SELECTIVE ELECTROCHEMICAL REDUCTION OF CO_2 TO HIGH VALUE CHEMICALS

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DELIVERABLE REPORT

4.1 - REPORT ON THE IMPACT OF REACTION INTERMEDIATES ON ECO2R SELECTIVITY TOWARDS ETHYLENE

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NATURE OF THE DELIVERABLE

R	*Report*	***X***
P	*Prototype*	
D	*Demonstrator*	
O	*Other*	

SUMMARY	
Keywords	*Reaction Intermediates, CO_2, ethanol, ethylene, acetaldehyde, glyoxal, acetate*
Abstract	*Electrochemical CO_2 reduction (ECO2R) on a copper catalyst leads to a wide product composition of various value-added chemicals such as CO, ethanol, and ethylene. A number of additional minor products have been reported, namely acetate, acetaldehyde, formate and glyoxal. These compounds are typically measured in only minor amounts of ~1% each. However, these compounds play an important role as reaction intermediates to some of the major product pathways that we would like to manipulate to steer product selectivity.* *This deliverable investigates the effects of these reaction intermediates on the experimental selectivity of ethylene, the targeted product for WP4. Specifically, the controlled addition of reaction intermediates into an operational ECO2R system is performed for a number of crucial intermediates, and the resulting change in product selectivity measured. We find that the direct reduction of acetaldehyde and glyoxal in even minor concentrations at elevated current densities will shift electrons away from the target product ethylene. Measured ethanol and acetaldehyde concentrations indicate that this is also occurring during ECO2R without additives.* *The conclusions from these results provide strategies to increase the selectivity of ethylene formation via glyoxal and acetaldehyde scavengers, which remove the intermediates prior to their subsequent reduction to alcohols. If successful, such a strategy may shift ~10% of electrons from the alcohol to hydrocarbon pathways.*
Public abstract for confidential deliverables	

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REPORT ON THE IMPACT OF REACTION INTERMEDIATES ON ECO2R SELECTIVITY TOWARDS ETHYLENE

CONTENT

1 INTRODUCTION

This deliverable report describes the experimental testing and evaluation of the controlled introduction of reaction intermediates into a steady-state electrochemical CO_2 reduction (ECO2R) system to determine the effects on ethylene product selectivity. Specifically, the known ECO2R intermediate compounds formate, acetate, acetaldehyde and glyoxal were injected into the catholyte of a device operating at constant current densities >100 mA/cm^2 with the formed reduction products measured in-line.

The scientific context behind this deliverable originates from several mechanistic and fundamental experimental studies performed at lower current densities (<10 mA/cm^2), which identify minor products that may be critical for the formation of major products commonly observed during ECO2R. Specifically, products measured with selectivity's ~1% during ECO2R on copper such as acetate, formate, acetaldehyde and glyoxal may in fact be produced in much higher abundances. These intermediates are then reduced further to the major observed products (e.g. ethylene, ethanol, propanol) prior to them diffusing back to the bulk electrolyte. The complexity of the proposed reaction pathways for ECO2R can be seen in the compiled reaction pathways image in Figure 1, originally reported by Nitopi et al. [1].

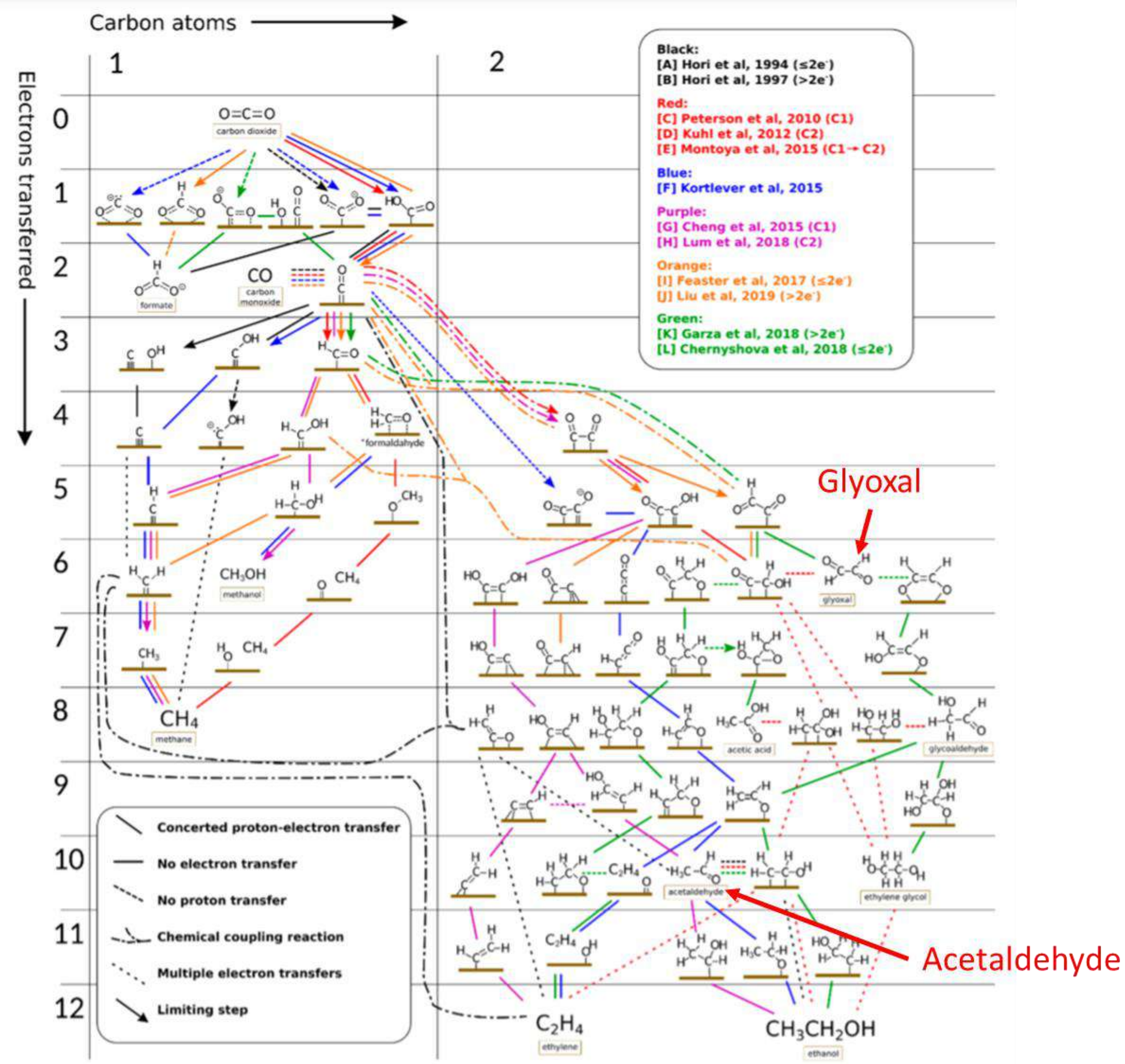

Figure 1: Figure referenced from Nitopi et al. [1] highlighting a collection of possible mechanistic pathways of CO_2 reduction to C1 and C2 products on polycrystalline copper, grouped into different colored reaction schemes taken from the works in the top-right legend. Both glyoxal and acetaldehyde are highlighted for their importance for to D4.1.

The pathways in Figure 1 were inspired by control experiments performed with Online Electrochemical Mass Spectrometry (OLEMS) [2] as well as H-cells with liquid product detection [3] that showed that acetaldehyde and glyoxal show direct reduction to alcohols. When coupled to computational models it is hypothesized that during ECO2R a similar reaction pathway through these intermediates is followed. There is additional work required to assess the influence for elevated current densities or changes to the electrolyte environment to influence the formation or desorption of these intermediates to promote or suppress ethanol formation. Understanding or influencing the mass transport or energetics of this pathway could in turn be used to increase ethylene selectivity.

Additionally, as acetate and formate will be at relatively high local concentrations at the electrode's surface as a by-product, it may play a role in changing the energy barriers of different reactions pathways by contributing to the reaction mechanisms and is therefore investigated.

Figure 2 below shows the baseline presence of liquid products within ECO2R in a gas-diffusion layer experiment at elevated current densities. The provided cell image further shows the comparative addition of intermediate species to the ECO2R catholyte reservoir. Further experimental details are provided within the following sections.

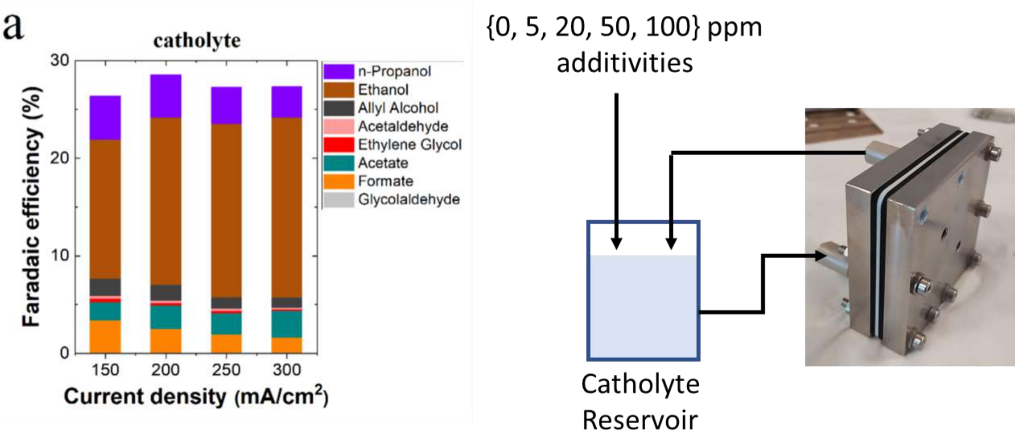

Figure 2: Overview of the minor liquid products reported by Ma et al. [4] during ECO2R on a copper catalyst at elevated current densities and a representation of the cell and simplified experiments performed within the deliverable.

2 SCOPE

This deliverable contributes to WP4 (ethylene production) and WP3 (ethanol production) by providing quantitative information on the importance of reaction intermediates on the ratio of ethylene:ethanol that is formed during ECO2R. Our task is to screen various reaction intermediates to determine if enhancing or interrupting the formation of various intermediate compounds will influence the selectivity of the formed products.

The deliverable requires the development of a procedure to provide quantitative and qualitative data on how the injection of reaction intermediate impact reaction selectivity. The scope of the deliverable is restricted to elevated current densities (100-400 mA/cm^2) where the formation of ethylene and ethanol is maximized in the control scenario. The experiments are further restricted to a flowing catholyte configuration to allow for intermediate additions to the catholyte.

3 RESULTS AND DISCUSSION

The following section presents the results and discussion for the performed reaction intermediate tests. All experiments were performed at a fixed current density and the specified reaction intermediates were added after the gas products were observed to be at steady-state as measured using the in-line gas chromatograph.

The experimental set-up for the electroreduction of CO_2 is shown in Figure 3. The cell used in all experiments was a PTFE-stack cell. Within the cell a 150 nm thick Cu-sputtered GDLs (corresponds to 0.13 mg/cm^2) were fixed onto a rubber gasket with exterior copper tape added as an electrical contact from its back side. The catholyte was 1 M $KHCO_3$ solution, circulating at 30 mL/min. The counter electrode was a Ni-foam to conduct oxygen evolution reaction (OER) in a 1 M KOH solution circulating at 30 mL/min. A cation-exchange membrane (Nafion®) was used to separate the electrolytes, minimize crossover of the intermediate-anions (such as formate and acetate) and transfer OH^- ions to complete the ionic circuit. The inlet CO_2 gas flow was set at 30 sccm by a mass-flow controller (MFC from Bronkhorst) and the outlet gas stream (unreacted CO_2 + products) was continuously measured with a mass-flow meter (MFM from Bronkhorst). The outlet gas stream then proceeded to a gas chromatograph (GC) which quantitatively measured the concentration of CO, CH_4, C_2H_4 and H_2, and provided qualitative measurements of any formed methanol, ethanol, acetaldehyde, acetone or n-propanol.

Our electrochemical protocol for performing the intermediate experiments were as follows. The electrochemical cell was first set to an initial open circuit voltage (OCV) for 60 seconds, followed by an electrochemical impedence spectroscopy (EIS) between 10 kHz and 1 kHz that lasts around 25 seconds. Immediately following this step, a chronopotentiometry (CP) step of 3600 seconds was applied at a constant current of 300 mA/cm^2 (equivalent of 675 mA) between the Cu-GDL and Ni-foam, cathode and anode, respectively. The reaction intermediates were injected into the catholyte beaker once the measured gas products reached a steady-state selectivity between injections. A final OCV step was conducted to measure the resting potential at the close of the experiment, and also to record the response of the MFM and GC during the recovery of the gas flow and change in the GC peak area, respectively.

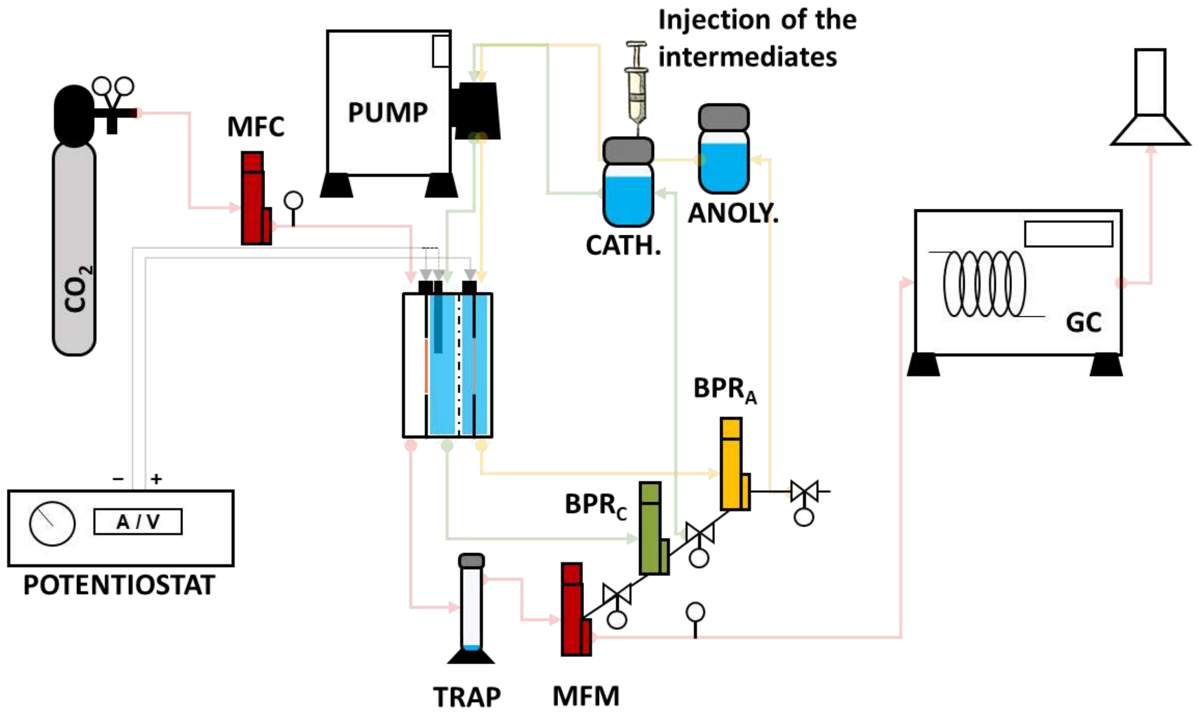

Figure 3: Experimental set-up used for the electrochemical CO2 reduction reaction. MFC and MFM are for the mass flow controller and measurement, BPR_C and BPR_A are the back-pressure regulators for catholyte and anolyte compartments. The intermediates were injected with a volumetric syringe at the catholyte beaker.

The concentrated stock solutions of the introduced intermediate products (2M for formate, acetate and glyoxal, 4 % wt. for acetaldehyde) were prepared in advance, in order to minimize a concentration gradient at the catholyte during the intermediate injections. We used 1M $KHCO_3$ as a catholyte because it is a strong electrolyte which can compensate high current densities (> 100 mA/cm$_2$) and also it has a near-neutral pH media. It is well-known that strong alkaline electrolytes yield a higher efficiency CO_2 electroreduction, however some of the intermediates were not stable in that media. For example, basic acetaldehyde solutions undergo aldol reactions to form multifunctional 3-hydroxybutanal and crotonaldehyde, following longer chain (polymerization) reactions.[5] Also we targeted below 3 % volume change for the 100 mL catholyte. The largest injection volume was 2.5 mL for the acetaldehyde – as higher concentrations require a special handling of this volatile and hazardous chemical. The back-pressure regulators (BPR) facilitated to establish a pressure balance at the liquid-membrane (BPR_A) and liquid-gas junctions (BPR_C), upon injection. Thus, we did not experience an overpressure that ruptures the membrane or causes an immediate flooding at the cathode during the injection of the intermediate solutions.

For 1 hour of electrolysis, 16 injections (by 4 minutes each) were taken by the gas chromatogram (GC). The time between the 4th and 5th GC injections were found to be a suitable period for intermediate injections thanks to the stabilization of the gaseous product distribution. To provide greater information regarding the influence of the reaction intermediates, the volatile effluents in the CO_2-off-gas were detected by the flame ion detector (FID) of our GC column. This approach allowed us to instantly monitor the concentrations of the volatile species right after each injection, rather than at the end of the experiment using NMR and HPLC for liquid analysis. Hence, our results gave the immediate effect of various reaction intermediates. Initial intermediate tests were done to estimate a reliable target concentration in the catholyte (i.e. 5, 20, 50 and 100 mM). According to the selectivity trends, we found that 50 mM was the most suitable target concentration to test the intermediates effect at the 100 mL catholyte. This value corresponds to 25 mM/cm^2 for the intermediate concentration vs. the geometric area of the cathode.

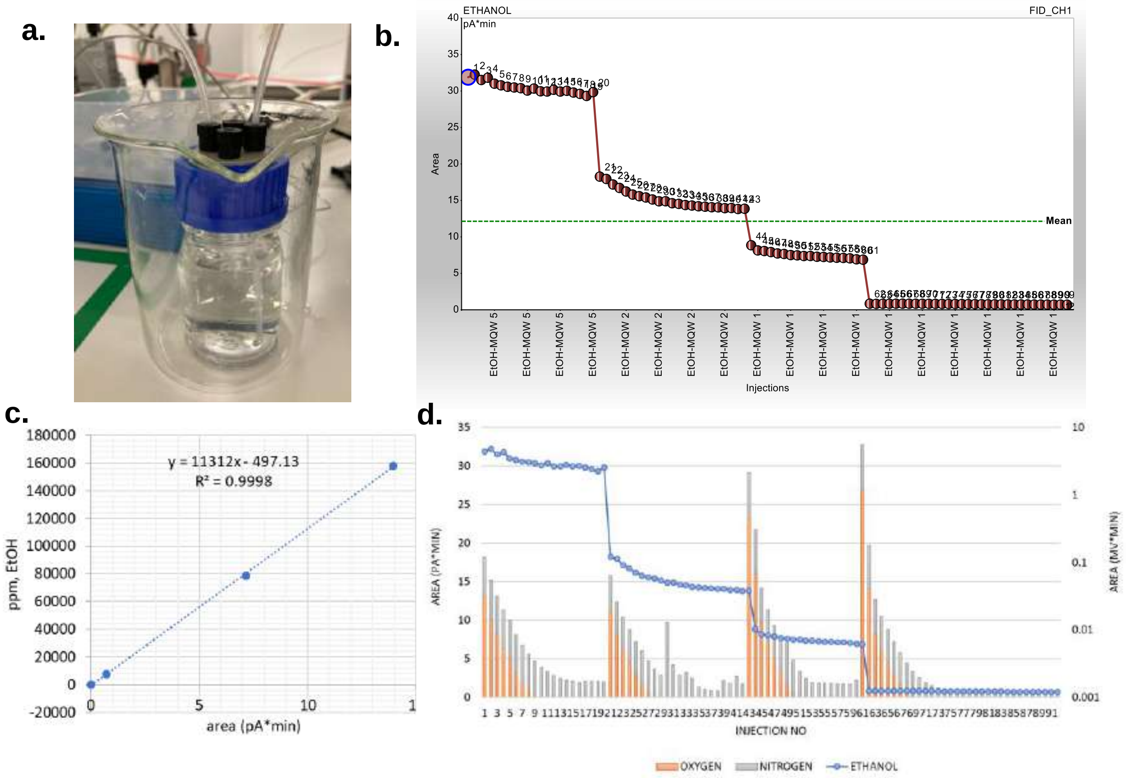

Figure 4: **a)** 100 mL solution of ethanol and MQ-water purged with He (not to interfere with N_2 or O_2 or to produce any other signal in the GC), **b)** Ethanol peak areas of the 92 GC injections **c)** Calibration plots for ppms of ethanol inside MQ-water vs. the GC-peak area **d)** Ethanol peak area in left-y axis and N_2 & O_2 area on the right-axis.

To perform the qualitative calibration of volatile compounds, control experiments were conducted by the GC injections according to the volatility principle of their liquid mixtures (Figure 4). In a partially filled container (such as 50 % vol. of ethanol in Milli-Q Water), liquid particles of ethanol would liberate from the surface and vaporize in the air above the liquid inside a beaker. As gas concentration accumulates in the head-space of the beaker, the distance separating individual molecules (ethanol vs. vapour/humidity-H_2O) decreases until Van der Waals and hydrogen bonds can drive clusters of molecules back into the liquid form (condensation). Eventually, vaporization and condensation reach a state of equilibrium, where no particles are lost but instead the gas phase is constantly being recycled into the liquid phase. Hence, we accelerate this by purging an inert gas into the mixture (Figure 4a) and deriving a semi-quantitative calibration of that mixture. An example is given in Figure 4 b-c, where we have used four different volumetric concentrations of ethanol (1, 10, 20 and 50 % vol. ethanol in MQ-Water). Nearly 20 injections (each of 4 min) were collected to ensure an equilibrium at the head-space that would be represented by a stable GC peak area for ethanol.

The results in Figure 4d show that water-vapour, nitrogen (N_2) and oxygen (O_2) content of the head-space can affect the stabilization time. Interestingly, O_2 shows a stronger effect to the ethanol equilibrium, which may correlate to the inert nature of N_2 (N-triple bond). During ECO2R the concentration of ethanol is expected to increase slowly as accumulation occurs within the catholyte beaker. These control experiments are then useful to track the varying concentrations and determine if the introduced intermediates are responsible for any of the observed changes in selectivity.

3.1 Formate Addition

In this section, we have checked the effect of formate ($HCOO^-$) on ECO2R towards ethylene. The injection of 50 mM potassium formate (or formate anion) into the catholyte beaker does not show a drastic effect on the selectivity of CO_2 products. The ethylene efficiency remains stable at 32 % as shown in Figure 5. The ethanol peak area rises during the experiment in a stable trend due to the continuous generation via ECO2R and the slow-equilibrium of the vapor phase. The effect of formate injection does not influence this trend (Figure 5c).

Observing the H_2 selectivity via hydrogen evolution reaction (HER), however, we observe a relatively quick increase within the 1-hour experiment in comparison with our results in other blank experiments. The accumulation or increment of anion concentration at the catholyte might affect the charge balance of the surface, pulling more potassium ions to surface layer. The drying of the salt-particles at the catalyst-pores can accelerate flooding by opening flow paths to the electrolyte. At this point, it is hard to determine whether formate ion specifically accelerates the flooding at the GDL or not, but an increase in HER is apparent. Nevertheless, it is evident that formate does not get reduced to a gaseous or liquid species such as ethylene or ethanol, or influence the pathways of these products.

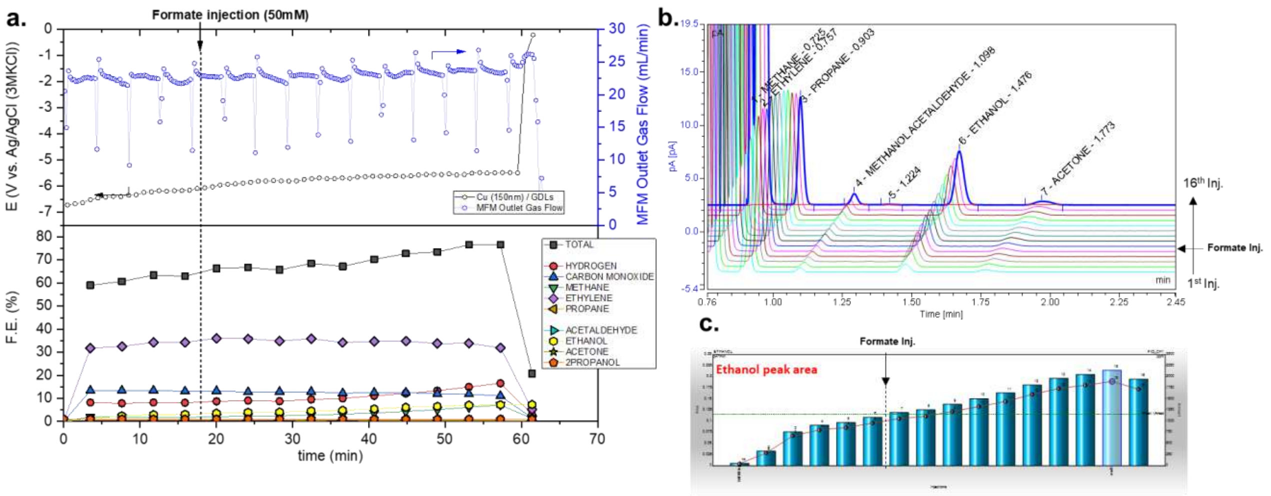

Figure 5: **a)** Cathode potential, outlet gas flow and faradaic efficiency of the products over the course of 1h experiment with **formate** injection between the 4th and 5th injection, **b)** waterfall plot of GC injections with an emphasis on the C2+ liquid products, **c)** Bar-graph of Ethanol peak area at each injection

3.2 Acetate Addition

In this section, we investigated the effect of acetate (CH_3COO^-) compound on ECO2R. We considered whether acetate anion, which is a C-C coupled simple hydrocarbon, might take part in a surface reaction or not, in order to produce a gaseous species or volatile effluent at sufficiently high potential. Hence, we introduced 50 mM potassium-acetate salt (or acetate anion) to the catholyte beaker between the 4th and 5th GC injections, shown in Figure 6a. No significant change either in electrode potential or faradaic efficiency of the products was detected. Further, the MFM outlet flow was not affected by the injection either.

In this experiment, however, we observed a semi-stable period for ethanol peak area following the injection of acetate, unlike the steady rise in the previous formate injection. If the C-C bond in acetate is an active intermediate towards ethanol path via glycol-aldehyde and ethylene-glycol such as in Figure 1, then central ethanol path via acetaldehyde would be impaired. Yet, liquid product analysis by NMR or HPLC would be required to postulate further on the selectivity, which might help to explain the lag in the ethanol peak area. As acetate is a negatively charged anion, when the anion is introduced into the bulk electrolyte (rather than formed at the electrode's surface) it is unclear the proximity of the anion form that is able to reach to the vicinity of the electrode's surface under a large negatively bias.

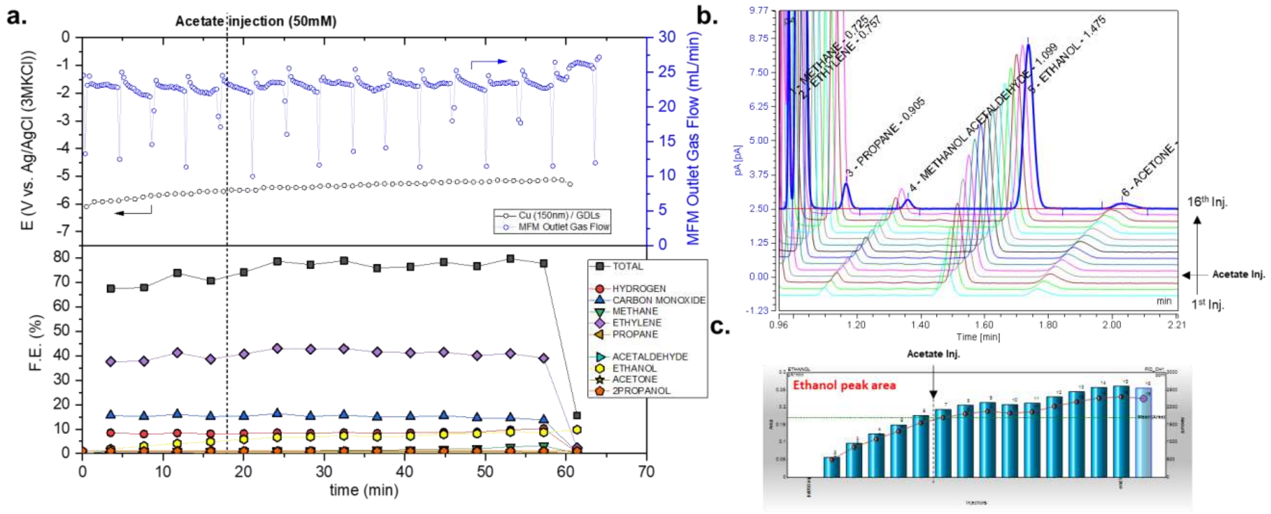

Figure 6: **a)** Cathode potential, outlet gas flow and faradaic efficiency of the products over the course of 1h experiment with **acetate** injection between the 4th and 5th injection, **b)** waterfall plot of GC injections with an emphasis on the C2+ liquid products, **c)** Bar-graph of Ethanol peak area at each injection

3.3 Acetaldehyde Addition

In this section, we investigated the effect of acetaldehyde (CH_3CHO) intermediate on ECO2R tests (Figure 7). During the course of electrolysis, 0.55 mL of the 40 % wt. acetaldehyde solution was injected into 1 M $KHCO_3$ catholyte to obtain a final concentration of 50 mM acetaldehyde in the beaker. Upon injection, we observed an instant spike in gaseous species (Figure 7a) which might result from the highly volatile acetaldehyde compound (boiling point of 20.9 °C). Also the rapid injection of this intermediate was necessary as the aldehyde solution is less stable than the other intermediate compounds therefore it is vital to introduce it to the electrolyte flow immediately.

Interestingly, the ethanol peak area showed an initial step back, then following by a steep rise (Figure 7c). This is also evident from the waterfall plot, where a sharp acetaldehyde peak appears at the 5th GC injection at 1.1 min, just before the ethanol peak area at 1.4 min. This was proceeded by a linear scale up of the ethanol concentration with the linear rise of the electrical charge (chronopotentiometry method; at a constant applied current of 300 mA/cm^2). These findings are consistent with the trends observed in higher ethanol concentration with acetaldehyde injection, observed by Bertheussen et. al. using a head space-gas chromatogram (HS-GC)[5]. Moreover, a significant contribution of our result is the on-line detection of acetaldehyde in the CO_2-off-gas stream, unlike the undetectable acetaldehyde peak in their HS-GC analysis. This is mainly a result of a different cell design, i.e. Cu-GDL vs. Cu-foil, where the volatile compounds could be carried from the reaction surface to the outlet port, together with the gaseous products and unreacted CO_2 from the same local environment. Also consistent with the DFT model by Koper et. al[6], aqueous acetaldehyde compared to its adsorbed counterpart requires 0.7 eV less energy for the following step which showed the thermodynamically most favorable pathway ethanol.

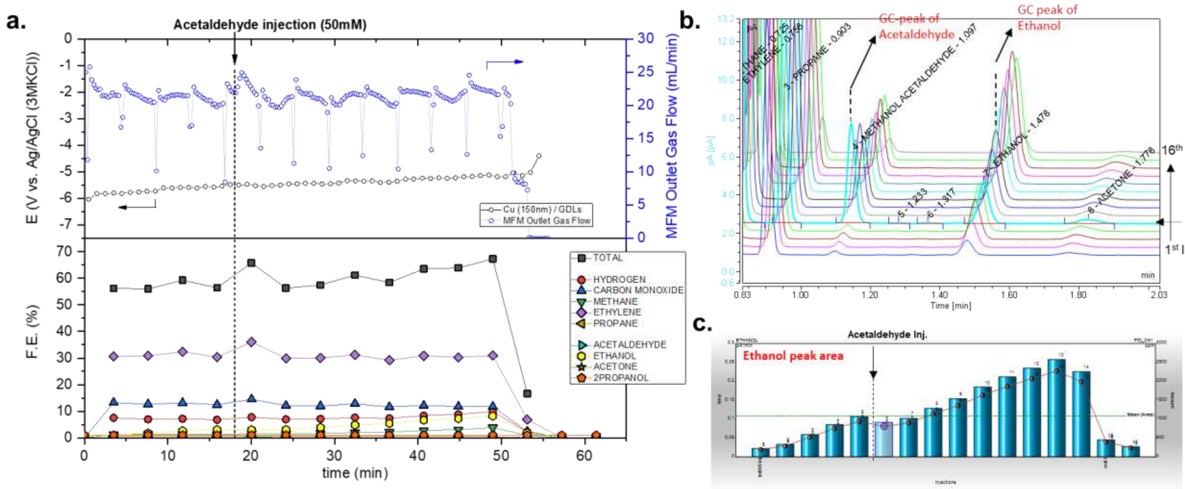

Figure 7: **a)** Cathode potential, outlet gas flow and faradaic efficiency of the products over the course of 1h experiment with **acetaldehyde** injection between the 4th and 5th injection, **b)** waterfall plot of GC injections with an emphasis on the C2+ liquid products, **c)** Bar-graph of Ethanol peak area at each injection

3.4 Glyoxal Addition

In this section, we investigated the effect of glyoxal injection (CHOCHO) on ECO2R test. In the run the injection was conducted between the 5th and 6th run, where all the products showed a steady state, and the faradaic efficiency of ethylene was near 40 %. After the injection, we observed a decreasing trend not only in ethylene efficiency but also in CO efficiency.

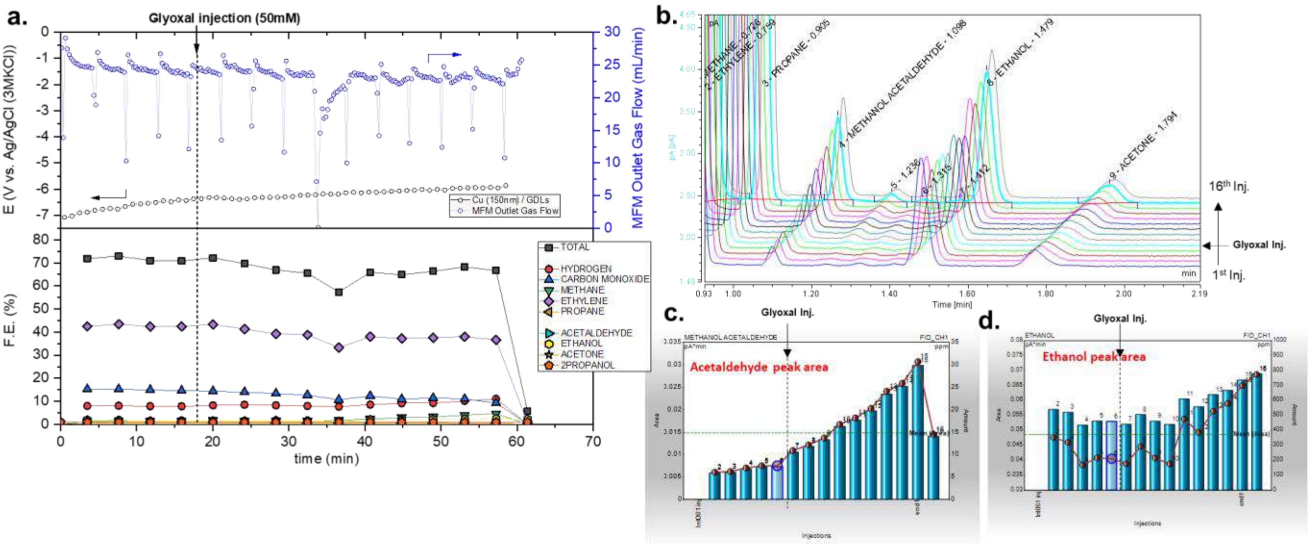

Figure 8: **a)** Cathode potential, outlet gas flow and faradaic efficiency of the products over the course of 1h experiment with glyoxal injection between the 4th and 5th injection, **b)** waterfall plot of GC injections with an emphasis on the C2+ liquid products, **c)** Bar-graph of acetaldehyde and **d)** ethanol peak area at each injection.

On the other hand, there was a steep rise in acetaldehyde concentration that coincides with the injection the glyoxal, which indicates that CHO-CHO compound would be able transform into the acetaldehyde, CH_3CHO on the Cu surface, presumably through the proton-electron coupled mechanism. This hypothesis is due to the linear increase of the acetaldehyde concentration under constant applied current density of 300 mA/cm^2. Furthermore, we noticed a delayed ethanol increment after only five injections which corresponds to roughly 20 mins and 810 C. If we consider a 2e- reduction (proton-electron coupled route) from glyoxal-to-acetaldehyde, 4.2 mM of glyoxal (ca. 10 % of the injected amount) would be active, if all the charge would be delivered to glyoxal. Yet, CO_2 reduction still proceeds and give C1 and C2+ products hence we can conclude that glyoxal is in competition with CO_2 at the surface and those precursors have different reaction paths; towards ethanol for glyoxal and ethylene for CO_2 active sites.

This conclusion is in line with the findings in the literature[1] that both glyoxal and glycoaldehyde reduction have been shown produce acetaldehyde and ethanol but not ethylene. Here in our study, we have shown that, glyoxal not only steers the reaction to ethanol, but also captivates the active sites for ECO2R and impair ethylene route.

4 CONCLUSIONS AND FUTURE WORK

This deliverable assessed the injection of formate, acetate, acetaldehyde and glyoxal on the selectivity of ethylene during ECO2R on a copper catalyst at elevated current densities. The acquired results both confirmed reports previously attained on the order of ~1 mA/cm^2, and provided potential operational approaches to limit the ethanol production pathway during ECO2R, thus increasing the share of electrons to ethylene.

We found that the addition of formate and acetate did not measurably impact the ethylene product selectivity of ECO2R, indicating that these compounds are end products once released from the electrode's surface, and do not substantially interact with surface-bound species or undergo further electroreductive or bulk reactions.

Conversely, both of the aldehyde compounds (acetaldehyde and glyoxal) resulted in increased ethanol production and a proportional shift in electrons away from carbon monoxide and ethylene. This confirms previous reports regarding the reduction of aldehydes within a ECO2R system and provides a quantitative assessment of the impact of gas product selectivity. The staged reduction of glyoxal can further be observed during the length of the experiment through the rise in both acetaldehyde and ethanol GC peak areas upon injection.

Future work following this deliverable will follow-up on the experimental findings from the acetaldehyde and glyoxal intermediate tests. Specifically, WP4 researchers will aim to provide aldehyde-scavenging compounds into the catholyte to remove any formed glyoxal and acetaldehyde species prior to the reduction into alcohols (ethanol and n-Propanol). Such an approach has the potential to stop the alcohol production pathways after 6 e^-'s (glyoxal) and 10 e^-'s (acetaldehyde) transfers, versus the 12 e^-'s of ethanol. The results from this deliverable indicate that in such a scenario ethanol production will be reduced in favor of acetaldehyde, while a larger share of electrons would be available for ethylene production, the targeted product of WP4.

5 REFERENCES

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