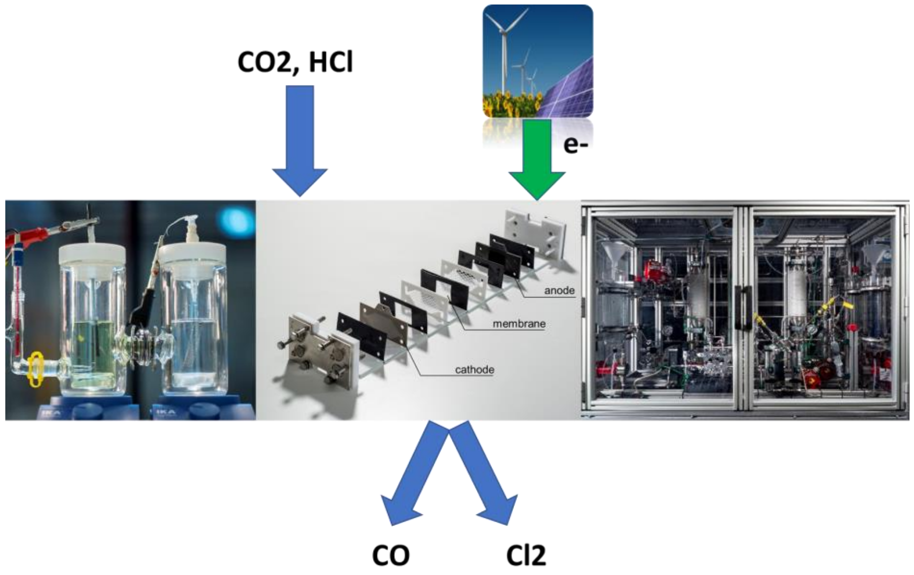
FINAL REPORT – PUBLIC



E-COUCH

Project number	TCCU118010
Projecttitel	Integration of large scale Electrochemical CO_2 Utilization with CHlorine production using green electricity
Penvoerder	TNO – Contact: E.J.M. Giling (erwin.giling@tno.nl)
Participants	Avantium, University of Amsterdam, TNO
Project period	1 Maart 2019 tot en met 1 Juli 2021
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Nederlandse samenvatting

Het doel van dit project is om een continu elektrochemisch proces te ontwikkelen om vanuit afvalstoffen (CO_2 en HCl) tegelijkertijd twee waardevolle chemische producten te produceren, door twee belangrijke elektrochemische processen te combineren: CO_2 -reductie tot CO en chloorproductie uit HCl, in één elektrochemische reactor. Het gebruik van CO_2 als C1-grondstof voor de vorming van waardevolle chemicaliën zoals koolmonoxide (CO) biedt het voordeel van een gemakkelijke, beschikbare en hernieuwbare koolstofbron, die niet-toxisch en overvloedig beschikbaar is; terwijl elektro-oxidatie van chloride tot chloor de mogelijkheid opent om chloor terug te winnen uit waterstofchloride of om dit laatste rechtstreeks te gebruiken in de chloreringsreactie, die veel wordt gebruikt in de polymeerindustrie. Hiermee draagt dit project bij aan meerdere doelstellingen van de Topsector Energie op het gebied van energie-efficiëntie, circulariteit en CO_2-hergebruik.

TNO, Avantium en UvA werkten in dit project samen om een combinatie van twee reacties in één electrolyzer te ontwikkelen en op te schalen: de gelijktijdige reductie van CO_2 tot CO aan de ene kant en de oxidatie van HCl tot Cl_2 aan de andere kant van de electrolyzer. Om tot een efficiënt zogenoemd gekoppeld ("*paired*") systeem te komen, is het cruciaal om uit te vinden hoe beide reacties zo goed mogelijk gekoppeld kunnen worden. De selectie van de optimale omstandigheden voor de gekoppelde reactie is beslissend voor het ontwikkelen van een efficiënt continu systeem. Daarom werd een studie voorgesteld van onder andere de geschikte elektrodematerialen, elektrolytoplossingen, membranen en toegepaste elektrische stromen, om het proces zo goed mogelijk technisch en economisch te optimaliseren. Op basis van de resultaten van de experimentele studie werd een opschalingsstap naar TRL4 gepland.

De projectactiviteiten zijn grotendeels volgens plan uitgevoerd, hoewel de covid-19-pandemie voor enige vertraging en verschuivingen in activiteiten heeft gezorgd. Als eerste is het experimentele programma uitgevoerd om de meest optimale omstandigheden voor opschaling te vinden, met behulp van kleinere reactoren. Vervolgens werd de levensduur van het kathodische systeem getest onder de meest optimale omstandigheden. Er is een stabiele Faraday-opbrengst waargenomen voor CO (86-90% Faraday-efficiëntie) gedurende 60 uur bij kamertemperatuur (21 graden).

Voor opschaling naar TRL4 is een nieuwe continue reactor met een elektrodeoppervlak van 100 cm^2 gemodelleerd, ontworpen, gerealiseerd en getest. Na optimalisatie en validatie van het proces in de nieuwe reactor zijn de waarden van de belangrijkste parameters experimenteel bepaald. Het project heeft aangetoond dat, vergeleken met de stand van de techniek, een betere Faraday efficiëntie (FE) voor CO en Cl_2 te bereiken is. De belangrijkste resultaten van het project zijn: FE naar CO: 75-80% @ 100 mA/cm2 en 60% @ 150 mA/cm2. FE richting Cl_2: 70-90% @ 100 – 150 mA/cm^2. Energieverbruik van ongeveer 3200 kWh/ton Cl_2 en 8200 kWh/ton CO.

De techno-economische evaluatie, waarin de businesscase voor een volledig systeem wordt doorgerekend, laat zien dat een positieve businesscase mogelijk is, met een geschatte productprijs van ~0,5 euro/kg voor een equimolaire mix van CO + Cl_2.

De volgende stap in de technologische ontwikkeling zou zijn om een opschaling naar prototype industriële schaal (TRL4-6) na te streven. Vervolgens moet een electolyzer stack met een oppervlakte van enkele m^2 totale elektrodegrootte worden ontworpen en getest in een TRL6-7 pilot plant, te bouwen op een relevante industriële locatie (bijvoorbeeld: bij Chemport Europe, Delfzijl).

Daarnaast moet in de volgende fase het gebruik van echte industriële processtromen of afvalstromen als elektrolyten worden onderzocht. Het is daarom aan te bevelen om aansluiting te zoeken bij een (industriële) partner die interesse heeft om dit proces verder op te schalen.

Public summary

The goal of this project is to develop a continuous electrochemical process using waste materials (CO_2 and HCl) to produce two valuable chemical products simultaneously by combining two large electrochemical processes: CO_2 reduction to CO and chlorine production from HCl, in one electrochemical reactor. The use of CO_2 as a C1 feedstock for the formation of more valuable chemicals such as carbon monoxide (CO) offers the use of an easy, available and renewable carbon source, which is non-toxic and abundant; while chloride electro-oxidation to chlorine opens the possibility of recovering the chlorine from hydrogen chloride or for using the latter directly in chlorination reaction, which is widely used in the polymer industry. This project thus contributes to several goals of the Topsector Energie related to energy efficiency, circularity and CO2 re-use.

TNO, Avantium and UvA partnered in this project to develop and scale-up a combination of two reactions in one electrolyzer: the simultaneous reduction of CO_2 to CO on one side and the oxidation of HCl to Cl_2 on the other side. In order to achieve an efficient paired system, it is crucial to be able to couple both reactions in terms of experimental conditions. The selection of the optimal conditions is a decisive parameter to obtain an efficient continuous system. Therefore, a study of the adequate electrode materials, electrolyte solutions, membranes and applied currents, among others, was proposed, to optimize the process in the interest of obtaining an economically beneficial process. Using the results of the experimental conditions study, a scale-up step to TRL4 was planned.

The project activities have been carried out largely according to the plan although the covid-19 pandemic caused some delays and shifts in activities. First, the experimental program has been carried out to find the most optimal conditions for scaleup, using smaller scale reactors. Then, the longevity of the cathodic system was tested under the most optimal conditions. A stable Faraday yield to CO (86-90% Faraday efficiency) for 60 hours at room temperature (21 degrees) has been observed.

For scale-up to TRL4, a new continuous flow reactor with a 100cm^2 electrode surface area has been modelled, designed, realized and tested. After optimization and validation of the process in the new reactor, the values of the key performance indicators have been experimentally determined. The project reached better Faraday efficiencies towards CO and Cl_2 compared to the state of the art. The project main achievements are: FE towards CO: 75-80% @ 100 mA/cm^2 and 60% @ 150 mA/cm^2. FE towards Cl_2: 70-90% @ 100 – 150 mA/cm^2. Energy consumption of about 3200 kWh/tonne Cl_2 and 8200 kWh/tonne CO.

The techno economic evaluation, assessing the business case for a full-scale system, shows that a positive business case is possible, with an estimated product price of ~0.5 Euro/kg for an equimolar mix of CO + Cl_2.

The next step in the technology development would be to pursue a scale-up to prototype industrial scale (TRL4-6), scaling up to ~1000cm^2 single cell surface area. Then a stack reactor with a surface area of several m^2 total electrode size needs to be designed and be tested in a TRL6-7 pilot plant, to be built on a relevant industrial location (e.g.: at Chemport Europe, Delfzijl).

Additionally in the next phase the use of real process streams or waste streams as electrolytes must be researched. It is therefore mandatory to connect with an (industrial) partner that is interested in scaling this process up further.

1. Introduction

1.1. Background

The excessive consumption of fossil fuels has led to an increase of the atmospheric concentration of carbon dioxide in the last decades. CO_2 is low-cost and globally abundant, hence the use of CO_2 as a source for carbon feedstock (CO_2 utilization) to produce chemicals and fuels is a large opportunity. Electrochemical methods for the conversion of CO_2 into chemicals have attracted a lot of attention due to the low temperatures and pressures needed to achieve the high and efficient conversion. Moreover, due to rapid roll-out of renewable energy, sector coupling (energy and chemistry sector) can lead to significant advantages, economic and ecological. An important advantage that makes electrochemistry attractive for industry is the ease of scalability which allows fast deployment.

The future is in renewable energy (RE) and to store it in platform molecules will be a critical part of the European energy and industry infrastructure. Conversion of CO_2 to value added chemicals is of high interest; its use as a C1 feedstock offers the possibility to produce platform molecules such as CO and C_2H_4 Electrochemistry is a powerful method of synthesizing organic products using RE, and is ideal for decentralized plants. One example is the largest electrolytic chlor-alkali process to produce chlorine which is widely used for synthesis of chlorocarbon based intermediates. However, the high overpotentials and low current densities needed to initiate the electrochemical reduction of CO_2 makes the electrochemical process currently economically unattractive.

In most cases the chemistry that occurs at the counter electrode yields a waste product, which holds little economic value (examples are the O_2 from CO_2 reduction process and HCl from chlor-alkali industry). A possible strategy to use the maximum potential of an electrochemical process can be achieved by pairing two reactions which both lead to valuable products. The formation of a valuable product in the counter reaction thus has the great potential advantage of saving resources and energy (needed to produce the oxidant and reductants for the two separate reactions). In this manner, the reduction of CO_2 can ultimately become a cost-efficient process

The counter reaction in CO_2 electrolyzers is usually water oxidation to oxygen, which has a minimal value, thereby, limiting the economic benefit that the process can offer. To overcome this issue, we propose to use paired electrolysis, where useful products are produced at both sides of an electrochemical reactor without consuming more electricity overall. The concept involves the electro-oxidation of Cl^- together with the electro-reduction of CO_2, giving rise to valuable chemicals in a highly efficient manner from essentially waste materials. The use of CO_2 as a C1 feedstock for the formation of more valuable chemicals such as carbon monoxide (CO) offers the use of an easy, available and renewable carbon source, which is non-toxic and abundant; while chloride electro-oxidation to chlorine opens the possibility of recovering the chlorine from hydrogen chloride or for using the latter directly in a chlorination reaction, which is widely used in the polymer industry.

1.2. Goal of the project

The goal the project is to develop a continuous electrochemical process (paired electrolysis) using waste materials (CO_2 and HCl) to produce two valuable chemical products simultaneously by combining two large electrochemical processes: CO_2 reduction to CO and chlorine production from HCl in one electrochemical reactor. A scheme of the process is showed in Figure 1. This process is a breakthrough regarding higher electron efficiency (can be larger than 170%, compared to standard 70%) and lower capital costs (per product produced up to 50% lower compared to standard). This process will be demonstrated up to TRL4. Detailed techno-economic evaluation is part of the project.

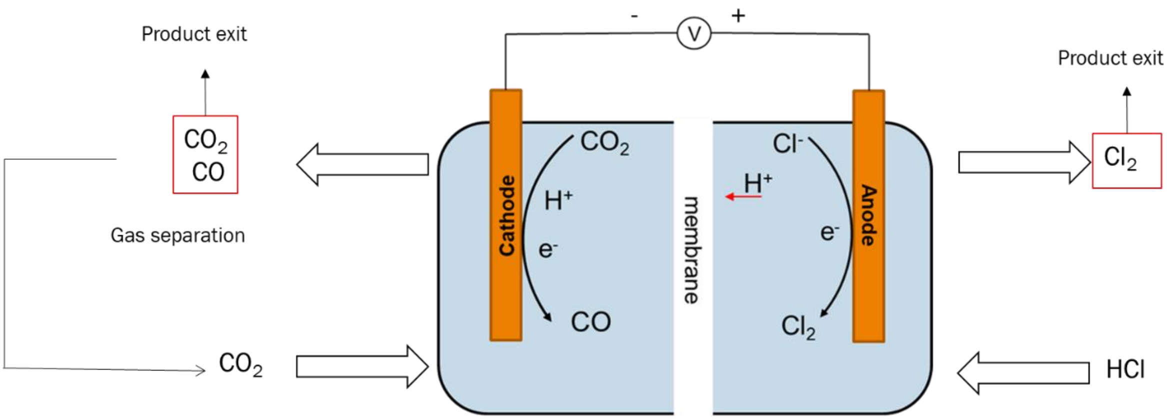

Figure 1: Schematic two compartment cell for paired electrolysis of CO_2/Cl^- to CO and chlorine.

The overarching objective of this project is to capture the opportunity of several major transitions in our society: cost and energy efficient **transformation** of CO_2, the **storage** of renewable energy into molecules, and **circularity**; the use of waste-streams as feedstocks for new processes and products. This project thus contributes to several goals of the Topsector Energie:

- Improvement of energy efficiency (by paired electrochemistry
- Flexibility of energy system (by storage of energy in molecules)
- Electrification and radically new processes (by using electrochemical processes and systems)
- Circular economy (by re-using CO_2 and waste streams, closing industrial chains)
- CO_2 emission reductions (by utilization).

2. Description of activities

TNO, Avantium and UvA propose the combination of two reactions, the reduction of CO_2 to CO on the cathode and the oxidation of HCl to Cl_2 on the anode. In order to achieve an efficient paired system, it is crucial to be able to couple both reactions in terms of experimental conditions. The selection of the optimal conditions is a decisive parameter to obtain an efficient continuous system. Thereby, a study of the adequate electrode materials, electrolyte solutions, membranes and applied currents, among others, is necessary to optimize the process in the interest of obtaining an economically beneficial process.

In this project, a novel concept of paired electrolysis will be designed and scaled up. Our cell will consist of a two compartment system divided by a membrane (as showed in Figure 1). In the cathodic compartment CO_2 will be reduced to CO while in the anodic compartment HCl will be oxidized to Cl_2.

$$\textit{Overall reaction: } 2\,Cl^- + CO_2 + 2\,H^+ \rightarrow Cl_2 + CO + H_2O \quad E = 1.46\ V$$

The use of CO_2 as a C1 feedstock for the formation of more valuable chemicals such as carbon monoxide (CO) offers the use of an easy, available and renewable carbon source, which is non-toxic and abundant; while chloride electro-oxidation to chlorine opens the possibility of recovering the chlorine from hydrogen chloride or for using the latter directly in chlorination reaction, which is widely used in the polymer industry. This project will lead to the technology development up to TRL 4. The overarching final goal is scale-up and commercialization of this process.

The result of this project will be a bench scale demonstration of continuous paired electrolysis of CO_2 and Cl^- and evaluation of technical and economic feasibility of the process. The project will deliver an optimal electrochemical reactor and hardware for such paired electrolysis, as well as the models that describe reactor performance. In Figure 2 a schematic overview is given of the E-COUCH project.

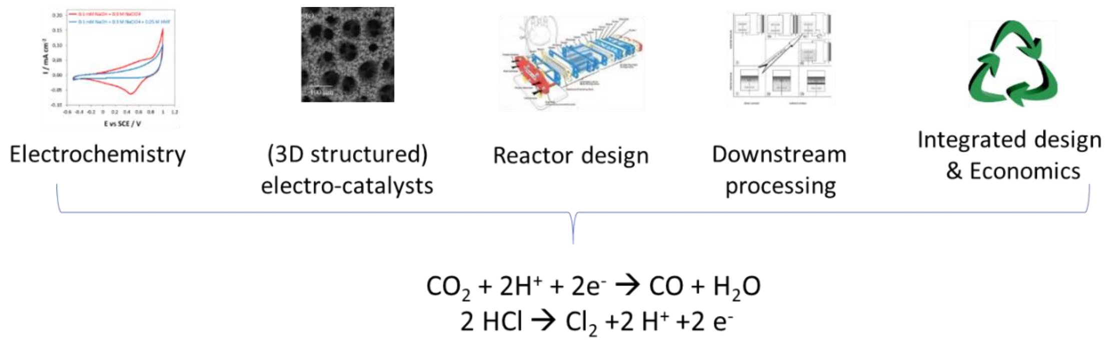

Figure 2: Schematic overview of the research activities within E-COUCH.

Importantly, the project will generate a required set of data, conceptual process diagram with mass and energy balances and important parameters for the further process scale up

In order to reach the goals of the project, the following activities have been carried out.

At the start of the project, TNO and Avantium have set the requirements and Key Performance Indicators. A preliminary Techno-Economic assessment of the reaction unit was performed based on existing knowledge. Important parameters to be optimized were identified.

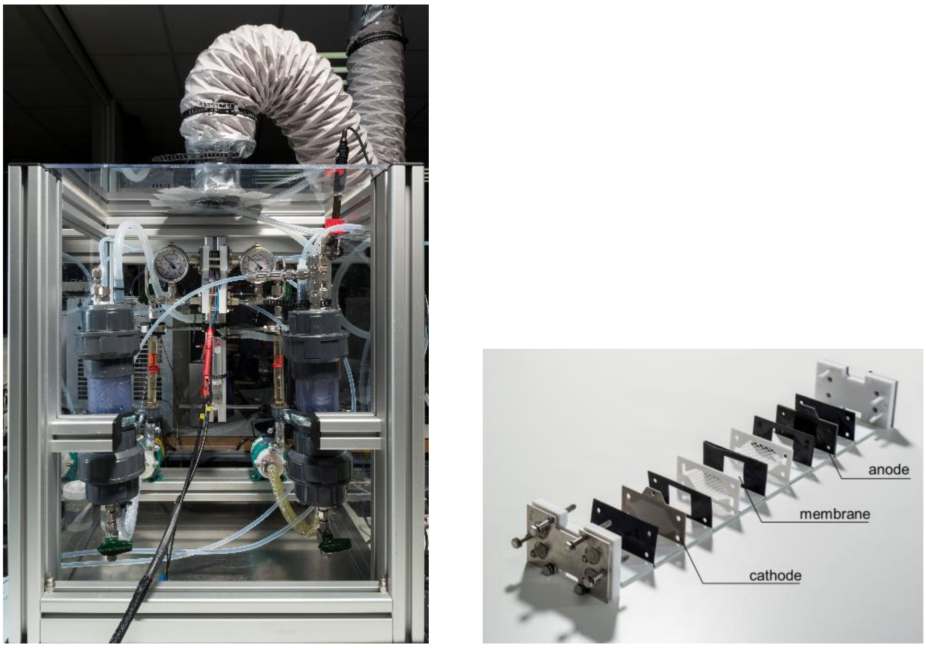

Figure 3: Laboratory equipment used for electrolysis in an electro cell 10 cm^2 flow cell (right).

Subsequently UvA and Avantium focused on the design and optimization of individual and paired routes. The main tasks were electrode and catalyst development and selection, determining operating electrochemical window and analytical characterization using 10cm^2 electrode area laboratory equipment (see Figure 3). The performance of selected catalyst materials for anodic and cathodic reactions were investigated.

After the requirements and specifications were set, TNO started with the electrochemical reactor design and realisation, integrating both reactions into a single electrochemical cell. Optimization of paired electrolysis was done. Several electrodes were prepared based on results of UvA and Avantium, then tested in existing electrochemical flow cells as well as in a newly constructed novel reactor (see Figure 4). Various 3D electrodes were tested and optimized with the goal to achieve industrially relevant performance (i.e. current density, efficiency). Reaction conditions (electrolyte, pH, temperature) were optimized.

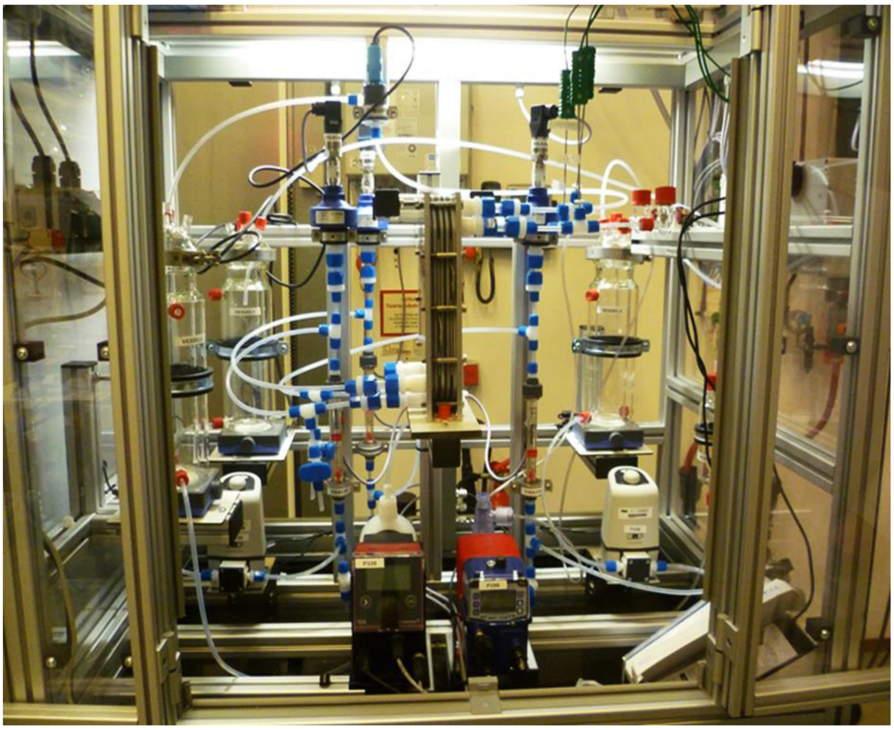

Figure 4: TRL4 100 cm^2 reactor test station

As a supporting task, electrochemical reactor modelling was performed, to understand interaction phenomena such as heat and mass transfer in combination with the electrochemical reactions occurring at electrode surfaces. Aspects influencing the reaction performance such as current density, selectivity, yield were investigated. With the models, predictions can be made for the reactor performance when scaled up and recommendation for scale up will be formulated. Models are validated with experimental tests.

An extensive test program has been carried out by the partners, testing in batch and continuous mode for characterization of the whole system. Continuous electrolysis was be performed in various electrolyser configurations, in order to optimize the reaction yield and efficiency. The electrolysis conditions were optimized and characterized. Various electrolyte options were tested, to minimize cell voltage, maximize economic feasibility and assess electrolyte recycling options. Additionally the stability of the reactor and its components over time was assessed.

Selected membranes were tested for use in paired electrolysis, to tests transport of reaction components, as well as the stability of the membranes at various operating conditions (pH, temperature).

The bench scale continuous paired electrolysis of CO_2 and Cl^- was demonstrated and a process concept established, based on the user requirements and the reactor design. The process concept entails the design of a process taking into account the feed and downstream processing needs.

An important part of the research was to do a thorough system analysis in order to assess the potential of this technology for grid balancing and CO_2 utilization and Cl_2 production, including the evaluation of the economic impact of the technology.

The roles of the participants in the project were as follows:

Naam deelnemer	Rol in project
TNO	Lead in Continuous electrode and reactor design, experimental scientific validation, techno-economic evaluation and project management. Participant in optimization of reaction conditions and concept process
Avantium	Lead in development of concept process. Participant in optimization and benchmarking of electrocatalysts, process conditions (together with UvA). Participant in input to Electrochemical Reactor Design.
UvA	Lead in optimization and benchmarking of electrocatalysts, process conditions (together with Avantium). UvA

3. Results

The main result of the project is an operational continuous bench-scale electrochemical flow reactor for coproduction of CO and Cl_2 including:

- Experimentally validated key performance indicators;
- Profitability of business case based on experimental results;
- Technology development implementation plan for scale-up;

Specific results reached in the project are:

- A stable Faraday yield to CO (86-90% Faraday efficiency) for 60 hours at room temperature (21 degrees) has been observed.
- A process design has been made for the full scale process.
- For scale-up to TRL4, a new continuous flow reactor with a 100cm^2 electrode surface area has been modelled, designed, realized and tested. After optimization and validation of the process in the new reactor, the values of the key performance indicators have been experimentally determined. The project reached better Faraday efficiencies towards CO and Cl_2 compared to the state of the art. The project main achievements are: FE towards CO: 75-80% @ 100 mA/cm^2 and 60% @ 150 mA/cm^2. FE towards Cl_2: 70-90% @ 100 – 150 mA/cm^2. Energy consumption of about 3200 kWh/tonne Cl_2 and 8200 kWh/tonne CO.
- The techno economic evaluation, assessing the business case for a full-scale system, shows that a positive business case is possible, with an estimated product price of ~0.5 Euro/kg for an equimolar mix of CO + Cl_2.

By taking this stepping stone towards commercialization, the project has contributed to several of the overall goals of the Topsector Energie as described above.

3.1. Outlook continuation, application, scale-up

The project has reached its goals and has shown that the technology can have a positive business case.

The next step in the technology development would be to pursue a scale-up to prototype industrial scale (TRL4-6), scaling up to ~1000cm^2 single cell surface area. Then a stack reactor with a surface area of several m^2 total electrode size needs to be designed and be tested in a TRL6-7 pilot plant, to be built on a relevant industrial location (e.g.: at Chemport Europe, Delfzijl).

In the next phase the use of real process streams or waste streams as electrolytes must be researched. It is therefore advisable to connect with an (industrial) partner that is interested in scaling this process up further.

Finally, the knowledge gained in the project on electrode and reactor design, both experimental and by modeling, can be applied to the development of other electrochemical systems.

3.2. Publications and dissemination

- 2019-09-15 Presentation “Electrochemical paired & CO production” at 12th European Congress of Chemical Engineering, Florence
- 2021-08 Presentation “Electrochemical paired & CO production” at International Society of Electrochemistry meeting
- Website: https://www.voltachem.com/news/new-ecouch-project-develops-route-towards-efficient-electrochemical-co2-utilisation
- Booklet: https://www.voltachem.com/images/uploads/_Voltachem_in_action_2019_lowres.pdf
- Publication in preparation