

Electrons to Close the Carbon Cycle

Publiek eindrapport

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Partners

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Samenvatting

Toepassing van hernieuwbare elektriciteit in de chemische industrie en in de staalproductie biedt kansen om de uitstoot van CO₂ te verminderen, die momenteel in grote hoeveelheden wordt gegenereerd als gevolg van het gebruik van fossiele grondstoffen (olie, gas en kolen).

Een van de mogelijkheden om elektriciteit te benutten is het ontwikkelen van een proces om CO₂ (en water) als grondstof te gebruiken en dit om te zetten in producten met toegevoegde waarde, zoals synthesesgas (een mengsel van CO en H₂), dat kan worden gebruikt voor productie van staal als alternatief voor klassieke op steenkool gebaseerde processen. Elektrochemische apparaten voor de omzetting van CO₂ bestaan typisch uit zogenaamde gasdiffusie-elektroden, op basis van voor waterstofbrandstofcellen ontwikkelde koolstofdoeken, die nanodeeltjes van koper bevatten, die als katalysator fungeren. Onlangs is aan de Universiteit Twente een nieuw concept ontwikkeld op basis van metalen, zogenaamde holle vezelelektroden (HFE's). De holle vezels bestaan uit aan elkaar gesinterde metaaldeeltjes, waardoor een poreuze, gasdoorlatende wand ontstaat met een hoog elektrisch geleidingsvermogen. Toen ze van koper waren gemaakt en onder doorstroomomstandigheden bij verschillende CO₂-gassnelheden werden gebruikt, vertoonden de holle vezels een uitstekende omzetting in CO, met een selectiviteit over H₂ van meer dan 70%. Deze resultaten zijn gepubliceerd in het toonaangevende tijdschrift Nature Communications ([doi:10.1038/ncomms10748](https://doi.org/10.1038/ncomms10748), *Three-dimensional porous hollow fiber copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction* | Nature Communications), en het concept van de holle vezels is gepatenteerd door de Universiteit Twente ([doi:10.1038/ncomms10748](https://doi.org/10.1038/ncomms10748), EP 3 380 651).

In dit project werd het concept van de holle vezelelektroden verder ontwikkeld, met focus op i) de kopergeïnduceerde omzetting van CO₂ naar CO (syngas), en ii) de Ti-geïnduceerde omzetting van stikstof (oxide) verbindingen in ammoniak.

Bij de elektrochemische productie van Syngas werden de prestaties van de holle vezels vergeleken met verschillende alternatieve configuraties op basis van (platte) koolstofdoeken, terwijl ook het effect van de samenstelling van het voedingsgas op de prestaties van de holle vezels in detail werd geëvalueerd. Om de hoeveelheid Cu die nodig is voor de constructie van een holle vezel te verminderen, werden bovendien titaniumvezels geprepareerd en gefunctionaliseerd met een dunne buitenlaag van gesinterde Cu-deeltjes.

Gasdiffusie-elektroden (GDE's) van vlakke koolstofdoek werden ontwikkeld met behulp van spraycoating van oplossingen die ionomeer van Nafion en Cu-deeltjes bevatten die vergelijkbaar zijn met die gebruikt bij de synthese van de HFE's, om een vergelijking tussen deze meer conventionele elektroden en de holle vezel technologie. Verschillende experimentele parameters tijdens de voorbereiding van deze elektroden, en in het bijzonder het oplosmiddel van de voorloperoplossing, bleken een belangrijke rol te spelen bij het bepalen van de uiteindelijke productverdeling bij elektrochemische CO₂-conversie. Interessant is dat ethyleen in significante hoeveelheden werd verkregen, als apolaire oplosmiddelen werden toegepast bij de bereidingsprocedure. Dit wordt verklaard door de lagere dekking van de Cu-deeltjes door Nafion-polymeer. Verder werden GDE's toegepast in een doorstroomconfiguratie, met 30% meer CO-productie ten opzichte van een doorstroomconfiguratie. De prestatieverbetering wordt toegeschreven aan een betere elektrolytmenging in de buurt van het katalytische oppervlak, waardoor CO effectief wordt verwijderd uit de buurt van het koperoppervlak, waardoor koppelingsreacties met ethyleen worden voorkomen. In die zin zijn de resultaten vergelijkbaar met HFE's. Ook het effect van elektrolyt op de vlakke plaat GDE's werd onderzocht door de prestatie van een op goud gebaseerde GDE in een KHCO₃ elektrolyt met en zonder op imidazolium gebaseerde moleculen te vergelijken. Hoewel wordt aangenomen dat het op imidazolium gebaseerde molecuul een stabiliserend effect heeft op een belangrijk reactietussenproduct, was de selectiviteit naar CO het hoogst in de KHCO₃-elektrolyt zonder imidazolium, toegeschreven aan een ander op carbonaat gebaseerd activeringsmechanisme.

Het effect van de aanwezigheid van CO in het CO₂-voedingsgas (relevant voor samenstellingen aangetroffen in de staalindustrie), op de prestatie van de HFE, werd in detail onderzocht. Een belangrijke conclusie is dat de aanwezigheid van CO de omzetting van CO₂ beperkt. Met andere woorden, er is een hogere energie-input nodig om dezelfde hoeveelheid CO₂ om te zetten in aanwezigheid respectievelijk afwezigheid van CO.

Ook bij N₂-activering is de toepasbaarheid van de HFE-technologie onderzocht. De beperkt beschikbare publicaties over elektrochemische reductie van N₂ tot NH₃ suggereerden massatransport van N₂ als een

van de grote problemen die moeten worden opgelost, en er verschenen verschillende publicaties die beweerden dat de vorming van NH_3 succesvol was. Daarom richtte het project zich in eerste instantie op de elektrochemische omzetting van N_2 in NH_3 , met behulp van speciaal geprepareerde holle titaniumvezels. De reactie lijdt echter aan een zeer lage activiteit die het moeilijk maakt om onvoorziene NH_3 -niveaus te overwinnen. Daarom detecteren de meest "succesvolle" experimenten die in de literatuur worden gerapporteerd NH_3 waarschijnlijk als verontreinigende stof, maar dan een elektrochemisch geproduceerd product. Het gebruik van gemodificeerde holle-vezelelektroden voor deze reactie onthulde dat niet het massatransport het probleem is, maar de katalytische activiteit van geteste elektrokatalysatoren voor de activering van het zeer stabiele N_2 -molecuul. Met het oog hierop werd het werk aan N_2 -activering omgeleid in de richting van NO_x -reductie. GEEN gas, wanneer het door de wanden van een Cu-Ti holle vezel wordt gevoerd, kan met succes worden omgezet in ammoniak. Wanneer genormaliseerd naar geometrische oppervlakte, zou de conversie van nitraat (NO_3^-) bevattende oplossingen naar ammoniak (NH_4^+) kunnen worden uitgevoerd met behulp van Ti HFE's met een vrij hoge selectiviteit en stroomdichtheid.

Tot slot lieten de Twentse onderzoeksgroepen zien dat vorming van ureum uit NO_3^- en CO_2 haalbaar is. Het werk onthulde echter ook de vorming van Cu --- CN-soorten, die oplosbaar zijn in de elektrolyt, en leiden tot herstructurering en deactivering van het elektrode-oppervlak. Verder onderzoek is nodig om manieren te vinden om het elektrode-oppervlak te stabiliseren.

Er heeft een systeemontwerp en procesevaluatie plaatsgevonden met betrekking tot de verkregen experimentele gegevens van de holle vezeltechnologie bij de omzetting van CO_2 naar CO. Verder is een elektrochemische cel ontwikkeld en gebouwd om de haalbaarheid van het concept op een grote(re) schaal. Meer specifiek werden meerdere vezels geconfigureerd in een quasi velachtige configuratie, om een beperkte afstand tussen de elektroden (kathode en anode) mogelijk te maken. De onderzoeken zijn uitgevoerd in een open samenwerking tussen de Universiteit Twente (UTwente), kennisinstellingen (TNO) en het bedrijfsleven (ArcelorMittal, Nouryon (Nobian), DOW, OCI) gefaciliteerd door ISPT.

Het onderzoek heeft het inzicht verbeterd in de technische haalbaarheid en schaalbaarheid, en de economische relevantie van elektrochemische omzetting van CO_2 en N_2 op basis van de gepatenteerde holle vezeltechnologie. De resultaten zijn ook vergeleken met alternatieve methoden voor het opslaan van elektriciteit, zoals bijvoorbeeld beschreven in het ISPT-voorstel 'elektrisch aangedreven activering van basischemicaliën'.

Bijdrage aan de doelstellingen van de regeling

Het E3C-project valt onder het door Topsector Energie in 2015 opgezette innovatiethema Systeemintegratie. Specifiek draagt het E3C-project bij aan de programmalijn: *elektrificatie en flexibilisering*

In de programmalijn ligt de focus op systeemintegratie door elektrificatie en flexibilisering van de industrie. Elektrificatie van de procesindustrie kan via power-to-heat, warmteproductie met elektriciteit (lijn 1a), en via power-to-products. De directe synthese van moleculen via elektrochemie (power-to-molecules), elektrische input van mechanische energie of elektrisch gedreven scheidingsprocessen zijn daarvoor belangrijke opties. Onderzoekthema's binnen deze programmalijn omvatten o.a. nieuwe elektrisch-gedreven processen voor omzetting en elektrochemische productie van kleine moleculen als energiedrager.

E3C draagt bij aan deze elektrificatie- en elektrochemiedoelstellingen van de industrie. Het hoofddoel E3C is het vinden van nieuwe wegen om elektrische energie om te zetten in chemische energie. In het project is onderzoek gedaan naar elektrochemische productie van kleine moleculen als energiedrager, namelijk NH_3 . Daarnaast is gekeken hoe middels elektrochemie CO_2 kan worden omgezet naar CO, wat daarna geschikt is voor omzetting naar andere producten.

Summary

Application of renewable electricity in the chemical industry and in steel manufacturing, offers opportunities to reduce emissions of CO₂, presently generated in large amounts as a consequence of the use of fossil feedstock (oil, gas and coal).

One of the options to utilize electricity is to develop a process for the utilization of CO₂ (and water) as feedstock, and convert this into value added products, such as synthesis gas (a mixture of CO and H₂), which can be used for production of steel as an alternative to classic coal-based processes.

Electrochemical devices for conversion of CO₂ typically consist of so-called gas diffusion electrodes, based on carbon cloths developed for hydrogen fuel cells, containing nanoparticles of Copper, functioning as catalyst. Recently, a novel concept on the basis of metallic, so-called hollow fibre electrodes (HFEs) was developed at the University of Twente. The hollow fibres consist of metal particles sintered together, so that a porous, gas-permeable wall is created with high electrical conductivity. When made of Copper, and operated in flow-through conditions at various CO₂ gas velocities, the hollow fibres showed excellent conversion to CO, with a selectivity over H₂ of more than 70%. These results have been published in the leading journal Nature Communications (doi:10.1038/ncomms10748, [Three-dimensional porous hollow fibre copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction | Nature Communications](#)), and the concept of the hollow fibres has been patented by the University of Twente (doi:10.1038/ncomms10748, EP 3 380 651).

In this project, the concept of the hollow fibre electrodes was further developed, with focus on i) the copper-induced conversion of CO₂ to CO (syngas), and ii) the Ti induced conversion of Nitrogen (oxide) compounds into ammonia.

In the electrochemical production of Syngas, the performance of the hollow fibres was compared to several alternative configurations based on (flat sheet) carbon cloths, while also the effect of composition of the feed gas on the performance of the hollow fibres was evaluated in detail. Furthermore, to reduce the amount Cu required for construction of a hollow fibre, titanium fibers were prepared and functionalized with a thin, outer layer of sintered Cu particles.

Flat sheet carbon cloth gas diffusion electrodes (GDEs) were developed using spray-coating of solutions containing ionomer of Nafion, and Cu particles similar to those used in the synthesis of the HFEs, in order to facilitate a comparison between these more conventional electrodes and the hollow fiber technology. Several experimental parameters during the preparation of these electrodes, and in particular the solvent of the precursor solution were found to play a major role in determining the final product distribution in electrochemical CO₂ conversion. Interestingly, ethylene was obtained in significant quantities, if apolar solvents, were applied in the preparation procedure. This is explained by the lower coverage of the Cu particles by Nafion polymer. Furthermore, GDEs were applied in a flow-through configuration, showing 30% more CO production with respect to a flow-by configuration. The improvement in performance is attributed to better electrolyte mixing at the vicinity of the catalytic surface, effectively removing CO from the vicinity of the Copper surface, preventing coupling reactions to ethylene. In this sense the results are comparable to HFEs. Also the effect of electrolyte on the flat sheet GDEs was investigated, by comparing the performance of a gold based GDE in a KHCO₃ electrolyte with and without imidazolium-based molecules. Though the imidazolium-based molecule is assumed to have a stabilizing effect on an important reaction intermediate, the selectivity towards CO was the highest in the KHCO₃ electrolyte without imidazolium, attributed to a different carbonate-based activation mechanism.

The effect of the presence of CO in the CO₂ feed gas (relevant for compositions encountered in the steel industry), on the performance of the HFE, was investigated in detail. An important conclusion is that the presence of CO limits the conversion of CO₂. In other words, a higher energy input is required to convert the same amount of CO₂ in the presence, or in the absence of CO, respectively.

The applicability of the HFE technology was also investigated in N₂ activation. The limited available publications about electrochemical reduction of N₂ to NH₃ suggested mass transport of N₂ as one of the big problems to be solved, and several publications were emerging that claimed successful NH₃ formation. Therefore, the project initially started focusing on electrochemical conversion of N₂ into NH₃, using specially prepared titanium hollow fibers. However, the reaction suffers from very low activity that makes it difficult to

overcome adventitious NH_3 levels. Therefore, the most “successful” experiments reported in the literature likely detect NH_3 as contaminant, rather than a product produced electrochemically. Using modified hollow fiber electrodes for this reaction revealed that not mass transport is the problem but catalytic activity of tested electrocatalysts for activation of the highly stable N_2 molecule. In view of this, the work on N_2 activation was diverted into the direction of NO_x reduction. NO gas, when fed through the walls of a Cu-Ti hollow fibre, could be successfully converted to Ammonia. When normalized to geometric area, the conversion of nitrate (NO_3^-) containing solutions to Ammonia (NH_4^+) could be performed using Ti HFES with quite high selectivity and current density.

Finally, the research groups in Twente showed the formation of urea from NO_3^- and CO_2 was feasible. However, the work also revealed the formation of Cu--CN species, which are soluble in the electrolyte, and lead to restructuring and deactivation of the electrode surface. Further research is needed to determine ways to stabilize the electrode surface.

A system design and process evaluation took place with regard to the acquired experimental data of the hollow fiber technology in the conversion of CO_2 to CO. Furthermore, an electrochemical cell was developed and constructed to evaluate the feasibility of the concept on a large(er) scale. More specifically, multiple fibers were configured in a *quasi* sheet-like configuration, to allow limited distance between the electrodes (cathode and anode). The studies were conducted in an open partnership between the University of Twente (UTwente), knowledge institutions (TNO) and the business community (ArcelorMittal, Nouryon (Nobian), DOW, OCI) facilitated by ISPT.

The research has improved insight into the technical feasibility and scalability, and the economic relevance of electrochemical conversion of CO_2 , and N_2 based on the patented hollow fiber technology. The results have also been compared with alternative methods for storing electricity, as described, for example, in the ISPT proposal 'electrical driven activation of base chemicals'.

Discussion

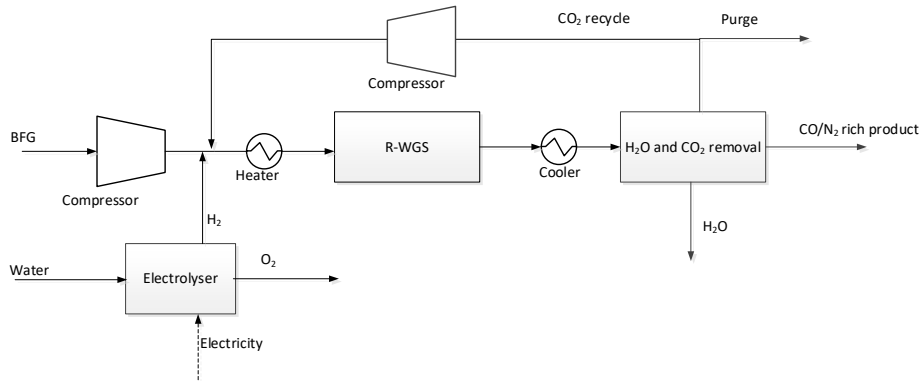
Results

WP1 Techno-economical evaluation (ECN-TNO)

In this work package the techno-economic evaluation of the electrochemical reduction of CO_2 to CO was performed. Within this TEA study the low temperature CO_2 -electrolysis on the basis of the E-tripleC technology was compared to three other different routes for CO production in a steel mill environment, in which CO is produced from blast furnace gases and recycled to partially replace coke. The selected capacity of the Steel Mill was based on a Western Europe plant producing 4 million ton per year of hot roll coil (HRC), using processes that are typical to any average steel mill (International Energy Agency Environmental Projects (IEAGHG), Iron and Steel CCS study (Techno-economics integrated steel mill), 53 (2013) 1689–1699. doi:10.1017/CBO9781107415324.004). The four different CO_2 to CO routes examined in the TEA were the following:

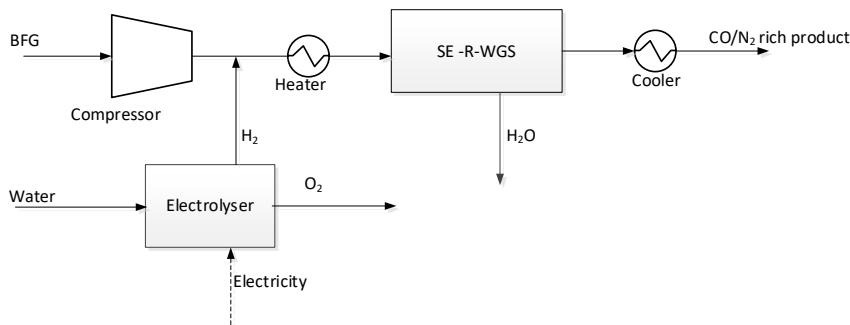
1/ Indirect CO synthesis (water electrolysis and reversible watergas shift (RWGS)):

For the route via Reverse Water Gas Shift (RWGS) reaction: $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$, H_2 produced in the electrolyser route, is added to a RWGS reactor (see figure below). The RWGS reaction is equilibrium limited, and part of the CO_2 will remain unconverted (calculated thermodynamic conversion of CO_2 to CO at 800 °C is 14%). RWGS reaction product will be cooled and water will be removed from the gas. Depending on the allowed amount of the steam in the final CO product, technology for water removal has to be selected. Unconverted CO_2 will be removed from the stream, recompressed and recycled back to the reactor. Proton Exchange Membranes (PEM) electrolyser was considered as H_2 -source in this study, as the H_2 product can be delivered at pressures of approx. 30 bara, which is required for the in-situ steam separation concept considered in this study.



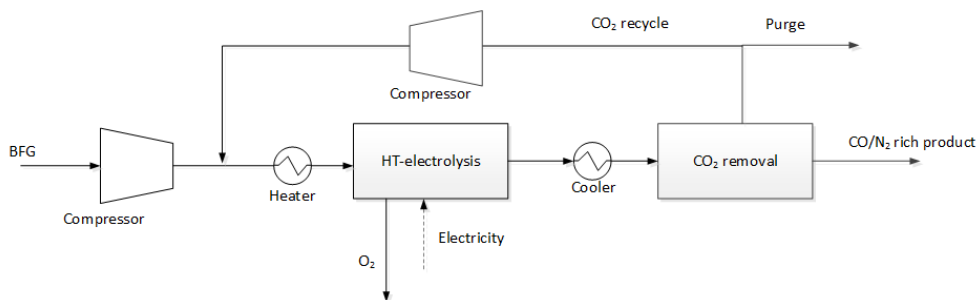
2/ Indirect CO synthesis (water electrolysis plus separation enhanced reversible watergas shift (SE-RWGS)):

This route is a variation on the first route. Since the CO₂ conversion in the RWGS reactor is limited, an separation enhanced watergasshift reactor by in-situ steam separation technology via adsorption in order to increase CO₂ conversion to CO (SE-RWGS) was considered in this study. There is no commercial technology available for in-situ steam removal. The reason for selecting this adsorption-based technology, is that TNO has developed knowledge on this technology, with a present technology readiness level (TRL) 4-5. In this concept, due to obtained high CO₂ conversion to CO, CO₂ removal step and thus CO₂ recycle can be omitted.



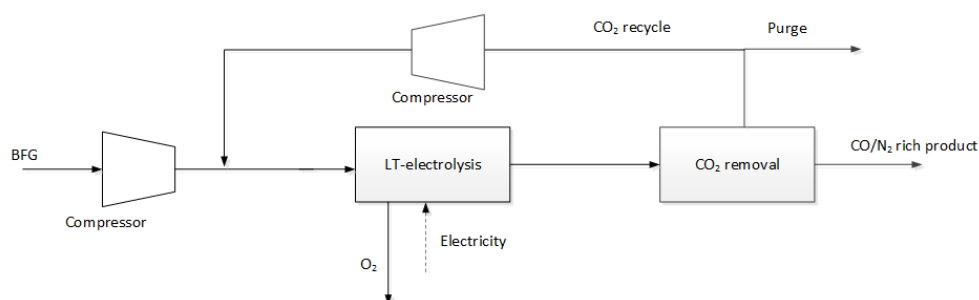
3/ Direct CO-synthesis in High Temperature Electrolyser:

In the case of High Temperature (HT) CO₂ electrolysis route, compressed BFG is pre-heated and directly fed to the HT electrolyser in which the following reaction occurs: $CO_2 = CO + 1/2O_2$. The electrolyser operates at relatively high temperatures (700-850 °C) to facilitate the electro-catalytic splitting of carbon dioxide into carbon monoxide and oxygen. The heat which is inevitably produced by Joule-heating by the electrical current compensates for the endothermic nature of the high temperature electrolysis process. The Danish company Haldor Topsøe is one of the large providers of this technology, showing currently a maximum production capacity of 100 Nm³/h of CO (equivalent to 560 kW) (Ref. Small-Scale CO from CO₂ using Electrolysis, Haldor-Topsøe brochure, 2017).



4/ Low Temperature CO₂ electrolysis (E-TripleC case):

The system using low temperature electrolysis on basis of the hollow copper fibres as a cathode¹ is presented in the figure below. BFG are compressed to the pressure level required in the electrolyser in which CO₂ reduction to CO takes place. Unconverted CO₂ is separated from CO/N₂, recompressed and recycled back to the process. In order to perform the techno-economic study on this system assumptions on input parameters were made: The Faradaic efficiency towards CO was taken as 75%, similar to the best reported and determined values for the use of Copper hollow fibre electrodes; the area specific resistance was taken as 4 ohm.cm² which was a factor of ten lower than the experimental value as obtained roughly from reference²; The CO to CO₂ conversion was taken as 60%; Assumed voltage drop due to internal resistance is 0.4 V. Assumed lifetime of the electrolyser is 80,000 h.



An overview of the results for the different studied CO₂ to CO routes is given in the table below.

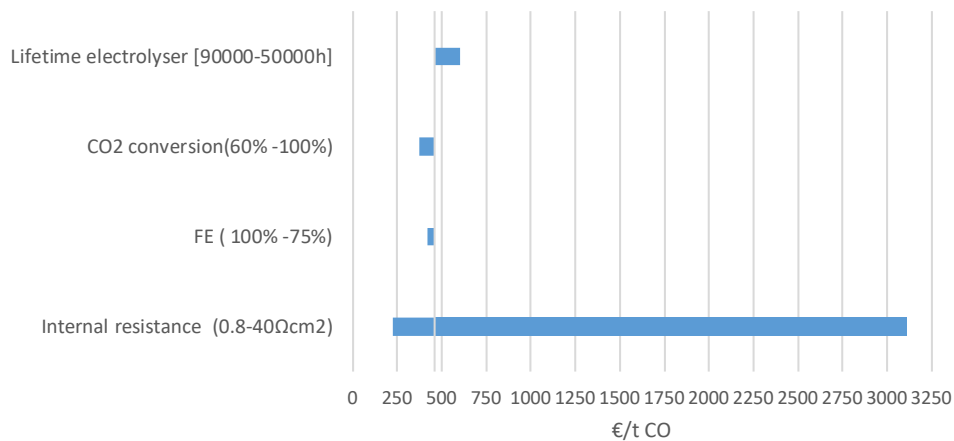
Case	Internal resistance [Ω·cm ²]	Product quality [molar composition]	Power consumption [kWh/kg CO produced]	Area electrolyser [m ²]	Production Costs [€/t CO]
Water electrolysis + RWGS reactor	0.2 - 0.3	H ₂ 15.85%, CO ₂ 6.14% N ₂ 44.6%	21.2	38,079	
Water electrolysis + SE-RWGS	0.2 – 0.3	H ₂ 1.9% CO ₂ 8.9% N ₂ 51.3%	3	5,402	208
HT-CO₂ electrolysis	0.9	H ₂ 3.7% CO ₂ 4.3% N ₂ 50.1%	2.5	52,033	332
E-TripleC	4	H ₂ 7.28% CO ₂ 0.93% N ₂ 51.11%	4.5	82,949	463

¹ R. Kas, K.K. Hummadi, R. Kortlever, P. de Wit, A. Milbrat, M.W.J. Luiten-Olieman, N.E. Benes, M.T.M. Koper, G. Mul, Three-dimensional porous hollow fibre copper electrodes for efficient and high-rate electrochemical carbon dioxide reduction, Nat. Commun. 7 (2016) 10748. doi:10.1038/ncomms10748.

The table shows that for the E-triple-C case the expected CO production costs are reaching values slightly higher than for the other alternative cases. The higher value is due to relatively large electrolyser area required (16 times larger than for water electrolysis) for the E-triple-C case.

The table shows that product gas will contain significant amount of N₂ (> 40%mol), and some CO₂ and H₂. The presence of hydrogen is critical as injection of H₂ in the blast furnace leads to decrease in the temperature in the blast furnace² because H₂ is only partly consumed to reduce iron oxides to iron because of thermodynamic constraints caused by the water-gas shift reaction. As a result part of the H₂ may stay unconverted, resulting in explosive product gas mixture. This suggests that the faradaic efficiency in the conversion of CO₂ to CO should be ideally close to 100%.

To evaluate the most critical parameters affecting the production costs, a sensitivity study was done taking into account the following parameters: lifetime of electrolyser, CO₂ conversion, Faradaic efficiency (FE) and internal resistance. From the sensitivity study it was concluded that the parameter which had the highest impact on the CO production costs was the cell internal resistance. Other parameters studied as stack lifetime, Faradaic efficiency, CO₂ conversion, have a minor impact on production costs.



The performed techno-economic analysis comparing the E-triple-C case to alternative cases to produce CO shows that, in order to stay economically competitive, the internal resistance for E-triple-C case should be reduced from the experimentally derived value of 40 Ω·cm² to 0.8 Ω·cm². In the latter case, the calculated CO production costs are 228 €/t CO, that is reasonable if the CO industrial cost price of 437 €/t CO is taken into account. Calculated CO production costs for water electrolysis + SE-RWGS were of 208 €/t CO were in the range of the E-triple-C costs. HT-CO₂ electrolysis has higher production costs of 332€/t CO.

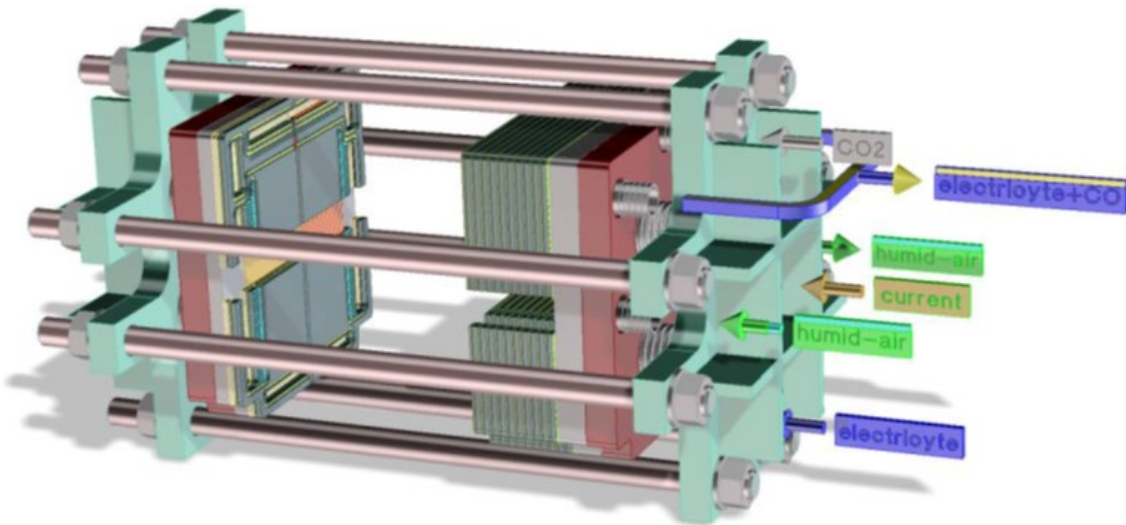
WP2 Conceptual stack design (ECN-TNO)

In this work package, a conceptual design for a CO₂-electrolysis stack has been developed. The main challenge was to incorporate the hollow copper fibres in the design while fulfilling essential requirements like uniformity of the current density over the cell and between cells, distribution of reactants over a large number of cells. Establishing good electrical conductivity over many cells connected in series is another challenge in scaling-up to a complete stack. Hereafter follows a short description of the conceptual design on headlines, e.g. the overall stack design, the arrangement of the hollow tubes on the cathode side and the bipolar plate/manifolding design.

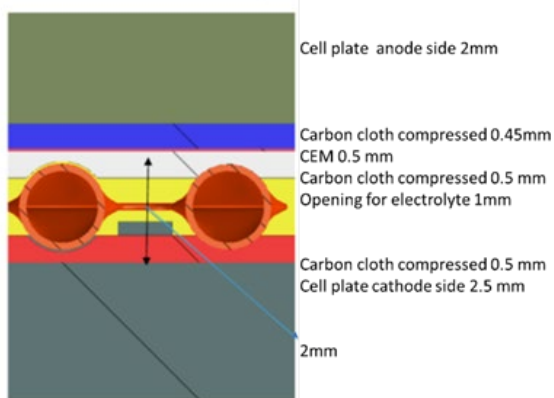
The figure below shows a drawing of the stack. The stack has cells with a bipolar configuration, where hollow-fibres are used as cathode, and Ir based electrode as an anode: The electrolyte and CO₂ is fed at the cathode side, while humidified air is fed at the anode side. All gas and liquid connections are on one side of the stack. The power supply connections are on both sides. Stack size was estimated to be

² C. Yilmaz, J. Wendelstorf, T. Turek, Modeling and simulation of hydrogen injection into a blast furnace to reduce carbon dioxide emissions, Journal of Cleaner Production 154 (2017) 488-501.

comprised of 40 cells, of which 11 have been drawn: 10 cells on the connection side and 1 cell at the end. The assumed dimensions of the active part of cell is 165x190mm, dimension of plates with connections are 245x250mm.



The following figure addresses the incorporation of the copper hollow tubes in the design. The figure shows the cross section perpendicular to the length of the hollow copper tubes of one repeating stack unit: graphite bipolar plate-carbon cloth-hollow tubes-carbon cloth-cation exchange membrane with Ir-anode catalyst-carbon cloth-graphite bipolar plate. The figure shows two copper hollow tubes at a distance of 2 mm. Compressed carbon cloth used between membrane and hollow fibres has dual functionality: to prevent damage of the membrane by hollow fibres, and to provide mechanical stability to fibres. Because of that carbon cloth is also placed between the fibres and the cathode side of the bipolar plate. In addition the carbon cloth takes care of a better distribution of the current between the tubes and over the length of the tubes.



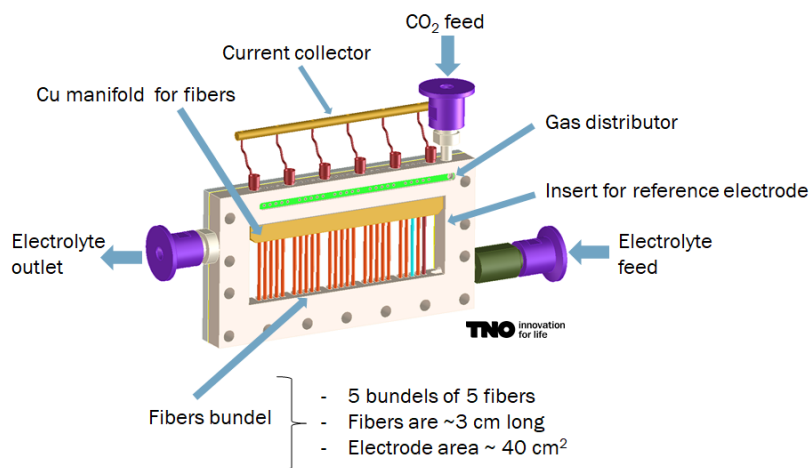
The graphite bipolar plate design includes both optimized manifolds and sealing arrangement in order to take care of the CO₂ and electrolyte supply to the cathode side; the humidified air supply to the anode side and the outlet flow of the CO-product from the cathode side.

The end-plates of the stack consists of an arrangement of copper plates taking care of the current/voltage supply, an insulation layer and thick metal plates over which the clamping force can be applied. The contacting and sealing between the different stack components is being ensured by providing a clamping force over the stack by electrically insulated pull rods between the end plates.

WP3 Cell development and testing (TNO)

In WP3, the scaling-up from a single cell testing to a stack of fibers was carried out experimentally, after discussion and deliberation with the scientists involved in work package 2. First, the reactor was designed with the selected geometry to be able to accommodate up to 25 fibers in the so-called fibers array. The design of the cell was evaluated taking in account several aspects such as: inter-fiber space to ensure that gas bubbles from one fiber do not interfere with the one adjacent, homogeneous distribution of CO₂ gas stream over every fiber, homogenous liquid electrolyte distribution over electrolyte chambers and efficient removal of unreacted gas to avoid creation of a gas blanket that can act as electric insulator, minimization of ohmic losses by reducing to the maximum the inter-electrode distance, need of a reference electrode to control the working electrode potential, flexibility on fiber assembly due to non-homogenous shape/curvature/and length of fibers, homogeneous electric distribution over the length of the reactor, leak tight compartments, easiness for reactor assembly and interchange of fibers, pressure drop along the cell depending on the flow rate, and chemical compatibility of the components.

Once the basis of design was finalized, the engineering design phase started and a detailed reactor design was created and the reactor prototype was constructed. The following figures shows the designed flow cell, and the constructed reactor.



After construction of the reactor, a test-plan was drafted with the intention of testing important aspects of the electrochemical process such as: effect on voltage or current applied, effect on electrolyte flow-rate, effect on number of fibers and effect on distance between fibers during performance of CO₂ reduction to CO. However, several challenges were faced with led to failure of most of the experimental tests.

The main problems encountered were the following:

- Related to reactor:

- Fragility of gas and liquid inlets and outlets connectors, which decrease the easiness of reactor assembly and testing
- Assembly of reactor and specially troubleshooting is time intensive
- Related to fibers:
 - Fragility of the fibers which leads to breakage of them.
 - Lack of homogeneity between fibers which leads to non-homogenous gas distribution between fibers and therefore need of different settings between fibers.

Based on the challenges encountered, we foresee improvement opportunities in relation to:

1. Manifold and fiber design

The glue (which connects the fibers to the manifold) lead to leakage issues, which could have been solved by soldering the fibers to the base, as well as soldering the tips of the fibers closed. However, this would not avoid mid-fiber breakage, and in the case a fiber broke, new soldering would be needed, greatly increasing repair time. Another option to eliminate this problem is for each fiber to have its individual gas regulator (given that each fiber opens its pores at different pressures and also is able to withstand different pressures) but this again increases complexity to a probably undesired level and non-realistic conditions in case of a scaled up process.

2. Decrease reactor assembly time.

Even with the improvements made by TNO Petten, which improved the mechanical strength of inlet and outlet lines (which decreases repair time) the assembly of the reactor is still time intensive (>40min), and therefore in an event of fiber failure, the experiment preparation time is increased even more.

3. Fiber homogeneity:

Breakage of fibers or glue that connects the fibers to the manifold occurred at different pressures. This makes it difficult to determine at what CO₂ flow (and therefore fiber pressure) the reactor should operate. In some tests the glue at the base and tip of the fibers failed, at higher pressures, and in others, the fiber itself broke. The mechanical strength is fiber dependent and therefore the behavior of each fiber differs from one another.

4. Increase fiber mechanical strength.

Possible use of copper covered titanium hollow fibers which might increase the mechanical strength of the fiber.

WP4 (UT/Copper hollow fibers, Anne):

Copper hollow fibers were prepared via dry-wet spinning of a polymer solution of N-methylpyrrolidone, Polyetherimide, Polyvinyl Pyrolidone, and copper particles of sizes in the range of 1-2 μm. To remove template molecules and to sinter the copper particles, the time of calcination was varied in a range of 1 - 4 hours at 600 °C. This calcination temperature was determined based on Thermal Gravimetric Analysis (TGA), showing completion of hydrocarbon removal at this temperature. Furthermore, the temperature of the subsequent treatment of the fibers in a flow of 4% H₂ (in Ar) was varied in the range of 200 °C to 400 °C, at a fixed time of 1 h. Temperature programmed reduction experiments (TPR) were used to analyze the hydrogen treatment. The Faradaic Efficiency (FE) towards CO in electrochemical reduction of CO₂ was determined at -0.45 V vs RHE, using a 0.1 M KHCO₃ electrolyte. A calcination time of 3 hours at 600 °C and a hydrogen treatment temperature of 280 °C were found to induce the highest FE to CO of 73% . Optimizing oxidation properties predominantly affects porosity, favoring the CO₂ gas distribution over the length of the fiber, and hence the CO₂ reduction efficiency. Treatment in H₂ in the range of 250 to 300 °C is proposed to affect the content of residual (subsurface) oxygen in Cu, which leads to favorable properties on the nanoscale.

The impact of the operating conditions in terms of the electrochemical conversion of CO₂ into CO was assessed with respect to the CO₂ feed concentration, CO feed concentration and a combination of both. It was observed that CO is not converted at the studied potential (-1.1 V vs Ag/AgCl) and that the

performance of the fibres increases when more CO₂ in the feed is present. Furthermore, having a mixture of CO₂ and CO fed to the fiber decreases the CO₂ conversion rate. Further investigation of the effect of waste gasses on electrochemical CO₂ conversion with copper hollow fibers is envisioned for the remainder of the corresponding PhD project.

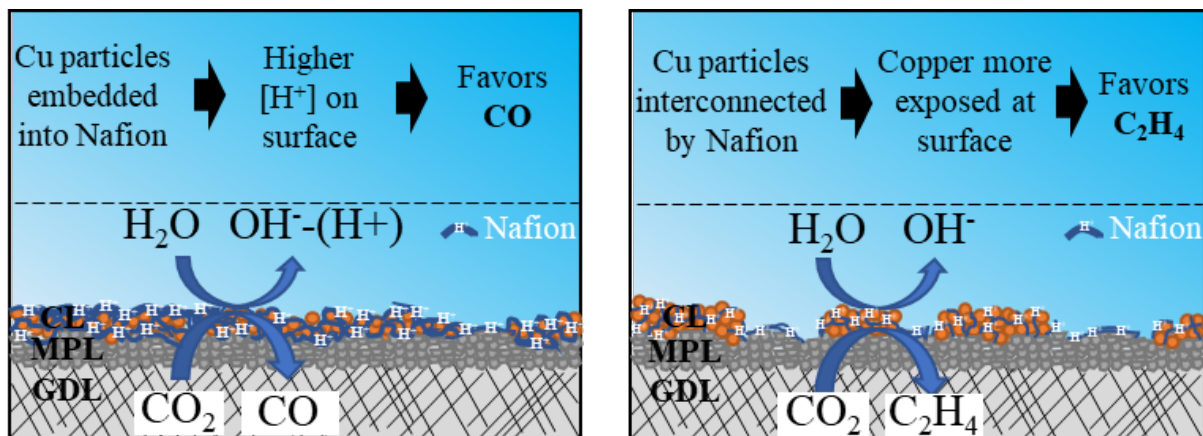
The effect of the catholyte was briefly investigated in terms of electrolyte concentration and cation type, and is thought to be of importance with respect to the performance of the copper hollow fiber. Further investigation of this topic is envisioned for the remainder of the corresponding PhD project.

Flat porous copper sheets were developed using a similar procedure as the Cu hollow fiber preparation, aiming at quick introduction of the porous copper catalyst in a conventional GDE reactor and to study the effect of geometry on the CO₂ conversion rate. However, the sheets appeared to be very brittle and did not exhibit high CO₂ to CO conversion rate. There is room for further research here, as process conditions and preparation procedure could be further optimized.

Cu was spray coated on Ti hollow fibers to create fibers for CO₂ conversion that have improved mechanical stability over the Cu hollow fibers. Oxidation of the Cu is required for the Cu layer to be active for CO₂ conversion. The Cu @ Ti hollow fibers showed similar performance to the copper hollow fibers in terms of selectivity, although the partial current density of the copper hollow fibers is superior over the Cu @ Ti hollow fibers. Also the morphology obtained (similar to shown in Figure 3) appears beneficial to obtain higher current densities in comparison the Cu fibers, but additional experiments are required to further assess these aspects.

WP4 (UT/Flat sheets, Liniker):

Cu-based gas diffusion electrodes (GDE) show excellent performance in the electrochemical reduction of CO₂ to ethylene. We evaluated how the solvent of ink formulations containing Nafion-ionomer and unsupported Cu particles, affects the polymerized Nafion-Copper distribution in the as-prepared GDE and the obtained performance in the electrochemical reduction of CO₂. Isopropanol (IPA), dimethyl sulfoxide (DMSO), ethylene glycol (EG), or N-methyl-2-pyrrolidone (NMP)) were used. Microscopic analyses of the Cu-GDEs demonstrate that NMP and DMSO lead to exposed islands of copper, with Nafion acting predominantly as an inter-particle binder. Such geometry is confirmed by the relatively high electrochemical surface area (ECSA) and the low charge-transfer resistance (R_{ct}). IPA or EG induce the formation of Cu-catalyst particles embedded into, and covered by (polymerized) Nafion films, in agreement with the relatively low ECSA, and high R_{ct}, likely due to significant polymerization and agglomeration of Nafion in the ink formulation induced by the protic solvents, prior to preparation of the catalyst layer. When evaluated in the electrochemical reduction of CO₂ at -1.1 V vs the reversible hydrogen electrode (RHE), the exposed particles prepared using NMP and DMSO lead to higher FE towards ethylene than EG or IPA-based GDEs (23.5% and 19.2%, vs 10.2% and 13.4%, respectively). The lower ethylene FE for Nafion covered systems, is tentatively attributed to the acidity and highly effective transport of protons by Nafion. The results are graphically illustrated in the following Figure:



Aiming to improve CO₂ transport across copper-based gas diffusion electrodes, we investigated how flow by and flow through regimes would affect the activity (measured by current density) and selectivity (measured by faradaic efficiency) of CO₂RR of cloth based electrodes. We first studied the effect of the ionic membrane used to separate cathodic and anodic chambers in a flow cell reactor. We observed that anionic membranes (Sustanion) provided roughly the same conductivity as cationic membranes (Nafion) while enhancing the faradaic efficiency towards CO and ethylene by 30% when compared to Nafion membranes in a flow by configuration. We then selected Sustanion to evaluate the effect of CO₂ transport regimes in flow by and flow through conditions, in which we observed that flowing CO₂ through Cu-GDE electrodes improved the faradaic efficiency towards CO another 30%, reaching a maximum of 85% at -0.85 V vs RHE (around 50 mA/cm²). We believe that the improved electrolyte mixing at the vicinity of the gas-liquid-catalyst interface enhances CO₂ transport to the active copper sites, while enabling a fast product removal, favouring CO desorption and avoiding further CO dimerization to produce ethylene. The findings at this topic can contribute to improvements on mass transport limitations on flow cell electrolyzers and to a more rational design of materials such membranes that can greatly impact the final product.

In another topic we investigated the effect of imidazolium-based molecules in aqueous systems to decrease CO formation overpotential, then enhancing the energy efficiency of the CO₂ reduction reaction (CO₂RR). Usually, imidazolium (IM)-based compounds are used in non-aqueous solvents, such as acetonitrile, to act as co-catalyst and reduce the adsorption energy of the radical CO₂⁻ on the catalyst surface. In this work, we have used gold as catalyst (very selective to CO) coated onto gas diffusion electrodes as active phase. In the first part of this work we investigated the catalytic activity of Au-GDEs on 0.3 M KHCO₃, reaching remarkable 94% faradaic efficiency towards CO at -1.1V vs RHE (30 mA/cm²). This result although promising is expected and seen in literature. In the second part of this work we added imidazolium-based molecules (dimethyl-IM and methyl-pentyl-IM) as co-catalysts in the electrolyte to evaluate how activity and selectivity would change. We observed a negative effect on CO formation and a positive effect on hydrogen evolution reaction (HER) for both imidazolium molecules tested. Recently there has been a paper showing the same behaviour as the one observed by us, but not many explanations were given on why imidazolium-molecules work so well in non-aqueous systems but have a negative effect on aqueous electrolytes, such as KHCO₃. Based on a recent study reported in the literature, one of the reasons is that imidazolium promotes the reduction of KHCO₃ molecules, leading to HER to take place, while CO₂ reduction was less affected. We will use surface enhanced Raman spectroscopy to provide insight on the potential window where either HER or CO₂RR occur in the absence of imidazolium-based molecules and if these potentials change in the presence of them.

WP5 (UT/N₂ activation, Piotr):

Porous Ti based hollow fibres with low electrical resistivity (4.1-9.6 μΩ·m), orders of magnitude smaller than reported for Ti-fibres in the literature, were produced by dry-wet spinning of a mixture of Ti-particles, Polyethersulfone (PES) and N-methylpyrrolidone. Utilizing a two-step thermal decomposition of PES, consisting of treatment in air at 475 °C, followed by treatment in Argon at 800 °C, hollow fibres of entirely metallic Ti are obtained, as confirmed by XRD, SEM-EDS, and TGA-MS analyses. Carbonization of the polymer under an inert atmosphere can be used to produce a Ti/TiC-composite. To obtain a Ti/TiN composite, the porous Ti-tubes can be treated in nitrogen atmosphere at 800 °C. The porosity, pore size distribution, and bending-strength of the fibres were determined for a low (800 °C) and high (1100 °C) degree of sintering. The presence of TiC or TiN, likely in an outer, but crystalline shell, results in lower resistivity than of the pure Ti fibres, which can be attributed to the insulating layer of TiC or TiN preventing capacitive effects at the Ti/air interface. The developed preparation methodology results in porous metallic and composite Ti based fibres, which are very suitable for electrochemical applications.

Reduction of nitric oxide was investigated using Cu electrodes in acid and neutral pH conditions. Using Electrochemical Mass Spectrometry (EC-MS) in stagnant electrolyte the favorable formation of ammonia (and hydrogen) in acidic electrolyte is revealed, while N₂O and N₂ are formed in significant quantities at neutral conditions. Additional performance evaluation of Cu hollow fiber electrodes using 10 vol% NO supplied through the porous electrode structure, are shown to be in agreement with EC-MS data at low gas flow rates. However, with increasing flow rate, almost 90 % of faradaic efficiency and a NH₃ production rate of 400 μmol h⁻² cm⁻² were obtained in neutral electrolyte at -0.6 V vs RHE likely due to enhanced

availability of NO at the electrode surface suppressing hydrogen evolution reaction. This approach opens a new way for localized green ammonia production where conversion of waste NO to valuable fertilizer is possible.

In performing electrochemical reduction of CO₂ over Cu electrodes, the anions present in solution typically do not participate in the formation of reaction products. NO₃⁻ is an exception, and previous reports indicate the formation of urea in certain process conditions. We found by use of Surface Enhanced Raman Spectroscopy and Electrochemical Mass spectrometry that simultaneous reduction of NO₃⁻ and CO₂ on Cu surfaces forms carbon-nitrogen triple bonds in the form of cyanide. Cyanide likely forms soluble Cu-CN complexes, which cause catalyst surface instability. The Raman peak position of C≡N is dependent on the oxidation state of the Cu surface, and Cu-C≡N can be oxidized by anodic polarization yielding NO. The implications of these observations for a process for electrochemical formation of urea, are discussed.

Technical and organizational issues

Most of the initial project aims have been performed: from component, cell, stack analyses towards the process and economic modelling level. In the beginning of the project we did set out to look at anode processes, but the anodic reaction was not further assessed. Therefore, we decided to really focus on the cathode. Furthermore, nitrogen reduction studies failed: reported literature data could not be reproduced. Instead, the focus was shifted towards NO_x reduction, which did turn out to be successful. Here, the formation of a CN intermediate, leading to urea was discovered.

What is still open, is to understand the effect of the electrolyte on the performance, the effect of impurities of the feed gas on performance (other than CO and CO₂) and a performance evaluation of an array of hollow fibres.

There was a very strong collaboration between the different PhD students involved: the E3C team was functioning well and having many joint meetings where knowledge was shared. Analytical devices and facilities were shared. Discussions between University of Twente and TNO were fruitful. Finally, ArcerlorMittal provided insightful feedback on weekly reports for CO₂ reduction evaluation.

Lessons learned

We learned to start from simple (model) reactions first to evaluate catalysis, rather than directly focus on solving mass transport limitations in electrodes by application of fiber technology.

The subject could have changed from N₂ to NO_x activation earlier in the timeline of the project. Action could have been taken earlier here to switch gears.

With respect to the work performed on flat sheet GDEs: design and manufacture of homemade reactors consume time and resources, which could have been avoided by buying commercially available reactors.

Reproducing state-of-the-art results require deeper know-how and infrastructure, typically not mentioned in published scientific papers.

The collaboration with TNO regarding stack evaluation could have been intensified earlier, to establish a working system.

Conclusions and recommendations

Findings

- The level of CO in the feed of CO₂ should be as low as possible, to prevent thermodynamically limited conversion of CO₂.

- Deposition of Cu on Ti-hollow fibres has led to successful conversion of CO₂ to CO, but this requires an oxidation (in air at elevated temperature) and -reduction step (in diluted H₂ at elevated temperature) to obtain a Cu surface electrochemically active towards reduction of CO₂.
- The hydrodynamics of the hollow fibre morphology have been better understood. This is related to the pore size distribution and pressure exerted from the inside out.
- An aprotic solvent for mixing Nafion ionomer and Cu particles, leads to better distribution of Cu particles on flexible carbon supports than a protic solvent, due to the influence of the solvent on polymerization properties of the Nafion ionomer.
- Also for carbon felts or cloths, flow through electrolysis improves performance in terms of CO₂ conversion to ethylene or CO.
- Electrochemical activation of nitrogen is extremely challenging, and previous, positive, reports in the literature should be critically assessed.
- Reduction of NO gas to form ammonia is feasible using a functionalized Ti hollow fibre, and is one particular example of the favorable creation of a triple boundary between gas, solid, and liquid at the outer wall of the fibre. Electrolyte composition and flow rate of NO determine reaction selectivity.
- Reduction of nitrogen oxides in solution using Ti hollow fibres provides the highest current density enhancement in flow through configuration reported to date. High selectivity to ammonia can be achieved.
- Simultaneous reduction of Nitrogen oxides and CO₂ on Cu electrodes leads to the formation of urea. However, Raman spectroscopy has demonstrated the formation of Cu-C---N complexes, which might influence Cu morphology and reduce the stability of the electrochemical processes.

Possibilities for further activities, research and/or spin off

- Further Investigation of the role of the electrolyte (cations specifically) on electrochemical CO₂ conversion.
- Continue research on urea production from NO_x reduction and CO₂, checking reproducibility and cost, at a system view (not leading to ammonia emissions).
- Explore cyanide chemistry.
- Hydrodynamics on a single fibre level is now reasonably understood. The influence on mass transfer properties and hydrodynamics of having multiple fibres in series should be further investigated.
- There is room for system integration: pairing CO₂ conversion with an anodic reaction other than O₂ production. For example, CO₂ reduction to ethylene electrochemically in combination with anodic conversion of ethylene to partially oxidized ethylene (ethylene oxide) could be studied.

Communication / dissemination

Activities and public references

Communication of the results of the project have been targeted at multiple stakeholder groups:

- Experts actively involved in innovation and deployment of electrocatalysis
- (Broader) process technology community

The experts have been reached through multiple communication channels and means:

- Dissemination via project pages etc on websites of ISPT and participating partners;
 - the E3C project page at the ISPT webpage (<https://ispt.eu/projects/e3c/>)
- News items published on websites and in journals;
 - [Topsector Energie: Minuscule buisjes sluiten de CO2-kringloop in de industrie, May 2021](#)
- Conferences, both scientific and non-scientific;

- NCCC 2018, 2019, 2020, 2021
- NH3 event 2018, 2019
- ECS Meeting 2020
- Negative emissions symposium UT
- NPS2018
- ESEE2021 (poster award)
- Symposium in Fuel cells and electrolyzers, Magdeburg-Germany 2019 (poster award)

Publication in scientific journals.

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- K. H. R. Rouwenhorst, P. M. Krzywda, N. E. Benes, G. Mul, L. Lefferts, in *Techno-Economic Challenges Green Ammon. as an Energy Vector*, 2020, 41–83.
- P. M. Krzywda, A. Paradelo Rodriguez, N. E. Benes, B. T. Mei, G. Mul, submitted to *ChemElectroChem*
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- A.C. Sustronk, N.E. Benes, G. Mul, submitted to *Electrochemical Science Advances*
- K. Hummadi, A.C. Sustronk, R. Kas, N.E. Benes, G. Mul, *Catalysts*, 2021, 11 (5), 571
- L. de Sousa, C. Harmoko, N. Benes, G. Mul, accepted for publication at *ACS ES&T engineering*, 2021

Tabel KPI

KPI	Score
TRL at start project	2
TRL at end project	4
Project success ³	2
Amount of publications	6 + 3 submitted + 5 in preparation
Amounts of patents	0
Amount of developed prototypes	1

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³ 1: the project has been completed in accordance with the original scope. All milestones have been achieved. ; 2: the project has been completed satisfactorily, but the content of the milestones has changed; 3: the project has not been completed and is definitively closed