



SELECTIVE ELECTROCHEMICAL REDUCTION OF CO₂ TO HIGH VALUE CHEMICALS

Grant agreement no.: 851441

Start date: 01.01.2020 – Duration: 36 months

Project Coordinator: Dr. Brian Seger - DTU

DELIVERABLE REPORT

4.3 REPORT ON MODIFYING CATALYST LAYER THICKNESS, MORPHOLOGY, SURFACE STRUCTURE FOR HIGH EFFICIENCY ETHYLENE PRODUCTION AND SUPPRESSION OF COMPETING REACTIONS		
Due Date	31-01-2022	
Author (s)	Thomas Burdyny; Erdem Irtem; Mengran Li; Kailun Yang	
Workpackage	4	
Workpackage Leader	Thomas Burdyny	
Lead Beneficiary	TUD	
Date released by WP leader	15-01-2022	
Date released by Coordinator	16-01-2022	
DISSEMINATION LEVEL		
PU	Public	X
PP	Restricted to other programme participants (including the Commission Services)	
RE	Restricted to a group specified by the consortium (including the Commission Services)	
CO	Confidential, only for members of the consortium (including the Commission Services)	
NATURE OF THE DELIVERABLE		
R	Report	X
P	Prototype	
D	Demonstrator	
O	Other	

SUMMARY	
Keywords	Electrochemical CO ₂ reduction; catalyst structure and thickness; current collection
Abstract	<p>This deliverable reports aims to explore the potential of catalyst layer manipulations to promote evenly-distributed CO₂ electrochemical reduction, which in turn optimizes multi-carbon product formation.</p> <p>Copper (Cu) is the only catalyst to produce noticeable amount of multicarbon products such as ethylene and ethanol, but is extremely sensitive to the local reaction environment and overpotentials. By positioning the catalyst layer at the liquid-gas interface, the gas-diffusion electrodes can achieve industrially relevant current densities. Consequently, through-plane and in-plane local variations in local pH, local CO₂, catalyst availability, and electric field are then also important to control.</p> <p>In this report, we studied the roles of these local variations by changing the catalyst thicknesses and current collection for the gas-diffusion electrodes and evaluating their performance in a liquid flow cell operating at high current densities up to 300 mA cm⁻². We identified that a moderate Cu thickness is highly desired to promote multicarbon because it can balance the transport of water, ions, and CO₂ within the catalyst structure to achieve an optimal local pH, and sufficient catalyst, water and CO₂ local availability. We also highlight the importance to homogenize the current distribution in-plane for to minimize energy loss and ensure a more negative cathode potential across the electrode in plane to drive CO₂ electrochemical reduction for C₂₊ products.</p> <p>This report is complementary to our D4.2 report by providing in-depth insights for the design of 3D-structured catalyst layer for industrially applicable gas-diffusion electrodes. The experimental results will also contribute to the data input and model validation for WP7.</p>
Public abstract for confidential deliverables	

REVISIONS			
Version	Date	Changed by	Comments
1.0	17-01-2022	Thomas Burdyny	

REPORT ON MODIFYING CATALYST LAYER THICKNESS, MORPHOLOGY, SURFACE STRUCTURE FOR HIGH EFFICIENCY ETHYLENE PRODUCTION AND SUPPRESSION OF COMPETING REACTIONS

CONTENT

1	Introduction	4
2	Scope.....	5
3	Results and Discussion	6
3.1	Varying Catalyst Layer Thickness to Impact Through-Plane Reactions	6
3.2	Homogenizing in-plane Activity by Varying Current Collection.....	10
4	Conclusions and future work	12
5	References	13

1 INTRODUCTION

This deliverable report describes the effects of in-plane and through-plane variations in the copper (Cu) catalyst layer on the performance of overall gas-diffusion electrodes (GDEs) to reduce CO₂ at high current densities. Specifically, this report investigates the changes of Cu reactivity and product selectivity over Sigracet gas-diffusion layers by various Cu thicknesses and in-plane electric potential distributions.

Scientific background

Copper catalysts for electrochemical CO₂ reduction are extremely sensitive to the reaction environment (e.g., local CO₂ availability and local pH), applied potentials, and surface morphology.¹ By using operando characterisations, recent studies²⁻⁴, including our Deliverable Report D4.2, have shown that the Cu surface undergoes significant in-situ surface reconstruction that could benefit the production of C₂ products by forming (100) facets, increasing surface roughness and increasing local pH. However, these studies only provide information about the catalyst-bulk electrolyte interface, and are challenging to understand the roles of through-plane and in-plane variations in the 3D structured catalyst layer.

There are a few recent experimental and modelling reports that highlight the importance of the through-plane inhomogeneity across the catalyst layer in determining the local CO₂ concentration⁵⁻⁷ and local pH⁷ (Figure 1). As shown in Figure 1c, the CO₂ concentration decreases within the catalyst layer as the distance from GDE interface decreases. Conversely, the local pH decreases via an opposite direction due to the acidification by CO₂ (see Figure 1b). The local CO₂ concentration was reported to influence the product selectivity: a moderate CO₂ concentration could benefit the production of multi-carbon products. In addition, a high local pH has been reported to favour multicarbon productions due to the lowering of overpotentials vs. RHE by 59mV/pH unit for C₂+ products.^{1,6} In most of these studies^{5,7}, nevertheless, the catalyst layers contain both Cu or oxide-derived Cu nanoparticles and other

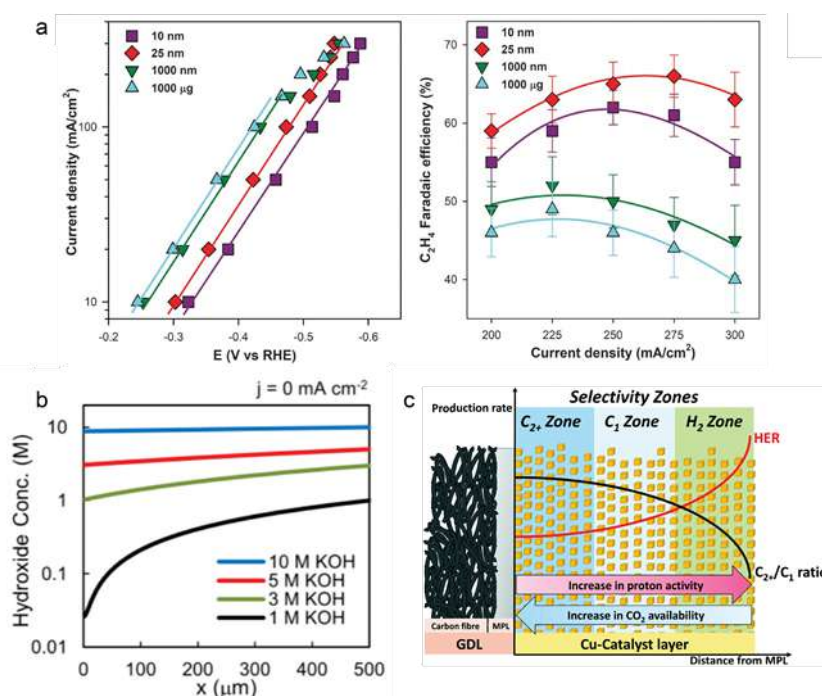


Figure 1: (a) The reported effects of Cu thicknesses on the performance of GDEs in KOH catholyte.⁶ (b) Calculated local hydroxide ion pH in catholytes with different pH values when current density = 0 mA cm⁻².⁶ (c) Reported different reaction zones in the catalyst layer in a flow-through configuration in bicarbonate electrolytes.⁷ Reproduced from Ref. 7 with permission from the Royal Society of Chemistry.

additives such as ionomers, which should have significant impacts on the through-plane compositional and structural variations but cannot be easily ruled out in these studies.

Due to the structural inhomogeneity of the in-plane catalyst layers, importantly, there should be local variations across the catalyst layer in the electric field and local reaction environment. Such in-plane local variations can exert a significant impact on the performance of large-size electrodes for industrial applications. However, it remains underexplored for the understanding of the relationship between in plane local variations and overall electrode performance.

Hence, this report seeks to understand the roles of through-plane and in-plane local variations on the performance of Cu-based GDEs in a flow electrolyzer operating at current densities up to 300 mA cm^{-2} . To rule out the potential impacts from additives and ionomer in the catalyst layer, we chose to deposit only Cu onto the gas-diffusion layer by magnetron sputtering. The new insights generated from this report are anticipated to be important to develop large size electrode for industrially relevant CO_2 electrolyzers, and minimizing catalytic materials, which do not contribute to the desired reaction.

2 SCOPE

This deliverable contributes to WP4 (ethylene production) and WP7 by providing qualitative and quantitative information on the roles of local through-plane and in-plane variations on of the Cu catalyst layer on a GDL during CO_2 electrochemical reduction at high current densities. Our task is to identify the role of the local variations in the catalyst layer on the performance of the GDE to reduce CO_2 at high current densities, as illustrated in Figure 2.

The configuration of the flow electrolyzer in this deliverable is restricted to liquid flow cell, where a flowing catholyte is fed in between the membrane and the electrode. The reactivity of the GDEs were measured under chronopotentiometry (constant current densities), while the product selectivities were measured by gas chromatography and high-performance liquid chromatography. The work is limited to Sigracet GDL with a microporous layer (MPL), which is commonly used in the field of CO_2 electrolysis.

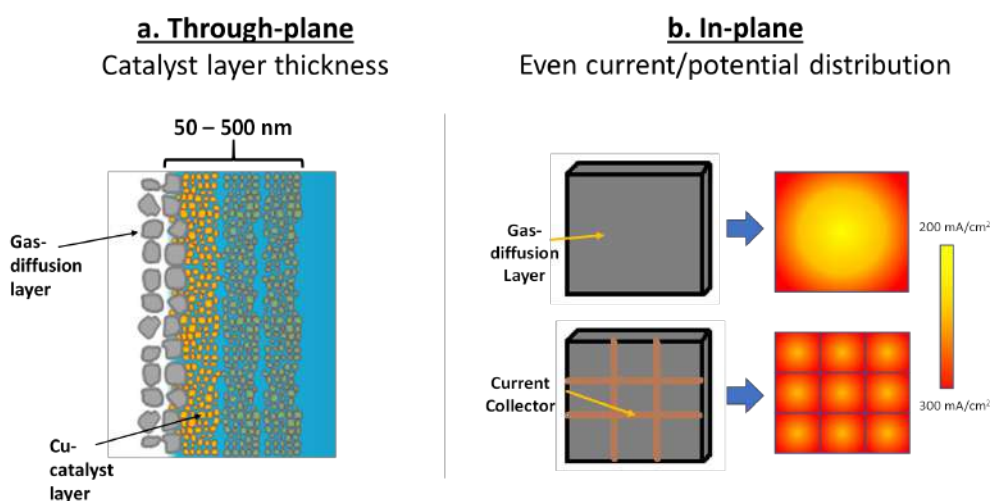


Figure 2: Schematic of (a) through-plane and (b) in-plane experimental protocol design to elucidate the role of local inhomogeneity on the performance of CO_2 electroreduction at high current densities.

3 RESULTS AND DISCUSSION

The experimental setup used for electrochemical reduction of CO₂ and product analysis are presented below in Figure 3. A mass flow controller (MFC) was used to feed CO₂ gas flow to the reactor at 40 mL/min, whereas a mass flow meter (MFM) at the reactor's outlet port measured the "product + unreacted CO₂" flow. As the MFM is calibrated for CO₂, the flow rate was corrected using the gas factor of this mixture that was determined by a gas chromatogram (GC). Back-pressure regulators (BPR) were used to offset the pressure drop amongst the three compartments of the flow cell which are; CO₂ gas, catholyte and anolyte channels, as displayed respectively from left-to-right in Figure 3. A glass beaker with 5 mL volume was used connected to the gas outlet port in order to trap humidity, salt water or pervaporate accumulation to the sampling loop of the GC.

A custom-made flow cell with a 2.25 cm² (1.5 x 1.5 cm) geometrically active reaction area (for cathode, membrane and anode) was utilized in this set of experiments. A strong alkaline solution (1 M KOH, 100 mL) was used for catholyte to maximize C₂₊ selectivity. The same solution and concentration was utilized for the anolyte to decrease the cell voltage at high current density (300 mA cm⁻²) and remain below the maximum power limit of the potentiostat machine (PARSTAT 4000, Princeton Applied Research Inc., 2A and 10 V limit for a single electrode and 45 V for the cumulative voltage limit, also known as compliance voltage). A peristaltic pump was used to circulate electrolytes between the beakers and flow-cell channels in accord with the pressure offset by the BPR system.

Magnetron sputtering (AJA International Inc.) with a copper target (MaTeck Germany, 99.9% purity) was used to form reproducible nano-sized thin films on gas diffusion layers (GDL from Sigracet 38BC, IonPower). Copper nanoparticle catalyst coated gas diffusion electrode with varying nominal sputtering thickness (Cu-X-GDE; where X = 10 to 500 nm) was used as the working electrode (cathode) and a nickel metal foam was used as the counter electrode (anode). To separate cathode and anode compartments, a cation exchange membrane (Nafion 115) was used for its stability at a given alkalinity, while effectively transferring K⁺ (and H⁺) ion for the charge balance of the cell. The bulk pH for both electrolytes did not undergo a significant change during 30 minute experiments (pH_f = 14 ± 0.3). A non-aqueous Ag|AgCl reference electrode ($E_{Ref.} = 0.198 \text{ V vs. SHE}$) was used to measure the working electrode potential.

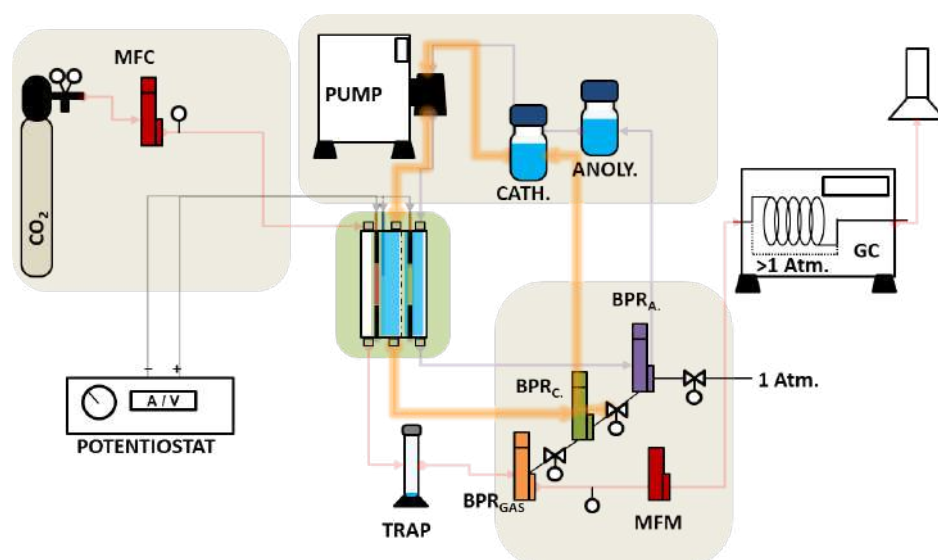


Figure 3: Schematic illustration of the testing system for the electrode measurement.

3.1 Varying Catalyst Layer Thickness to Impact Through-Plane Reactions

In order to understand the relationship between catalyst layer thickness and reaction selectivity towards CO₂ reduction, experimental operating conditions were fixed with the exception of the Cu-film thickness (see previous *SELECTCO2 Deliverable Report D.4.3. – Report on modifying catalyst layer thickness, morphology, surface structure for high efficiency ethylene production and suppression of competing reactions - 17/01/2022 – Version 1*

part for experimental protocol). A systematic investigation of each “Cu-X-GDE” electrode type was then conducted at a constant current of 300 mA cm^{-2} . The results are supported by three separate replicate tests, providing the error bars shown in Figure 4.

The faradaic efficiency of ethylene in Figure 4a reveals a critical maxima at 39.6 % for 60 nm nominal thickness. At 25 nm, its efficiency drops nearly to 30 % followed by complete loss of C_2H_4 selectivity when the nominal film thickness is 10 nm. Interestingly, CO activity remains at $11 \pm 2 \%$ across different Cu-film thickness (25 – 250 nm), yet almost half of its activity is lost once the film thickness drops to 10 nm.

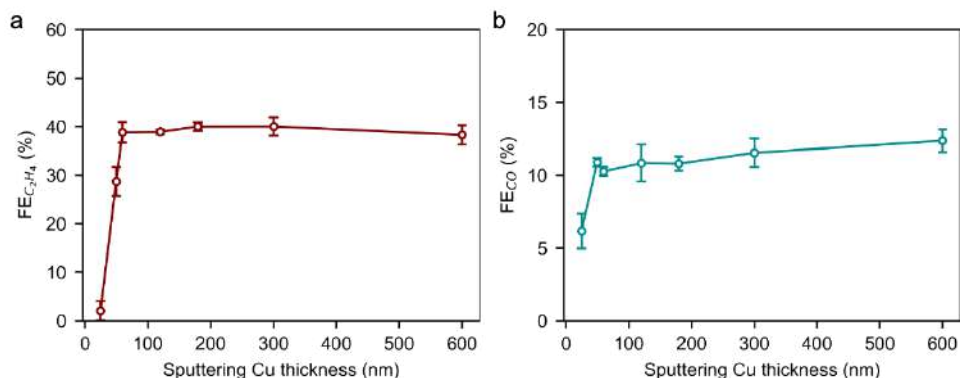
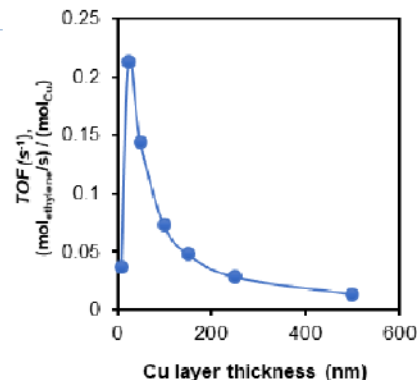


Figure 4: The effect of Cu-film thickness modification of CO₂ electroreduction reaction in terms of faradaic efficiency of (a) ethylene and (b) carbon monoxide. The applied current density is 300 mA cm^{-2} during 30 minutes in 1 M KOH electrolyte at 40 sccm CO₂ gas flow. Error bars represent the averaging of the GC injections where HER is minimal for each of the three experiments with different GDEs.

It appears that CO₂ electroreduction goes under a mass-transport limitation beyond a certain copper layer thickness. In case of a “triple-phase boundary (TPB) condition”, CO₂ reduction is described to occur via direct bonding of a gas molecule to a catalytic site where electrons and protons would meet in harmony. In such a scenario, one would expect a simultaneous increase of the partial current density with the layer thickness at a constant applied current density of 300 mA cm^{-2} . Yet, ethylene partial current density was limited to ca. 120 mA cm^{-2} for copper layer nominal thickness of 50 nm and beyond. Looking from an atomistic point of view, our back-of-the envelope calculations show a higher turn-over frequency for thinner films as well. Due to the dependency to protons for CO₂R, not only the supply of CO₂ but also the diffusion of H₂O as a proton source is an important limiting factor. Therefore, it is not a surprise to observe an effective utilization of the metallic site at much thinner films.

Table 1: Ethylene faradaic efficiencies of various thickness copper electrodes, and accompanying graph for TOF. It should be noted that TOF is based off total number of copper atoms rather than surface copper atoms.

Cu (nm)	Cu (g)	Cu (mol)	FE _{Ethylene} (%)	I _{Ethylene} (A)	Rate _{Ethylene} (mol/s)	TOF (s ⁻¹) (mol _{Ethylene} /s) / (mol _{Cu})
10	2.02E-05	3.17E-07	2%	0.01	1.16E-08	0.04
25	5.04E-05	7.93E-07	29%	0.20	1.69E-07	0.21
50	1.01E-04	1.58E-06	39%	0.26	2.28E-07	0.14
100	2.02E-04	3.17E-06	40%	0.27	2.30E-07	0.07
150	3.02E-04	4.75E-06	39%	0.27	2.29E-07	0.05
250	5.04E-04	7.93E-06	39%	0.26	2.26E-07	0.03
500	1.01E-03	1.58E-05	37%	0.25	2.15E-07	0.01



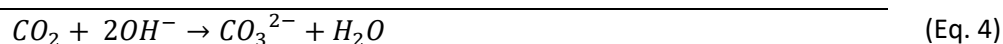
* Model was estimated for a FCC (4 atoms/unit cell) Cu particles with a compact and uniform layer formation, using theoretical density of Cu = 8.96 g/cm^3 , atomic weight of Cu = 63.55 g/mol , GDE area = 2.25 cm^2 .

Nevertheless, the increased population of copper nanoparticles with thicker layers do not result in a higher population of TBP sites, thus indicating an alternative boundary condition. Such a scenario was previously described by Nesbit and Burdyny et al.⁸ as “double-phase boundary condition (DPB)” where CO₂ gas might diffuse from the gas-phase to liquid-phase by the 10s to 1000s of nanometers and be reduced at the liquid-solid interface at the active Cu-site. In our particular phase, the catalyst layer was not supported with any ionomer additives, which promote the transfer of ions (H⁺ or OH⁻) taking part in CO₂ reduction or acting as a CO₂ activator by a nucleophilic attack from the lone electron pairs (e.g. pyridinic or imidazolium groups). For this reason, the diffusive mass-transport limitation observed at this point is a direct consequence of the catalytic property of the copper metal.

One should also consider the high local electrolyte concentration, which may lower the CO₂ solubility and diffusion rate. Considering the combined effects of CO₂ supply, H₂O supply and limited OH⁻ migration, we expect that CO₂ reduction would originate primarily at the catalyst-liquid boundary layer. It is well-known that CO formation is one of the earlier intermediary steps of CO₂ reduction with the transfer of two electron and two protons:



Hence, for every single CO molecule produced, two hydroxyl molecules are generated at the same reactive site. Ideally, negatively charged ions would migrate to the anode to balance with oxygen evolution reaction (OER). Yet, the rate of carbonate formation (HCO₃⁻/CO₃²⁻) through CO₂ capture (or CO₂ neutralization) with the electrochemically formed OH⁻ may occur prior to its discharge from the active Cu-site. Thus, another two molecules of the CO₂ reactant would be neutralized with OH⁻ and may decrease the activity of this metal site by forming metal salts at a critically high concentration according to the equations below (for pH > 10) :



On the other hand, it is postulated that the CO* dimerization reaction (or CO* coupling) is the rate-determining step for C₂₊ products.⁹ Thus, not only the abundance of this intermediate but also the residence time of this adsorbed species is critical for the rate-determining step. Cu film thickness lower than 50 nm (Cu10- and Cu25-GDE) can pose a risk for the population of CO* adsorption sites and decrease the abundance of the meeting points for the coupling reaction.

Conversely, it appears that thicker layers (600 nm) do not sufficiently meet the transport of CO₂ reactant gas throughout the catalyst layer. As a result, a limited CO₂ local concentration leads to a reduced surface coverage of *CO, which is much more sensitive towards C₂₊ products than CO due to the requirement of dimerization.¹⁰ A plateau of CO₂ reduction selectivity is observed, and the potential is not shown to be substantially decreased despite a much larger surface area of catalyst. Interestingly the H₂ evolution does not increase, indicating that the electrode potentials are still low enough to avoid hydrogen evolution on the catalyst areas deplete of CO₂.

Figure 5 shows the high resolution FE-SEM images of those GDEs which are at this critical activity region. Cu100nm-GDEs display an overlap of agglomerated Cu-nanoparticles from 50 – 100 nm in size. The under layer of carbon particles are only visible at lower magnifications seen in Figure 5f. Obtaining a well-focused image at high resolution was difficult for 10 nm thin film due to the local charging effects. This would imply that the copper particles do not effectively distribute the electrons. As the MPL is composed of carbon particles blended with non-conductive PTFE polymer, these charged copper nanoparticles may then not be electrically connected to the conductive carbon in the GDE. High electric fields then result from charge accumulation during imaging.

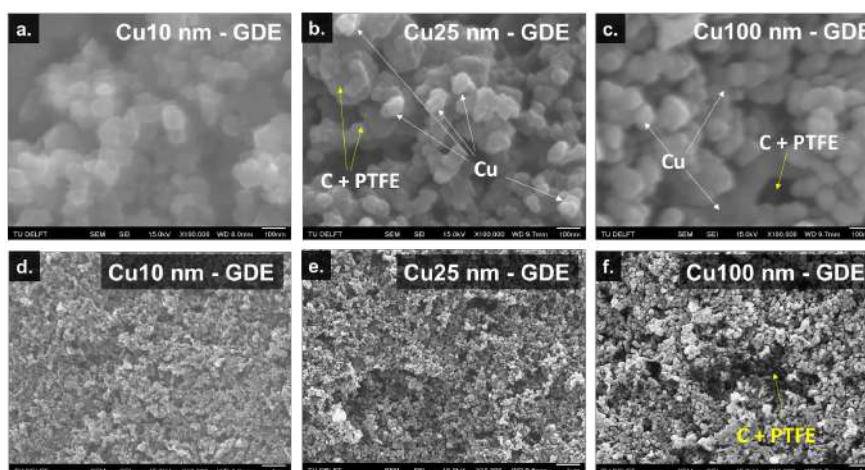


Figure 5: High-resolution FE-SEM images of copper thin-film coated gas diffusion electrodes (GDEs) with varying nominal thickness; (a, d) 10 nm, (b, e) 25 nm and, (c, f) 100 nm. Cu particles are sputtered over a microporous layer of GDE; a composite carbon layer made up of carbon nanoparticles (< 50 nm) blended with ~20 % wt. PTFE binder.

From the above inclinations, a decrease of ethylene selectivity for the films below 50 nm could then also result from an insufficient *CO surface coverage for dimerization and Cu catalyst availability. A thin Cu catalyst layer has a lower local pH due to the CO₂ acidification at the catalyst-MPL. As CH₄ is highly dependent on local pH and tends to be produced at low local pH, which can be confirmed by Figure 6b. In contrast, low local pH suppresses C₂₊ products,^{1,6} and promotes HER over the thinnest Cu electrodes, as shown in Figure 6a. In line with the FE-SEM results, the low coverage of Cu-particles and dominance of the C + PTFE phase also promotes HER.

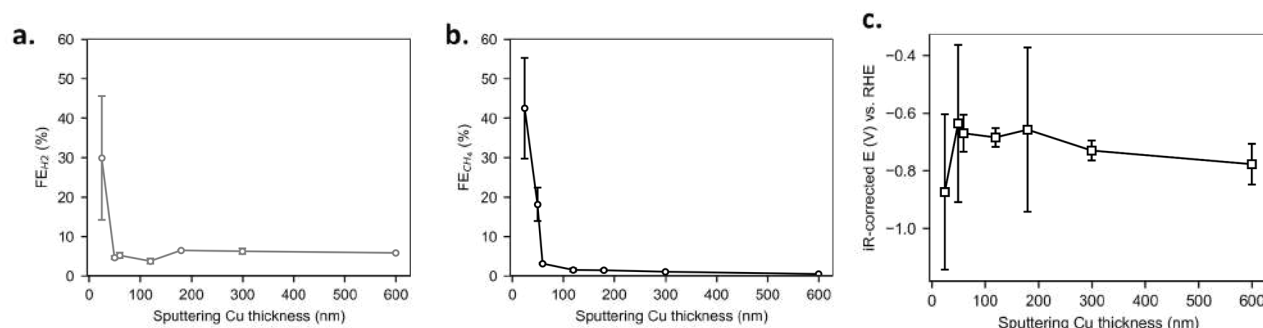


Figure 6: Faradaic efficiency of (a) hydrogen (H₂) and (b) methane (CH₄), along with (c) average of electrode potentials. The applied current density is 300 mA cm⁻² during 30 minutes in 1 M KOH electrolyte at 40 sccm CO₂ gas flow. Error bars represent the averaging of three experiments with different GDEs but taken from the identical sputtering session.

Interestingly, in Figure 6b, the activity of CH₄ does not become null but changes from a low average of 3 % to a maximum of 42 % from Cu50nm-GDE to Cu10nm-GDE, respectively. This would imply that Cu-nanoparticles are still active towards CO₂ adsorption and proceed with the subsequent steps of electron/proton uptake. In Figure 6c, we have also observed a larger overpotential for the tests conducted for Cu10nm-GDEs with an average of – 0.9 V vs. RHE, where a significant deviation of the cathode potential (~450 mV) was noted. For the rest of the electrodes, a rather stable electrode potential was recorded at – 0.7 V vs. RHE.

Combining our experimental findings and physical characterization methods, we can schematically depict a proposed influence of Cu-catalyst film thickness on selectivity during high-rate CO₂ electroreduction testing in a strong alkaline electrolyte. The selectivity results of C₂₊ products (and their precursor CO) indicate a favourable advantage of a shorter diffusion path for the CO₂ gas. At a constant current of 300 mA cm⁻², the average working electrode potential of thicker layers is – 0.7 V vs. RHE, which indicates the activity of a certain area in contact with the electrolyte. Hence, as higher current densities are reached, local CO₂ concentration and water management to

SELECTCO2 Deliverable Report D.4.3. – Report on modifying catalyst layer thickness, morphology, surface structure for high efficiency ethylene production and suppression of competing reactions - 17/01/2022 – Version 1

ensure sufficient water supply and subsequent OH^- removal needs to be considered. Otherwise, the bulk of the copper particles are not active towards CO_2 reduction.

At layers thinner than the nominal thickness of 50 nm, while C_{2+} activity drops, the selectivity of methane (CH_4) rises drastically. This would indicate a complete change of the rate-determining step of CO_2 reduction due to external factors occurring around the same catalytic site. The most significant change in GDE property was the drop in electrical conductivity observed during electron microscopy and also as an extra overvoltage of 0.2 V in the tests. It was shown before that, at higher overpotentials, the formation of CH_4 becomes the dominant process, hence steep increase of methane selectivity is similar to trend observed for polycrystalline copper electrodes.¹ Moreover, the promotion of H_2 from water electrolysis indicate a higher abundance of surface protons, most likely catalyzed by Cu and carbon nanoparticles.

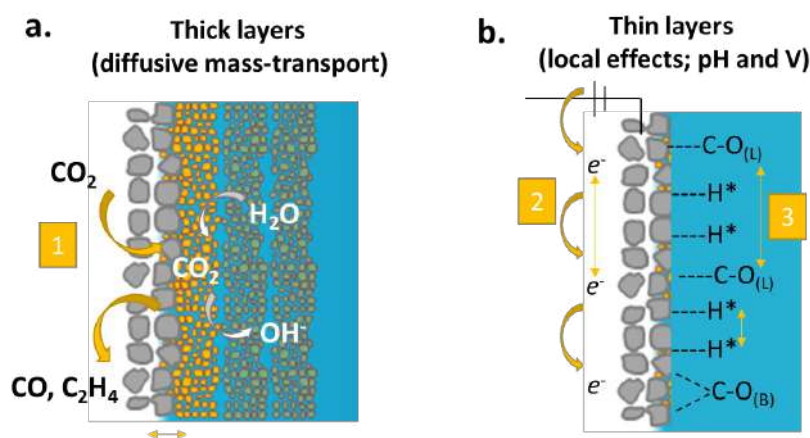


Figure 7: Schematic representation of the proposed influence of catalyst layer thickness on reactive species and products with indications for two separate cases; **(a)** thick layers that are beyond 250 nm and **(b)** thin layers with a thickness lower than 25 nm.

3.2 Homogenizing in-plane Activity by Varying Current Collection

This section presents the experimental results on the effects of in-plane local variations on CO_2 reduction performance by varying the current collections on the GDEs. Many groups have reported the relationship of potential vs selectivity while using Cu as an electrode for CO_2 reduction, but the reaction selectivity across the planar direction of an experimental catalyst has always been assumed to be identical.¹ Here we test this assumption while aiming to optimize C_2 product selectivity by creating a homogenous in-plane reaction potential.

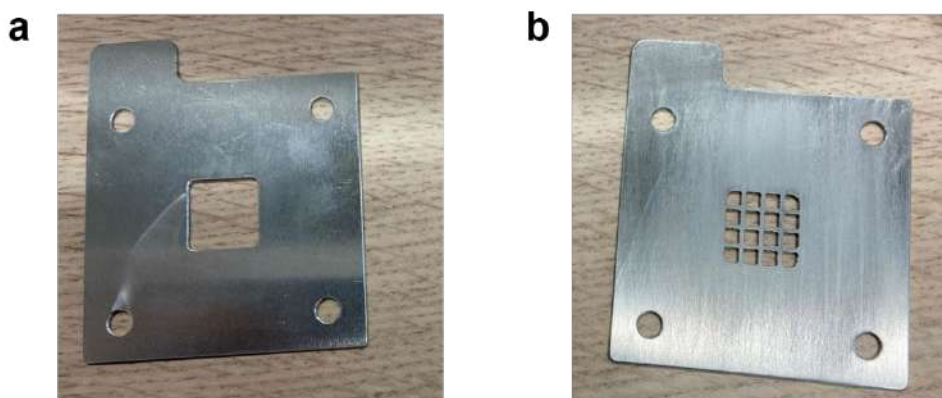


Figure 8: **(a)** Current collector with edge current collection. **(b)** Current collector with centre current collection.

During electrochemical CO₂ reduction, 100 nm thick sputtered Cu on Sigracet 39BC gas diffusion layers (1.5 cm * 1.5 cm, active surface area of 2.25 cm²) were used as the testing GDEs in a flowing electrolyte cell. Both 1 M KHCO₃ and 1M KOH were used as electrolyte separately. CO₂ inflow was 30 mL/min, electrolyte flow rates were both 10 mL/min. The tests were operated for 30 minutes under constant current densities (i.e., 25, 50, 100, 150, 200 mA cm⁻²), and GC injections reached steady state after 10 minutes. Catholytes were collected after the test and directly analysed by HPLC for liquid products. Figure 8 shows the two Aluminium current collectors used in this work. Figure 8a represents edge collection (in the case of PTFE based GDE or carbon based GDE where only edges are under electrical contact). Figure 8b shows a current collector with grids in the middle, which can also provide electrical contact, thus it is hypothesized to give a more homogeneous in-plane current distribution.

Figure 9 shows the Faradaic efficiency of main products detected while using 1 M KHCO₃ as electrolyte. Two opposite trends are observed: the Faradaic efficiency of H₂, CO and formate are slightly higher in the edge collection case than in the centre collection. However the Faradaic efficiency C₂H₄, CH₄, ethanol, n-propanol and acetate are slightly higher (especially for C₂H₄) using centre collection. This can be explained by potential distribution difference between these two scenarios. When using edge collection, the potential on the edges are expected to be the highest, with the centre point having the lowest potential due to the in-plane resistance of the GDE itself. The low potential area will favour the production of H₂, CO and formate. However, when using centre collection, the potential is expected to be distributed on GDE surface more evenly. Electric contact not only comes from in-plane conductivity, but also the current collectors. Thus we hypothesize there will be a larger fraction of the catalyst at a higher potential which favours the production of C₂H₄, CH₄, ethanol, n-propanol and acetate, instead of CO.

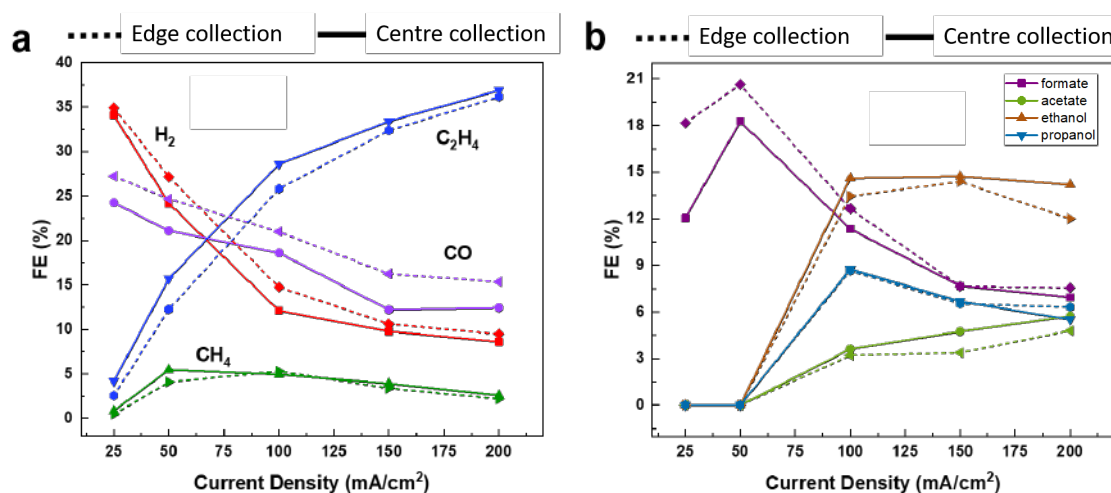


Figure 9: (a) Faradaic efficiency of gas products and (b) liquid products as function of current density in 1 M KHCO₃ electrolyte.

To investigate the influence of electrolyte on the conductivity of gas diffusion electrode, thus the current/potential distribution, we changed the electrolyte to 1 M KOH. Figure 10 shows that the CO FE is still higher using edge collection, while C₂H₄ is higher using centre collection, similar to the results in 1 M KHCO₃ electrolyte. However there are little differences in production of H₂ and CH₄. As for liquid products, more liquid products are detected under 50 mA cm⁻² in centre collection case, a trend which reverses at higher current densities. Overall, slightly more liquid products were produced while using the edge current collection (Figure 11).

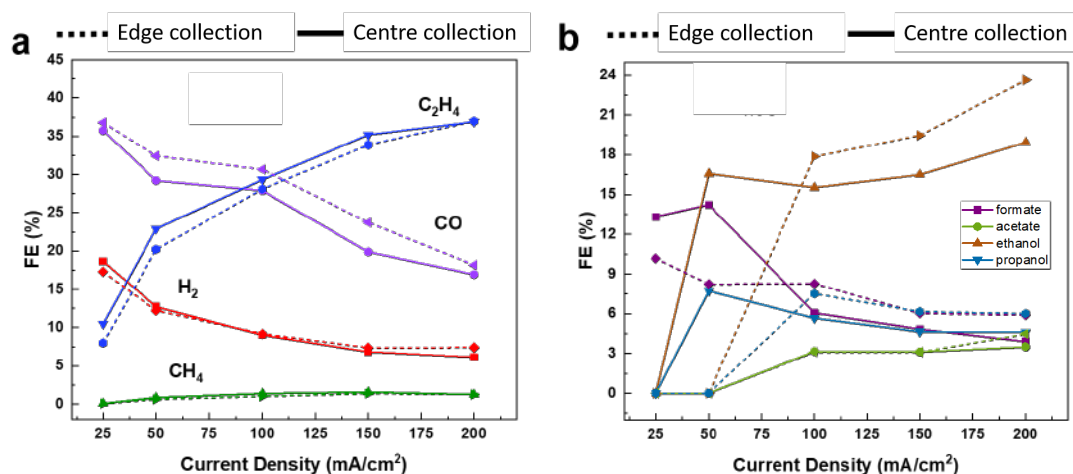


Figure 10: (a) Faradaic efficiency of gas products and (b) liquid products as function of current density in 1 M KOH electrolyte.

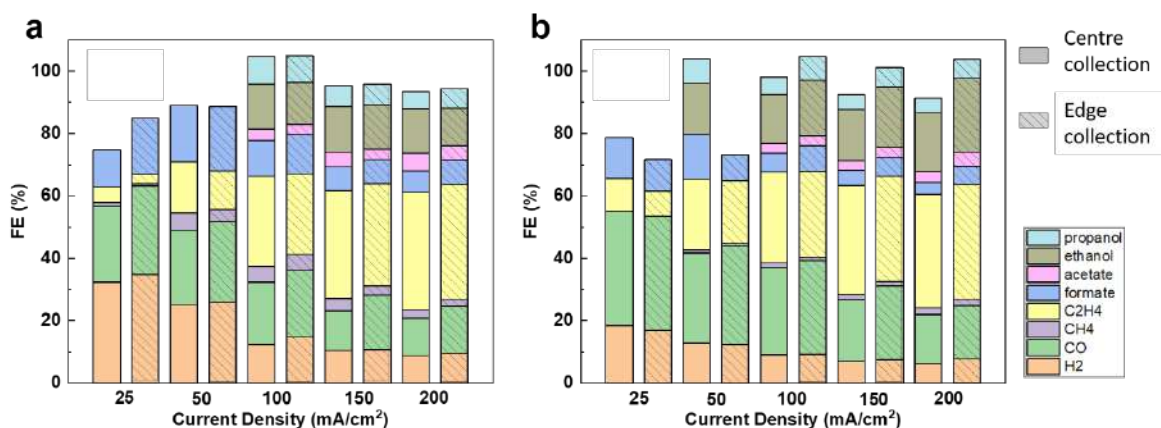


Figure 11: Total Faradaic efficiency gas and liquid products as a function of current density in (a) 1 M KHCO₃ and (b) KOH electrolytes.

4 CONCLUSIONS AND FUTURE WORK

In conclusion, this work reports the important roles of through-plane and in-plane local variations in 3D structured pure Cu catalyst layer in determining the performance of carbon GDEs for CO₂ electrochemical reduction at high current densities. We also highlight in this report manipulating the catalyst layer structure and current collection, we could further optimise the CO₂ reduction efficiency towards C₂₊ products at industrially relevant current densities.

Considering C-C coupling as a rate-limiting step towards C₂₊ products, we conclude that very-thin layers (< 10 and 25 nm) has significantly less chance for interactions of CO* adsorption sites due to the low local pH and availability of Cu catalyst. On the other hand, thicker layers showed an increase in CO ratio, which is also a precursor for the C₂₊ products. The consecutive drop of high carbon products is a result of the insufficient residence time of local CO and limited local CO₂ availability close to the electrolyte bulk. In the light of those findings, the effect of catalyst layer porosity (from sub-micron to tens of microns) and hydrophobicity on product selectivity needs to be further evaluated. We postulate that increased porosity would increase the abundance of intermediary products such as CO* (or CHO*, COH*) and give enough time for proton and electron uptake. This could be achieved by co-deposition of sacrificial atoms at different ratios¹¹, followed by their dissolution to obtain a high degree of control over a large

and rough substrate area, such as a microporous layer of GDLs. On top of that, by having a fixed catalyst layer thickness, GDLs with different degree of porosity can be utilized to confirm this postulation, which would be a more practical testing methodology in contrast to the tedious catalyst layer preparation method of the former approach.

The results in the in-plane studies highlight that local in-plane variation has an impact on the product selectivities and can be improved by improving the current collection. Due to the resistance of GDE, the edge current collection can cause a potential drop from the edges to the centre along the GDE surface. By using a current collector with an electric connection also in the middle, such difference can be mitigated. More detailed experimental work and analysis coupled with modelling work will be followed so a more quantitative description of the current/potential and products distribution can be understood. Collaboration with researchers from Prof. Sophia Haussener's group regarding the model has been initiated. In the next step, more results will be drawn from the model, which hopefully could help investigate factors that could not be observed or explained by experimental results.

5 REFERENCES

- 1 Nitopi, S. *et al.* Progress and Perspectives of Electrochemical CO₂ Reduction on Copper in Aqueous Electrolyte. *Chemical Reviews* **119**, 7610-7672, doi:10.1021/acs.chemrev.8b00705 (2019).
- 2 Huang, J. *et al.* Potential-induced nanoclustering of metallic catalysts during electrochemical CO₂ reduction. *Nature Communications* **9**, 3117, doi:10.1038/s41467-018-05544-3 (2018).
- 3 Arán-Ais, R. M. *et al.* Imaging electrochemically synthesized Cu₂O cubes and their morphological evolution under conditions relevant to CO₂ electroreduction. *Nature Communications* **11**, 3489, doi:10.1038/s41467-020-17220-6 (2020).
- 4 Lee, S. H. *et al.* Oxidation State and Surface Reconstruction of Cu under CO₂ Reduction Conditions from In Situ X-ray Characterization. *Journal of the American Chemical Society* **143**, 588-592, doi:10.1021/jacs.0c10017 (2021).
- 5 Tan, Y. C., Lee, K. B., Song, H. & Oh, J. Modulating Local CO₂ Concentration as a General Strategy for Enhancing C₂ Coupling in CO₂ Electroreduction. *Joule* **4**, 1104-1120, doi:10.1016/j.joule.2020.03.013 (2020).
- 6 Dinh, C.-T. *et al.* CO₂ electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. *Science* **360**, 783-787, doi:10.1126/science.aas9100 (2018).
- 7 Möller, T. *et al.* The product selectivity zones in gas diffusion electrodes during the electrocatalytic reduction of CO₂. *Energy & Environmental Science* **14**, 5995-6006, doi:10.1039/D1EE01696B (2021).
- 8 Nesbitt, N. T. *et al.* Liquid–Solid Boundaries Dominate Activity of CO₂ Reduction on Gas-Diffusion Electrodes. *ACS Catal.* **10**, 14093-14106, doi:10.1021/acscatal.0c03319 (2020).
- 9 Garza, A. J., Bell, A. T. & Head-Gordon, M. Mechanism of CO₂ Reduction at Copper Surfaces: Pathways to C₂ Products. *ACS Catal.* **8**, 1490-1499, doi:10.1021/acscatal.7b03477 (2018).
- 10 Liu, X. *et al.* pH effects on the electrochemical reduction of CO₂ towards C₂ products on stepped copper. *Nature Communications* **10**, 32, doi:10.1038/s41467-018-07970-9 (2019).
- 11 Zhong, M. *et al.* Accelerated discovery of CO₂ electrocatalysts using active machine learning. *Nature* **581**, 178-183, doi:10.1038/s41586-020-2242-8 (2020).