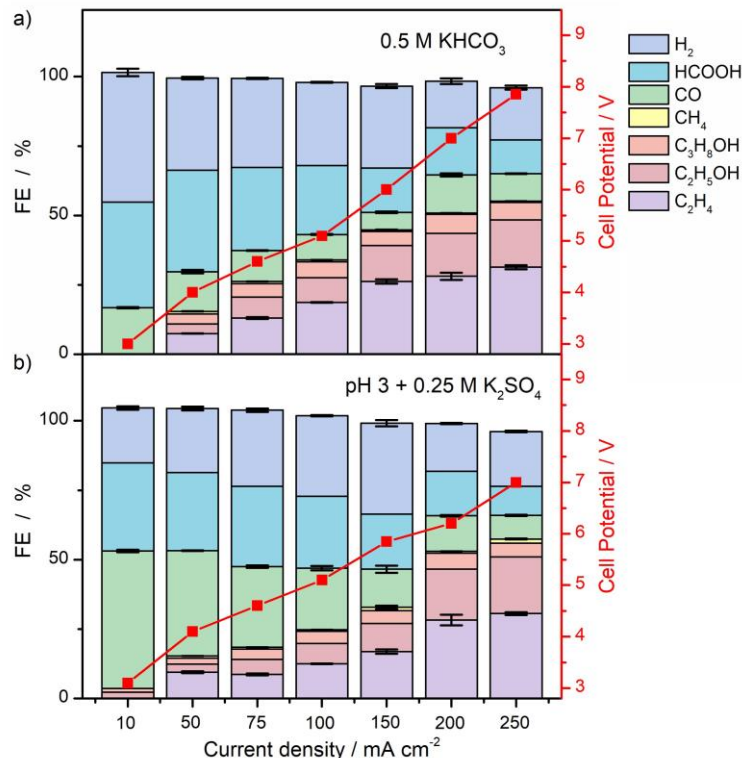


Figure 5.2 Effect of bulk pH on CO₂RR performance. FEs of H₂, HCOOH, CO, CH₄, C₃H₈OH, C₂H₅OH and C₂H₄ (left axis) as well as cell potential (right axis) as a function of total applied current density on Cu GDE in CO₂ saturated a) 0.5M KHCO₃ (pH 7.2) and b) pH 3 electrolyte with the presence of 0.25 M K₂SO₄ (pH 3.0).

To study the effect of bulk pH on CO₂RR, experiments were carried out in 0.5M KHCO₃ (bulk pH of 7.2 before electrolysis) and CO₂ saturated 0.25M K₂SO₄ (adjusted with H₂SO₄ to a bulk pH of 3 before electrolysis), respectively, where the cation concentrations were deliberately kept the same to exclude a bulk cation concentration effect on CO₂RR. Figure 5.2 shows the Faradaic efficiencies (FEs) for CO₂RR products as well as the cell potential in the two electrolytes as a function of total applied current density. As shown in Figure 5.2a, in 0.5M KHCO₃, H₂ and HCOOH are major products obtained during CO₂RR at low total applied current densities. Specifically, at 10 mA cm⁻², the FEs of H₂, HCOOH and CO are 46.6%, 38.1%, and 16.7% respectively. With increasing total applied current density, the FEs of H₂ and HCOOH decrease, while the total FE of CO and its further reduced products

increase. At the highest total applied current density of 250 mA cm^{-2} , the FEs of H_2 and HCOOH have reduced to 18.9% and 12.2% respectively, while the FEs of CO , C_2H_4 , $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_3\text{H}_8\text{OH}$ are 9.9%, 31.4%, 17.3% and 6.3% respectively. These results agree well with previously reported findings for Cu nanoparticle-based GDEs in bicarbonate electrolyte.¹⁷

Figure 5.2b shows the CO_2RR performance in the pH 3 sulfate electrolyte. At low total applied current densities (below 100 mA cm^{-2}), the primary products are HCOOH and CO . FEs of H_2 , HCOOH and CO are 19.7%, 31.7%, and 49.6% respectively at 10 mA cm^{-2} . These results suggest that H_2 formation is inhibited at low total applied current densities under these working conditions. This might be explained with the model recently proposed by Bondue et. al.¹⁸ According to their model, OH^- generated from CO_2RR could neutralize protons diffusing from bulk electrolyte to the catalyst surface to generate H_2O in pH 3 electrolyte and thereby inhibits H_2 formation during CO_2RR .¹⁸ This is in contrast with the H_2 production observed in 0.5M KHCO_3 at low current densities, where HCO_3^- acts as proton donor and is readily reduced to produce H_2 . Additionally, minor amounts of $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_3\text{H}_8\text{OH}$ are detected in the pH 3 electrolyte already at 10 mA cm^{-2} . With increasing total applied current density, the product distribution in the pH 3 electrolyte becomes similar to the one in 0.5 M KHCO_3 , especially at 200 and 250 mA cm^{-2} . These results suggest that the selectivity of CO_2RR on the Cu GDE remains consistent regardless of variations in pH or the composition of the bulk electrolyte at high total applied current densities.

The right axis of Figure 5.2 shows the cell potential obtained during CO_2RR in the 0.5 M KHCO_3 and pH 3 sulfate electrolytes, respectively. As expected, the cell potential increases in both electrolytes with the increasing total applied current density. Furthermore, the cell potential in pH 3 sulfate electrolyte remains lower than the cell potential in 0.5 M KHCO_3 . This is likely due to the higher ionic conductivity of the pH 3 electrolyte. (Specifically, the ionic conductivity of $1.167 \times 10^{-1} \text{ S cm}^{-1}$ in pH 3 with the presence of 0.25M K_2SO_4 is higher than the ionic conductivity of $5.895 \times 10^{-2} \text{ S cm}^{-1}$ in 0.5 M KHCO_3 despite the subtle electrolyte component change which occurs after CO_2 saturation.)

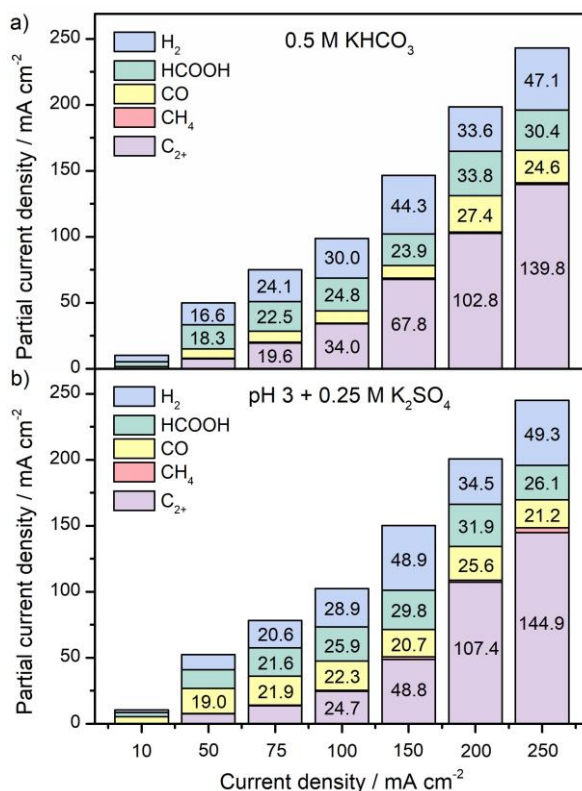


Figure 5.3 Partial current densities of H₂, HCOOH, CO, CH₄ and C₂₊ products (C₃H₈OH, C₂H₅OH and C₂H₄) as a function of total applied current density on Cu GDE in CO₂ saturated a) 0.5M KHCO₃ (pH 7.2) and b) 0.25M K₂SO₄ (pH 3.0).

Figure 5.3 shows the partial current densities of each CO₂RR product in both electrolytes. It clearly shows higher CO production in pH 3 electrolyte for lower total applied current densities, and similar product distributions in both electrolytes at higher total applied current densities. We ascribe this to the local pH regulation which is different between these two electrolytes at these lower current densities.

To study the stability of both electrolysis systems, long term electrolysis of CO₂RR at a total applied current density of 200 mA cm⁻² was performed on the Cu GDE in both electrolytes. The FE of C₂H₄ and the cell potential were chosen as indicators of CO₂RR performance. Left and right axis of Figure 5.4 shows FE of C₂H₄ (solid symbols) and cell potential (hollow symbols), respectively, as a function of time, in 0.5 KHCO₃ (green) and pH 3 electrolyte with presence of 0.25 M K₂SO₄ (pink). The results show that the cell potential in 0.5M KHCO₃ is more stable than in the pH 3 electrolyte. On the other hand, the FE of C₂H₄ in pH 3

electrolyte remains higher than in 0.5 M KHCO_3 for 14 hours (and especially for the first 8 hours).

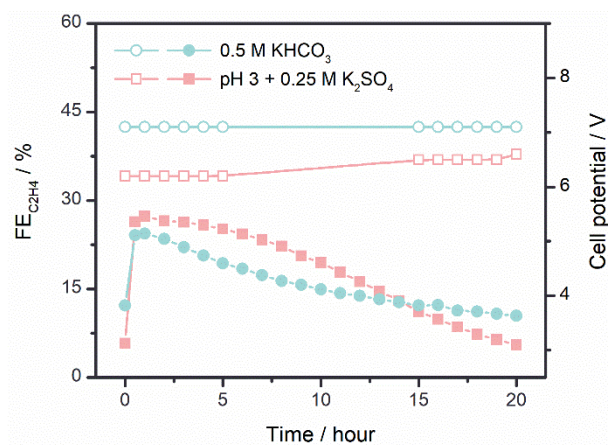


Figure 5.4 Comparison of CO_2RR performance at a total applied current density of 200 mA cm^{-2} on a Cu GDE in neutral and acidic bulk electrolyte: solid symbols representing FE of C_2H_4 corresponding to left axis and hollow symbols representing cell potential corresponding to right axis. Electrolytes: 0.5 KHCO_3 (green) and pH 3 electrolyte with presence of 0.25M K_2SO_4 (pink).

These results suggest that although less KHCO_3 precipitation is expected in pH 3 electrolyte, it does not necessarily lead to stable CO_2RR performance during long term electrolysis. Considering the fact that bulk pH before and after CO_2RR electrolysis remain relatively stable (see Table S1) and CO_2RR performance derived from long term electrolysis slowly went down over time, we assume that the loss of CO_2RR activity likely stems from electrode degradation during long term electrolysis.

To test our hypothesis, copper GDEs were characterized after long term electrolysis. The copper GDEs were rinsed with Milli-Q water at least three times and dried in the air immediately after long term electrolysis. Next, they were kept in sealed sample bags prior to SEM characterization. Figure 5.5 shows the characterization of copper GDEs after 20 hours electrolysis at a total applied current density of 200 mA cm^{-2} in 0.5M KHCO_3 and pH 3 sulfate electrolytes, respectively. Figure 5.5a, b show that surface catalysts remain as nanoparticles after long term CO_2RR experiments in both electrolytes. Figures 5.5c, d show

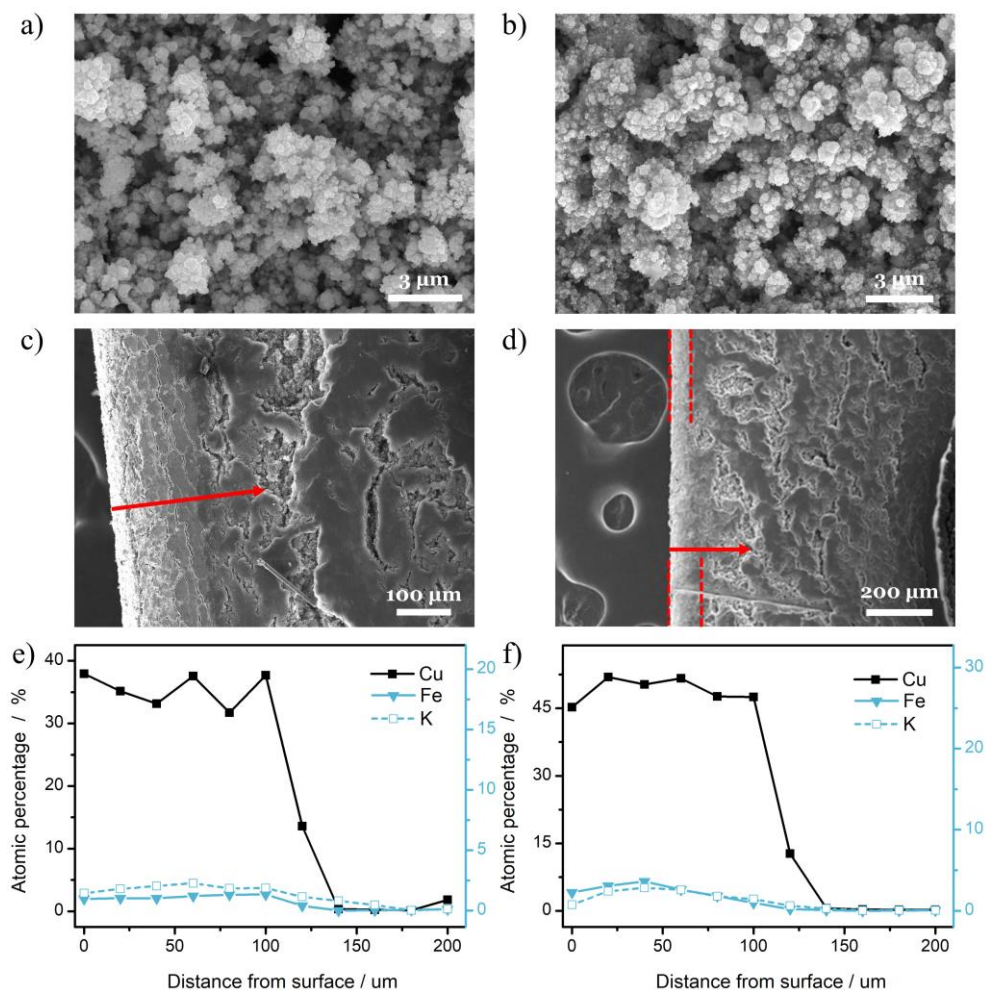


Figure 5.5 Characterization of copper GDEs after 20 hours long term electrolysis at a total applied current density of 200 mA cm^{-2} . a) Surface catalyst morphology, c) cross section and e) atomic percentages of Cu, K, Fe as a function of distance from top surface of catalyst layer obtained from EDX elemental mapping of a copper GDE after long term electrolysis in CO_2 saturated 0.5 M KHCO_3 ; b) Surface catalyst morphology, d) cross section and f) atomic percentages of element Cu, K, Fe as a function of distance from top surface of catalyst layer obtained from EDX elemental mapping of a copper GDE after long term electrolysis in CO_2 saturated pH 3 electrolyte with presence of $0.25 \text{ M K}_2\text{SO}_4$.

the cross section of the Cu GDEs after long term electrolysis in 0.5 M KHCO_3 and $0.25 \text{ M K}_2\text{SO}_4$ electrolytes, respectively. Figure 5.5c shows a well-preserved catalyst layer (around 100 μm) on GDE after long term electrolysis in 0.5 M KHCO_3 . On the other hand, it appears that the catalyst layer on copper GDE after long term electrolysis in pH 3 K_2SO_4 electrolyte was less intact, as shown by different distances between dashed lines in Figure 5.5d, which is

obtained from EDX mapping and indicates different thickness of the catalyst layer at different locations of the GDE. Supporting Figures D.1 and D.2 show further SEM images of the Cu GDE with catalyst layers of less than 50 μm and images of copper GDEs with a black deposit on the current collector respectively, which suggests a redeposition of Cu nanoparticles on the current collector during CO_2RR in the pH 3 electrolyte. In addition to the loss of Cu nanoparticles, the presence of KHCO_3 precipitation and Fe deposition originally from current collector (steel) in the catalyst layer are often considered as common reasons for causing loss of CO_2RR activity. Therefore, the atomic percentages of Cu (left axis), Fe (right axis) and K (right axis) obtained from EDX mapping along the arrow indicted in Figures 5.5c, d were obtained and are shown in Figure 5.5e, f respectively, with the positions chosen to have similar thicknesses of the catalyst layer. Figure 5.5e shows the presence of K throughout the catalyst layer as well as traces of Fe. In contrast, Figure 5.5f shows the presence of elements K and Fe in the top part of the catalyst layer. Additionally, it is worth noting that element Fe is higher on copper GDE after electrolysis in pH 3 sulfate electrolyte than on copper GDE after electrolysis in 0.5 M KHCO_3 in view of the ratio of atomic level of Fe and Cu in each GDE, which suggests more Fe deposition on the catalyst layer in pH 3 sulfate electrolyte under our working conditions.

5.3.2 Discussion

Our work shows that operating in acidic media is a promising method to decrease the CO_2 consumption caused by electrolyte without harming other important figures of merit such as the product distribution and electrode stability. Specifically, total FEs of CO_2RR products reach 80% on Cu GDE at total applied current densities of 200 and 250 mA cm^{-2} in both electrolytes. In the meantime, similar CO_2RR product distributions were observed under these conditions. However, electrolytes with different bulk pH affect the CO_2RR product distribution at low total applied current densities. In pH 3 electrolyte, CO and HCOOH are the main products, while H_2 and HCOOH are more pronounced in 0.5 M KHCO_3 , at the total applied current densities of 10 and 50 mA cm^{-2} . Additionally, minor C_2^+ products were observed in pH 3 electrolyte at a total applied current density of 10 mA cm^{-2} .

Previous work has shown that the selectivity and activity of a catalyst is highly sensitive to local pH¹⁹⁻²³ and cations²⁴⁻²⁷. Numerous experimental studies have shown that higher local pH conditions promote CO and multi-carbon products while suppressing H₂ and CH₄ on Cu catalysts.^{12, 20-23} In addition to the pH of the bulk electrolyte, buffer capacity of the electrolyte also plays an import role on the local pH during CO₂RR.^{8, 22-23, 28} Liu et al shows dramatic change of local pH in low buffered electrolytes with a rotating ring-disk electrode.²⁸ Burdyny et al investigated the pH near the GDE as a function of total applied current density during CO₂RR in commonly-used electrolytes, namely 0.1M KHCO₃, 1M KHCO₃ and 1M KCl, with a 1D reaction-diffusion model.⁸ The modelling shows a sudden increase of the local pH in the electrolytes with low buffer capacities at low current densities, which thereby leads to a high local pH in the low buffered electrolyte, and a similar ultimate alkaline local pH in all electrolytes (except a high local pH in high alkaline electrolyte) at high total applied current densities.⁸

These observations are in line with our experimental results. Considering the same cation concentration in both electrolytes and electrodes with the same preparation method in the present work, the observed different product distribution at low total applied current densities must be due to different local environment at the interface resulting from electrolyte. At low total applied current densities, HCO₃⁻ acts as a buffer species and a proton donor contributing to the H₂ production in 0.5 M KHCO₃. On the other hand, the rapidly increased local pH at the interface in low buffered pH 3 electrolyte leads to an inhibition of H₂ production because of the sluggish kinetics for water reduction in alkaline conditions. Under high total applied current densities, highly alkaline local environments at the interface are achieved, where HCO₃⁻ is consumed by excess OH⁻ formed during CO₂RR and no long acts as buffer at the interface. Consequently, a similar local environment at the interface is expected in both electrolytes. Therefore, a similar products distribution in both electrolytes are observed.

Although alkaline local environments at the interface are unavoidable in both electrolytes, less carbonate/bicarbonate are expected during the reaction as the bulk protons can to some extent neutralize the OH⁻ produced upon CO₂RR while in alkaline media both OH⁻ originated

from bulk electrolyte and generated from CO₂RR will be neutralized by CO₂. Our results shows that K⁺, which corresponds to carbonate/bicarbonate formation, is present in the catalysts layer after long term electrolysis in 0.5M KHCO₃ at a slightly higher level than in pH 3 electrolyte. In addition to K⁺, a higher content of Fe element, which is considered as metal impurity,^{15, 29} was observed on copper GDE after long term electrolysis in pH 3 electrolyte compared to 0.5M KHCO₃ electrolyte. This may be related to the higher instability of the current collector under acid conditions. However, the observed elemental difference does not seem high enough to explain CO₂RR performance over long term, as shown in Figure 5.4.

SEM characterization and EDX elemental mapping suggests a less stable catalyst layer in pH 3 electrolyte, which may be another factor contributing to the drop in CO₂RR performance in pH 3 electrolyte. It is known that Cu can be easily oxidized at open circuit potential. The formed Cu oxide dissolves in the acidic media and may be subsequently reduced back to Cu during electrolysis, which thereby leads to a less stable catalyst layer over long term electrolysis in pH 3 electrolyte. Further, this could also explain the black deposition on current collector after electrolysis. Therefore, we show the unavoidable interactions between the acidic reagent and the commonly used compartments, e.g. GDE, may result in inherently unstable CO₂RR electrolyzers.

5.4 Conclusions

In summary, we show that operating CO₂RR in acidic media is a promising approach to lower the CO₂ consumption and improve the energy efficiency without compromising the selectivity toward C₂⁺ products. Compared with commonly used bicarbonate electrolytes, our results in mild acidic electrolyte show an inhibition of H₂ production at low total applied current densities and similar CO₂RR product distribution at high total applied current densities. The similar CO₂RR product distributions at high total applied current densities in both electrolytes indicate a similar local pH at the interface under these conditions. In addition, our result shows the unavoidable interaction between the acidic electrolyte and Cu oxide may result in inherently unstable Cu catalyst layer on GDE. Our work thereby offers

new insights of CO₂RR in acidic media and points out the new challenge of employing acidic media in CO₂RR electrolyzers.

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