

**SELECTIVE ELECTROCHEMICAL REDUCTION OF CO₂ TO HIGH VALUE CHEMICALS****Grant agreement no.: 851441****Start date:** 01.01.2020 – **Duration:** 39 months**Project Coordinator:** Dr. Brian Seger - DTU**DELIVERABLE REPORT**

4.5 FINAL REPORT ON WP ACHIEVEMENTS IN TERMS OF ECO2R SELECTIVITY TO ETHYLENE AT HIGH CURRENT DENSITY		
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PU	Public	X
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NATURE OF THE DELIVERABLE		
R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

SUMMARY

Keywords	Electrochemical CO ₂ reduction; gas-diffusion electrodes; mass transport
Abstract	<p>This deliverable report describes the final ethylene performance achieved by combining the knowledge learnt in the previous deliverable reports. Specifically, each of the previous deliverables explored different experimental avenues for separately suppressing competing reactions. These include the use of additives to target the reduction of ethanol/acetate, optimizing catalyst layer thickness to minimize H₂ and CO, and varying the gas-diffusion layer composition to ensure optimal mass transport, conduction, and elevated current densities. The final ethylene selectivity was unable to meet the MS6 and MS7 targets of 75% and 90% Faradaic efficiency towards ethylene. However, using the experimental knowledge gained from the previous deliverable we were able to operate at substantially larger partial current densities for ethylene, and combined ethylene + ethanol Faradaic efficiencies as compared to the start of the project. Thus, we can provide a conclusive outlook and direction for the field as it related to optimizing C2+ selectivity on simple copper catalysts.</p>

REVISIONS

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FINAL REPORT ON WP ACHIEVEMENTS IN TERMS OF ECO2R SELECTIVITY TO ETHYLENE AT HIGH CURRENT DENSITY

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1 INTRODUCTION

This deliverable report combines the previous conclusions of Deliverable 4.1-4.4, and efforts from Work Packages 5 and 7, to optimize ethylene formation in a CO₂ electrolysis system using a sputtered copper catalyst. These previous deliverables aimed to increase ethylene selectivity primarily by targeting the reduction of competing reactions, as compared to directly promoting ethylene production. Most notably the competing reactions to be reduced include carbon monoxide (CO), hydrogen (H₂), ethanol and acetate. When combined, these competing reactions can consume >50% of a CO₂ electrolysis cells electrons, thus prohibiting ethylene Faradaic efficiencies near the SELECTCO₂ targets of 75% and 90% throughout the course of the project. The motivations for these efforts have been described in more detail versus existing literature in previous reports.

2 SCOPE

The scope of this deliverable is to report the highest achieved selectivity and current densities towards ethylene production as a result of WP4 progress and previous deliverable findings. As described in the below experimental results, scientific discussion and conclusion, we expand this scope to include a combined ethylene and ethanol Faradaic efficiency. Such expansion comes as a result of WP7 theoretical findings, and recommendations from the Scientific Advisory Board and Industrial Advisory Board.

3 RESULTS AND DISCUSSION

This section reports the combined findings that led to the most promising experimental results for ethylene formation in CO₂ electrolysis. As described in the following scientific discussion and conclusions section, we have also aimed to maximize the combined Faradaic efficiency of ethylene and ethanol.

Catalyst layer thickness and its influence on selectivity was described in Deliverable 4.3. In this report a catalyst layer thickness between 100 and 300 nm was found to minimize H₂ and CO production, while maximizing ethylene Faradaic efficiencies. Such a thickness allows for CO₂ access throughout the whole catalyst layer as described by the WP7 findings, while allowing for the active area to be maximized. Thus, we have used a 200 nm thickness for the combined results.

As discussed in Deliverable 4.1 and the additional findings described in the Midterm Report, we also found that the addition of a compounds with a free primary amine group (such as hydrazine or anthralamide) can reduce the Faradaic efficiency of CO substantially. Reducing CO output from ~12% to ~4%, and thus increasing the Faradaic efficiencies of C₂+ products including ethylene. While such results were promising, we were able to decrease CO production by a similar margin by switching to a membrane electrode assembly configuration and operating at a lower flow rate. An MEA configuration cannot allow for the addition of the described amine compounds due to a lack of catholyte in the system. An added benefit of the MEA configuration is a substantial reduction in cell voltage due to reduced ohmic losses from the removed catholyte channel. Thus, our best results do not utilize the findings of Deliverable 4.1.

3.1 Best values achieved for ethylene selectivity and current density.

The peak ethylene selectivity achieved in the project occurred in the first 18 months, reaching peak values between 50-52% during testing with a high catholyte flowrate of 1 M KOH. These tests were performed with a 2.25 cm² geometric catalyst area sputtered with 200 nm of a copper catalyst and using a Sigracet 38BB commercial gas-diffusion layer. Periodic tests using an e-PTFE gas-diffusion layer and a 50 nm copper catalyst layer were also able to reach 55-57% ethylene Faradaic efficiencies. However, due to the poor conductivity of the sputtered copper layer these catalysts degraded quickly, within the first 20 minutes of operation meaning that a good baseline selectivity could not be achieved. Such performance may have been able to be maintained for longer periods with

additional conductive layers added on top of the copper layer, but these effects were not pursued as there was not a clear avenue to increase ethylene selectivity further by reducing ethanol production. The activities also differed from the established deliverable workplan which was to develop different gas-diffusion electrodes in conjunction with WP5.

In addition to the peak ethylene selectivity, the variety of gas-diffusion electrodes developed in WP5 allowed for elevated current densities to be reached. We achieved ethylene partial current densities of 234 mA/cm² at a Faradaic efficiency of 39%, which were the highest in the project (**Figure 1**). In this case the gas-diffusion electrode utilized larger copper particles deposited with MPIP ionomers (denoted as Cu LPs with MPIP in Deliverable 4.4).

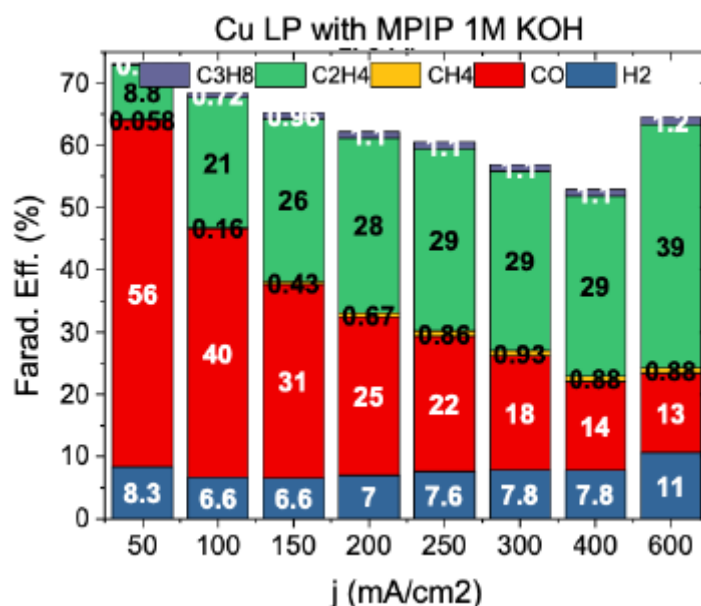


Figure 1: Gas product distribution for Cu micron-sized particles (LP) deposited with MPIP ionomer as a function of current densities when using 1M KOH as the catholyte.

3.2 Best values achieved for combined ethylene and ethanol production.

When considering the co-production of ethylene and ethanol together, we have achieved results that have more industrial importance. The approach utilizes an MEA configuration with lower CO₂ flow rates (**Figure 2a**). Such an approach allows for CO produced at the entrance regions of the channel to undergo further reduction to ethylene and ethanol. Utilizing the correct CO₂ flow rate can also prevent CO₂ shortages that lead to unwanted hydrogen evolution.

Analysing the results in **Figure 2a**, we can be seen that CO decreases greatly with lower flow rates as it is converted into further reduced products. As shown in previous reports CO is ~12% at 50 standard cubic centimetre per minute (sccm) flow rates. However, at 10 sccm CO is reduced to <3%. As a result of these further reductions, the production of oxygenates increases greatly at 10 sccm (**Figure 2b**), by as much as 14% as compared to the 50 sccm case. The combined ethylene + oxygenates then reaches a total of 84%, with ethylene + ethanol reaching ~72%. These results were achieved at a total current density of 200 mA/cm². Means of reducing acetate production (or preventing conversion of ethanol to acetate) would increase such a total Faradaic efficiency further and may be achievable by reducing the local pH of the reaction environment slightly.

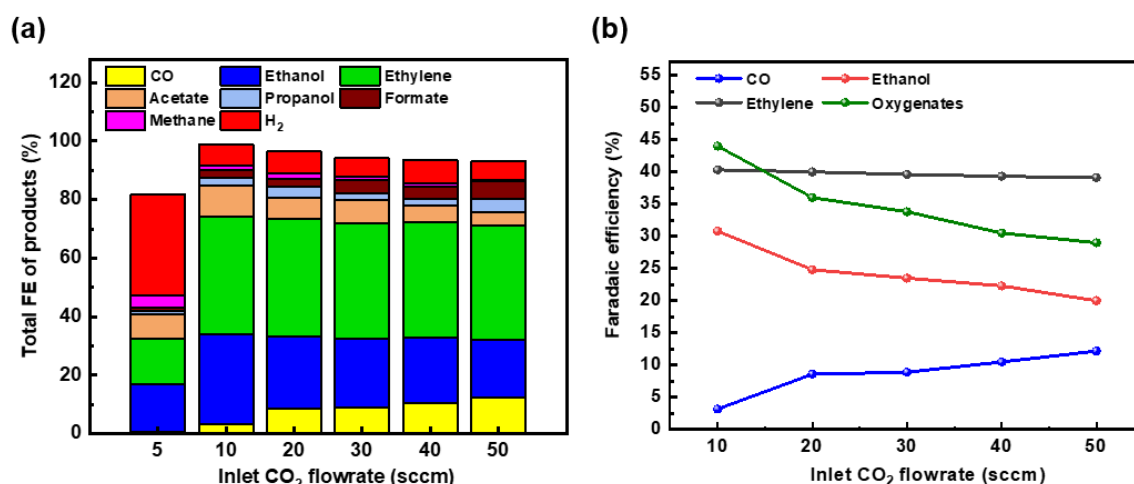


Figure 2: Peak multi-carbon product formation tests achieved through catalyst layer optimization and varied flow rate conditions. Here the combined ethylene + ethanol formation reached >70%. Further modifications of the anolyte concentration are expected to decrease acetate formation and further increase ethanol. Under these cases >75% ethylene + ethanol is then achievable. The anolyte is 1 M KOH, the current density is 200 mA/cm² and a Sustanion anion exchange membrane is used.

4 SCIENTIFIC REFLECTIONS ON THE INABILITY TO IMPACT THE ETHYLENE/OXYGENATES BRANCHING PATHWAY

As noted in the Midterm Report, the primary challenge facing the 75% and 90% ethylene Faradaic efficiency measurements is the co-production of oxygenates (ethanol, acetaldehyde and acetate), which have consistently consumed between 25-40% of the inputted electrons for the duration of the project. Thus, without direct experimental or catalytic control over the oxygenate/ethylene branching pathway, substantial ethylene selectivity's were not achieved despite the advancements made in WP4.

Within the SELECTCO₂ consortium Deliverable 7.5 outlined the branching pathway computationally and determined that the shared C-C coupling step is the rate-determining step for both ethylene and ethanol production. The two products then diverge at a shared *HCCO intermediate where protonation of the oxygen end leads to ethylene, while protonation of the carbon atom leads to oxygenated products (ethanol, acetate). These modelling conclusions imply that ethanol and ethylene cannot easily be promoted separated from one another as the branching pathway is kinetically downhill from the rate-determining step (see Figure 3). These conclusions are like those observed experimentally where ethylene and oxygenates are formed at similar ratios when observed.

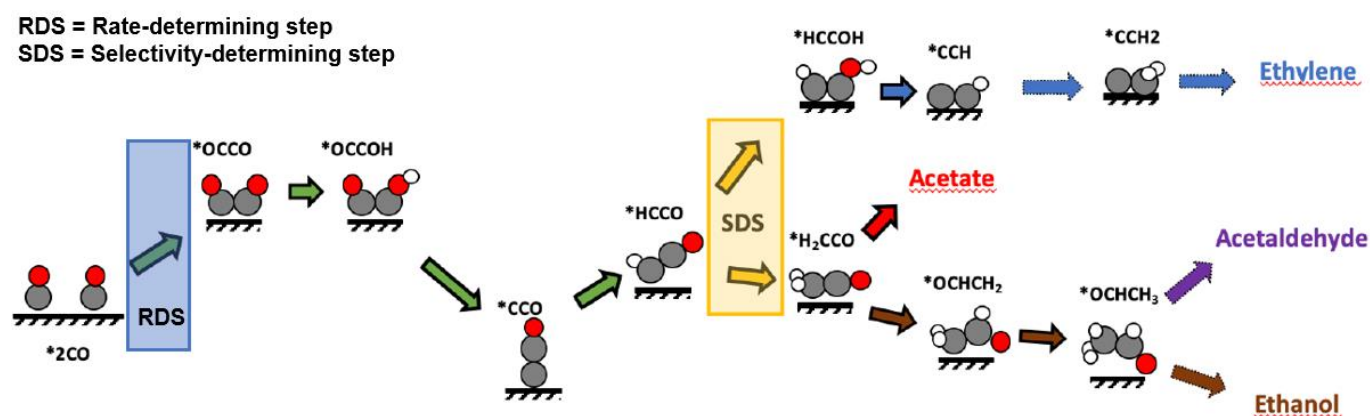


Figure 3: Schematic of the reaction pathways separating ethylene and ethanol as described in Deliverable 7.5, beginning from carbon monoxide dimerization. Here the selectivity-determining step (SDS) is kinetically after the rate-determining step (RDS).

In the final work for WP7, the DTU-Theory team extended the findings of Figure 3 to include kinetic barriers as compared to thermodynamic barriers alone. These efforts presented in

Figure 4 found that two parameters allow for the ethylene/ethanol branching pathway to be influenced to some extent. Notably DTU-Theory found that elevated local pH (the pH in the region where the electrochemical reaction takes place) and higher overpotentials should favour ethylene versus ethanol.

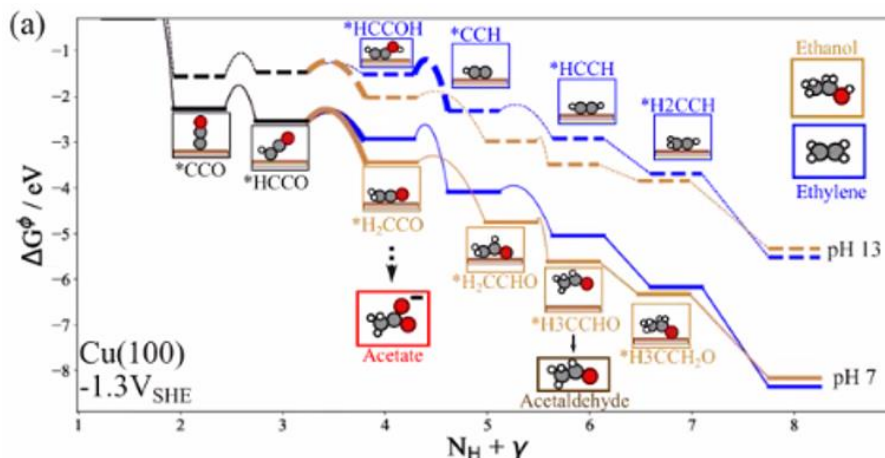


Figure 4: Comparison of ethylene and ethanol energetics including transition barriers as described by WP7 at a Standard Hydrogen Potential of -1.3 V. Here minor differences between ethanol and ethylene can be observed under different pH conditions, but not enough to completely shift the reaction towards or away from ethylene.

Despite these theoretical findings, however, these observations have already been experimentally observed in literature and have been taken into account in experimental work, as well as in the efforts of WP4. Specifically, during our experiments we operate with either pH = 14 electrolytes, or at elevated current densities which result in high local pH values at our cathode. Additionally, at elevated current densities of $>300 \text{ mA/cm}^2$ we are also operating at very high overpotentials. Thus, we had already enacted the new theoretical understandings of DTU-Theory through iteration and large data sets.

Despite these limitations, WP4 and WP3 have found alternative means of shifting the ratio of ethylene to oxygenates produced. These include the introduction of CO-producing metals such as silver, and by operating at lower flow rates. Unfortunately, both approaches are found to increase oxygenate production, rather than ethylene production due to their tendency to shift closer to carbon monoxide electrolysis product distributions. These observations then lead to primary conclusions for the SELECTCO2 Work Package 4 on selectivity ethylene production as described below.

5 CONCLUSIONS AND RECOMMENDATIONS

In conclusion, we have completed the final deliverable for WP4 targeting elevated ethylene selectivity from CO_2 electrolysis. The most notable factors to optimize ethylene selectivity were (i) optimization of the catalyst layer thickness, (ii) shifting to a membrane electrode assembly device, (iii) the use of lower CO_2 inlet flow rates to encourage CO reduction and (iv) the use of alkaline electrolytes and/or elevated current densities to push the local pH to higher values. Combined these led to ethylene Faradaic efficiency values in the range of 50-57% depending on the current density and exact operating conditions.

We have then concluded that achieving the targeted milestones (MS6 and MS7) required a substantial departure from current state-of-the-art approaches, as well as those proposed by WP4. From our findings we can promote two possibilities that are heavily encouraged for future research:

- 1) **Use of non-copper catalysts for multi-carbon CO₂ reduction:** To date copper and copper-based catalysts are the only catalysts capable of making multi-carbon products such as ethylene and ethanol. However, no researchers globally have clearly shown the ability to separately target ethylene or ethanol at meaningful current densities. A substantial departure from current research lines is then required to produce a new non-copper catalyst which can produce ethylene without by-product ethanol. Here molecular catalysts may provide a route forward due to their abilities to provide more controlled reaction pathways.
- 2) **Consideration of cumulative ethylene-ethanol Faradaic efficiencies:** As shown in WP4 we achieved combined C₂+ selectivity's of 72% at current densities of 200 mA/cm². While ethylene is the target product, industrial processes developed by Braskum (and others) exist which produce ethylene via ethanol dehydration (more details denoted in Deliverable 8.4). Thus, while the electrochemical reduction of CO₂ to ethylene seems to be limited to 50-60% with 25-30% ethanol co-production, the combined ethylene + ethanol selectivity can exceed 75%. Considering a post-electrolysis dehydration of ethanol to ethylene, such a combined route using our electrochemical results would allow for an overall CO₂ to ethylene selectivity in the range of those targeted. Such routes must be examined at higher technology-readiness levels as they combine multiple systems and separations together.