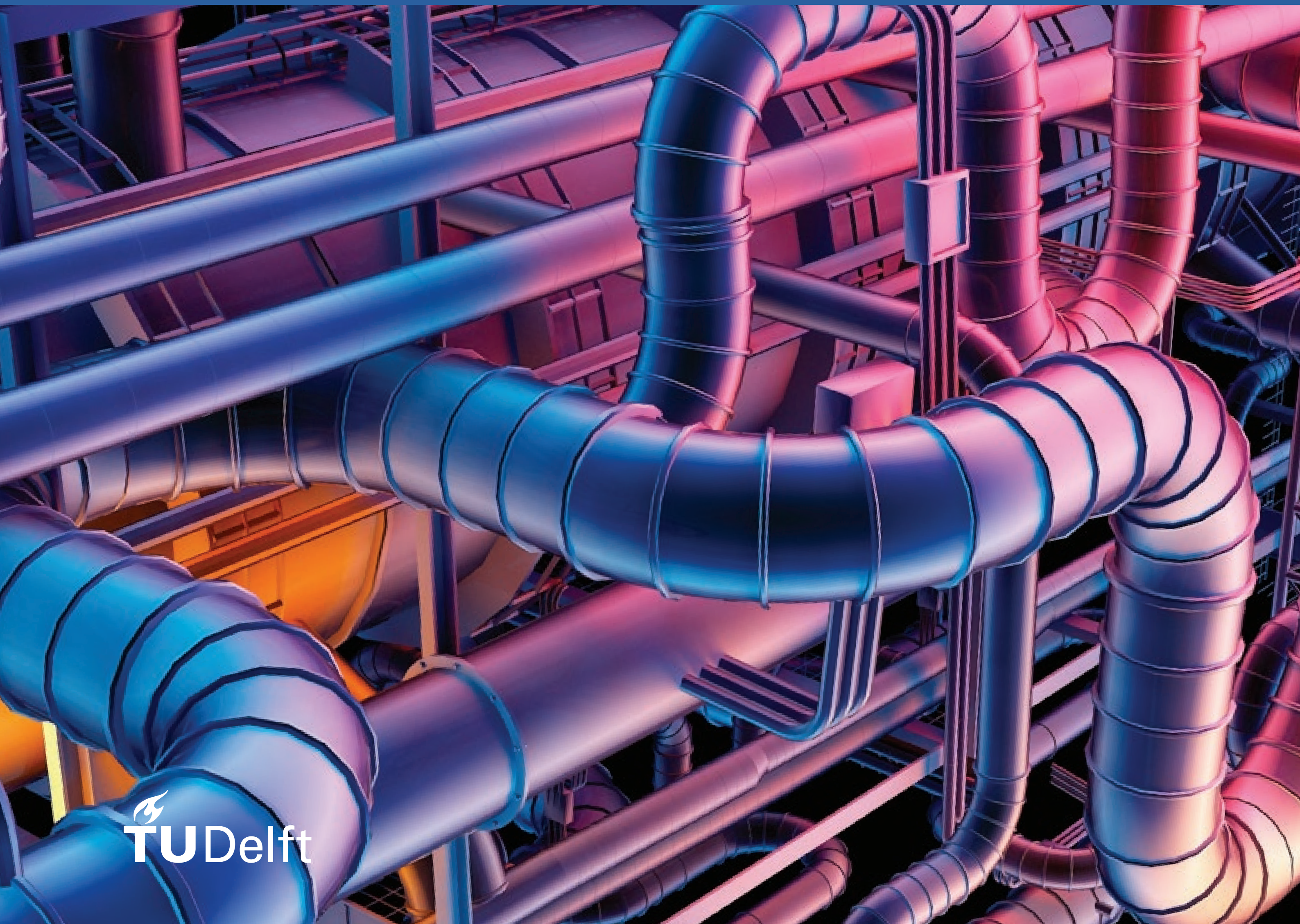
Large-scale conversion of renewable electricity into molecular bonds

e-Refinery

Challenges ahead and expertise available at TU Delft



TU Delft

e-Refinery NL

The Netherlands is increasingly aligning itself towards global sustainability goals. By formulating ambitions such as in the Dutch Transition Agenda (to arrive at a circular economy in 2050) and by joining global agreements such as the Paris Climate Agreement (to decrease greenhouse gas emissions from 2020 onwards), the country is looking ahead decades and planning for a CO_2-neutral (or even negative) sustainable system for both energy conversion and chemicals/materials production. As this transition has far-stretching implications for our industry and economy, it is vital to start building the required human capital and technology capacity as soon as possible. Timely investments into both will allow Dutch industry and science to keep existing or preferably attain new positions of leadership.

Electrification is a key enabler towards reducing CO_2 emission. The availability of renewable electrical energy does however not remove the demand for fuels, chemicals and other materials. In addition, the variability of nature calls for electricity storage to safeguard continuous electricity supply. Electrosynthesis is a promising approach to electrify the manufacturing of fuels, chemicals and materials and to contribute to energy storage. Given the Dutch strategic position in the international chemical, renewable energy and transport sectors, TU Delft sees exciting opportunities to establish a national consortium taking the first steps towards industrial-scale 'e-refinery' systems to convert electricity into molecular bonds.

Flexible energy storage in the form of chemicals produced by using electrical energy offers prospects for the energy sector to deal with the growing challenge of demand versus supply mismatch. The large-scale production of synthetic fuels, for example for heavy long-distance transport and aviation, platform chemicals and other materials using electrical energy from renewable sources addresses sustainability demands and is a decisive step towards creating a circular economy.

In this document, we explore the challenges that lie ahead, dividing them according to the three scales involved: the micro scale (Materials, Catalysts, Electrochemistry), the meso scale (Transport phenomena, Reactor Engineering & Process Intensification, Energy Technology & System Engineering) and the macro scale (Process and System Integration, Societal Embedding).

We envision a national consortium and a long-term (10+ years) research and development programme to tackle these challenges, in line with the recent advice by the Electrochemical Conversion and Materials (ECCM) committee to the Dutch Top Sectors HTSM, Energy and Chemistry. TU Delft started the e-refinery initiative and is motivated to play a key role in such a national activity. Across all the disciplines involved, from fundamental research to societal implementation, TU Delft has the expertise to pioneer the topic of electrosynthesis.

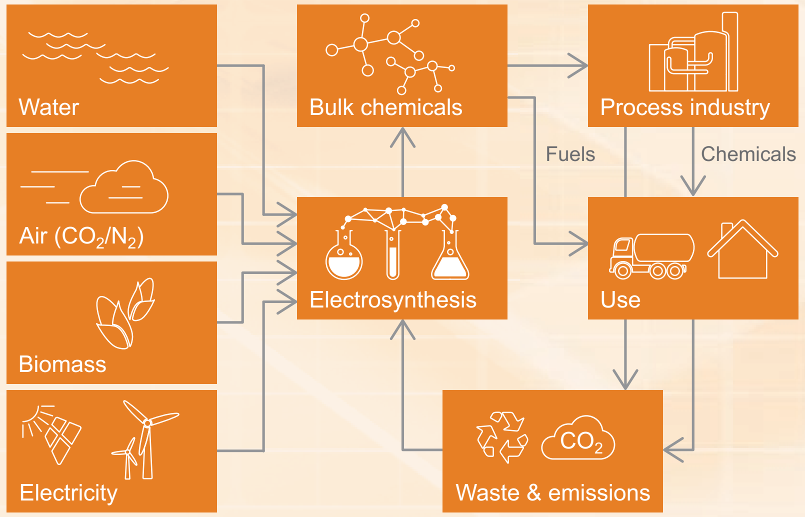
Chemicals from electricity

Electrosynthesis in chemical manufacturing is the synthesis of chemical compounds in an electrochemical cell, basically consisting of electrodes, an electrolyte and liquid or gaseous reactants. In short, it allows the production of chemicals using electricity.

The method was developed more than 160 years ago. Now, its green potential has been rediscovered. It makes sustainable and 'green' chemistry possible, particularly with the use of surplus power from renewable sources, such as wind or solar energy. Direct electrochemical conversion of feedstock to chemicals is one of the primary routes for electrification of the chemical industry and for providing flexibility in the coming era of varying supply and demand of renewable electricity.

The potential advantages of the electrosynthesis production route include high selectivity, scalability, less wasteful side reactions, less energy loss, less chemicals spent, often fewer reaction steps than conventional methods and integrability in existing industry. Nonetheless, historically, electrochemical synthesis has been limited to a narrow spectrum of reactions and chemicals, which is often attributed to a lag in chemical and engineering technology and the prohibitive capital costs, particularly of electrochemical reactors. One major exception concerns the chloralkali process where electrosynthesis of an aqueous solution of NaCl is used to produce the bulk chemicals chlorine and sodium hydroxide: one of the largest chemical processes worldwide.

Although commodity-scale implementation of the electrosynthesis technology is still far away, the first positive business cases in the production of high-value chemicals are emerging, with many more expected on the short term.



At the micro scale

Thrust 1: Materials, Catalysts, Electrochemistry

It is clear that the choice of electrode material, electrolyte and membrane determine to a large extent which product can be obtained from e-refinery systems. The three components are mutually dependent and should be chosen such that an inherently stable operation is obtained. The design of the electrosynthesis process requires in-depth knowledge of the processes involved from the atomic to the micro scale to ultimately enable production processes at large scales.

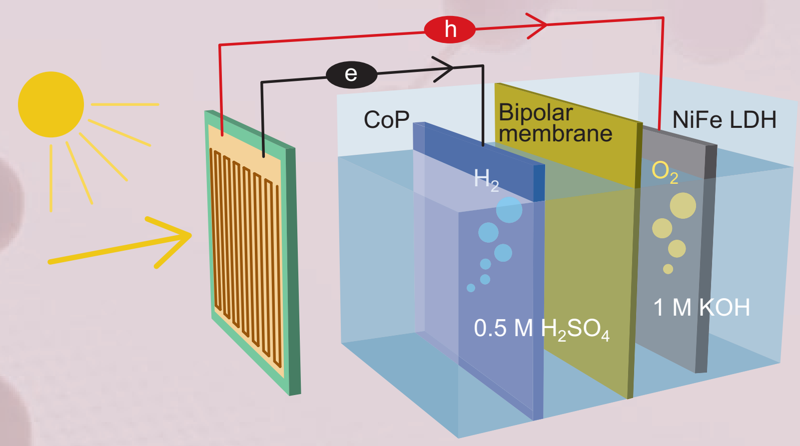
Local probing of processes at the micro scale
A detailed mechanistic insight into the processes taking place at the micro-scale during electrosynthesis is currently lacking. To address this issue, it will be essential to locally study the intrinsic kinetics throughout in the device, whether in the solid, liquid or gas phase. A targeted research programme in this area would leverage the leading Dutch position in the development and use of *in-situ* and *operando* characterisation techniques to analyse the structural development in time of the key functional materials (electrodes, electrolytes, membranes) at all length scales and over long periods of time. Specifically, to determine the chemical conversion pathways, it will be necessary to investigate the non-equilibrium electrode surface processes at the nano scale; this involves *operando* characterisation using advanced microscopy techniques. Similarly, for the membranes novel *operando* techniques are needed to study the transport behaviour within the membranes as well as their long-term stability.

Rational design
The materials used in electrochemical catalytic processes have yet to be designed and optimised. A rational design approach is needed of the key component materials (electrodes, electrolytes and membranes), including their morphological aspects, aiming for inherent stability, high efficiency and maximum selectivity.

This implies the development and use of new predictive computational tools, thermodynamic analyses and analogue reasoning in order to (1) develop non-noble metal catalysts which are impurity resistant, can deal with oscillating process conditions, have a low over-potential and show a high conversion speed; (2) develop (bipolar) membranes for specific process conditions; and (3) develop stable and inert electrolytes with high transport numbers. Finally, high-throughput methods need to be developed for the experimental verification of the predicted properties and further guidance.

Design for bulk
The goal of large-scale production of fuels and chemicals guides the design of the nano-structured materials involved in the e-refinery technology: the components need to maintain their uniform functionality over long timescales (for example, 5 years) and under relevant process conditions (for example, fluctuations in flow, material composition and energy supply). They should also be produced in a scalable manner (for example, utilising new processes for 3D printing, CVD/ALD, etc.) The availability of resources needs to be taken into account in selecting these materials.

Bipolar membranes for optimised electrochemical engineering
Efficient solar-to-fuel devices require electrocatalyst and photoelectrode materials to operate in a common electrochemical conversion environment. However, the optimal environment for the oxidation and reduction reactions are typically not the same, posing challenges to arrive at an efficient and stable overall system. Researchers at the Materials for Energy Conversion and Storage group at TU Delft study the importance of the electrolyte pH for the activation and performance of electrocatalyst and photoelectrode materials. Using a bipolar membrane to separate anode and cathode compartments to separately optimise both reaction conditions offers an attractive approach towards photoelectrochemical and electrochemical devices for highly efficient and stable solar-driven water splitting.



At the meso scale

Thrust 2: Transport Phenomena, Reactor Engineering & Process Intensification, Energy Technology & System Engineering

The next frontier is in translating the insights obtained by studying the microscopic-scale processes at work in the e-refinery system (Thrust 1) into practical tools to design, engineer and optimise the reactor component and process system design. Establishing general electrochemical engineering design rules, taking into account all materials and components involved, will allow assessing the potential of electrochemical synthesis routes, and allow predicting the effect of transients (in electrical current and material resources) on all aspects of the conversion process.

Transport phenomena
Electrosynthesis involves transport of chemicals and ionic/electrical charge across a range of length scales. Full process control requires a detailed determination of the limiting effects of mass, charge and heat transfer, including limitations caused by multi-component and multi-phase flow (Stefan flows, bubble transport). Moreover, it requires optimisation of the porous structures of electrodes and (possibly bipolar) membranes.

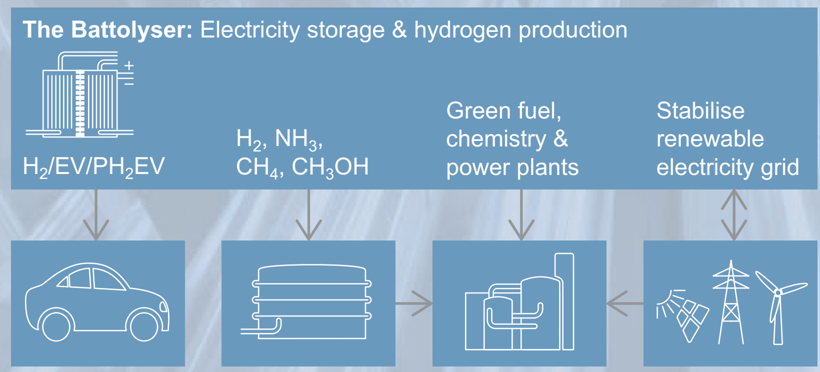
Reactor engineering & process intensification
The development of continuously operating electrochemical flow reactors poses several challenges. It requires assessing the geometry/configuration, advanced engineering and developing a scaling-up approach for these reactors. An optimal balance between operation towards maximal selectivity (potential-driven) and allowing for (*in-situ*) separation of useful products needs to be determined. An additional challenge is transient operation and intensification to deal with process fluctuations, pulsed reactions and the effects of fouling. This asks for comprehensive reactor models and experimental facilities to enable validation from the reactor level down to the *in-situ* electrode level.

Energy technology & systems engineering
Large-scale electrochemistry-based processes for fuels and bulk chemicals production are in an early stage of development. Challenges on the process systems engineering level include:

- finding solutions to deal with fluctuations in power characteristics related to process dynamics and control;
- determining the gas-cleaning requirements for a wide variety of CO_2 sources for carbon-based e-refinery products; and finally
- process integration (flows, recycles, heat, pressure levels) to arrive at optimal process system efficiencies.

Combining electricity storage and hydrogen production in a single system
To store sustainably generated electricity in the form of wind and solar power, batteries are best for short-term storage whereas synthetically produced fuels such as hydrogen and derived compounds are most suitable for long-term energy storage. Researchers at the Materials for Energy Conversion & Storage group at TU Delft developed the first integrated battery and electrolysis system. This so-called 'battolyser' stores and supplies electricity very efficiently as a battery. When the battery is full, it automatically starts splitting water into hydrogen and oxygen using electrolysis at an outstanding overall efficiency of up to 90%. The battolyser is effectively in service the whole time, storing power, producing hydrogen or supplying power to the grid. It provides an efficient, cheap, large-scale, robust way of storing electricity that can be switched back and forth between electricity and hydrogen as often as needed.

Work is ongoing to further improve the efficiency and to scale up the concept to the size of a shipping container, to prove that the technology is also suitable at the scale of the power produced by a large wind turbine and that it can be combined with downstream hydrogen use.



At the macro scale

Thrust 3: Process and System Integration, Societal Embedding

Simultaneously with Thrusts 1 and 2, a global assessment of the transition of classical petrochemical processes to the e-refinery concept is needed. Can we determine the pros and cons well in advance? How can the e-refinery concept be optimally integrated into the energy grid? This Thrust is concerned with the challenge of predicting and optimising the impact of the e-refinery concept towards reaching the sustainability goals for 2050.

Facilitating knowledge transfer

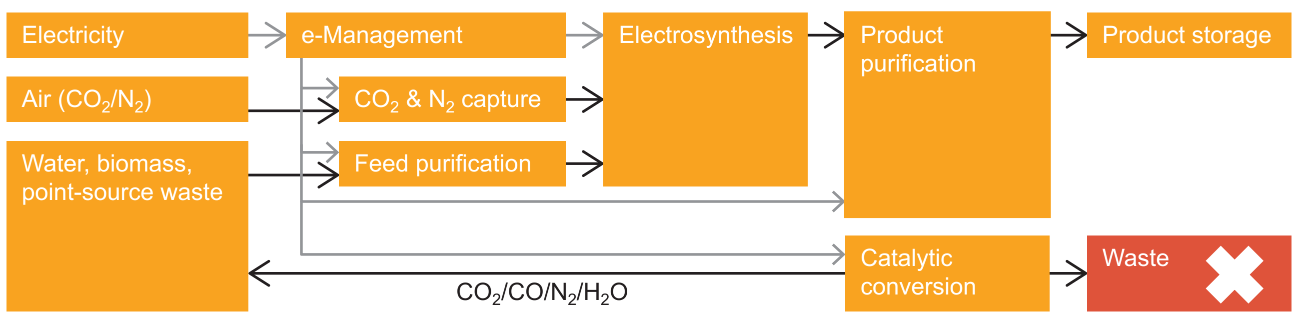
For a successful integration of e-refinery systems in the incumbent (energy) system, there is a need for understanding the complex interactions across multiple scales (from molecules to products), and for actively guiding technology development by implementing feedback loops that allow transferring and evaluating knowledge across the different scales where e-refinery technologies operate (macro, meso, micro).

Maximising synergies

To anticipate the introduction of e-refinery systems, it is vital to make a timely assessment of the relevant system constrains, including the use of current assets, matchmaking of supply and demand, evaluation of the environmental impacts, logistics and feedstock availability. We also need to identify and evaluate the trade-offs between short-term and long-term e-refinery configurations to identify potential hotspots, opportunities for synergies and non-regret options at the system level.

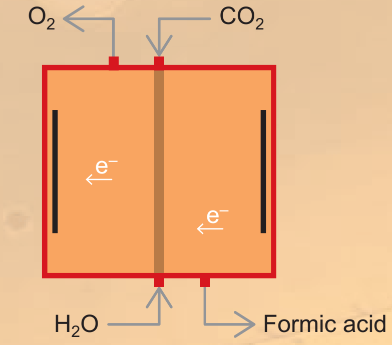
Preparing for technology uptake

Given the technological feasibility of e-refinery systems, how can we create the optimal conditions for them to be implemented? Towards this challenge, we need to develop new business models that speed up and/or support the uptake of the technologies and to assess incentives that can support their deployment. We also need to understand and develop institutional frameworks and governance tools to achieve effective large-scale diffusion as soon as the e-refinery technologies are commercially available and new actors become involved from the demand side.



Closing the CO_2 loop using formic acid

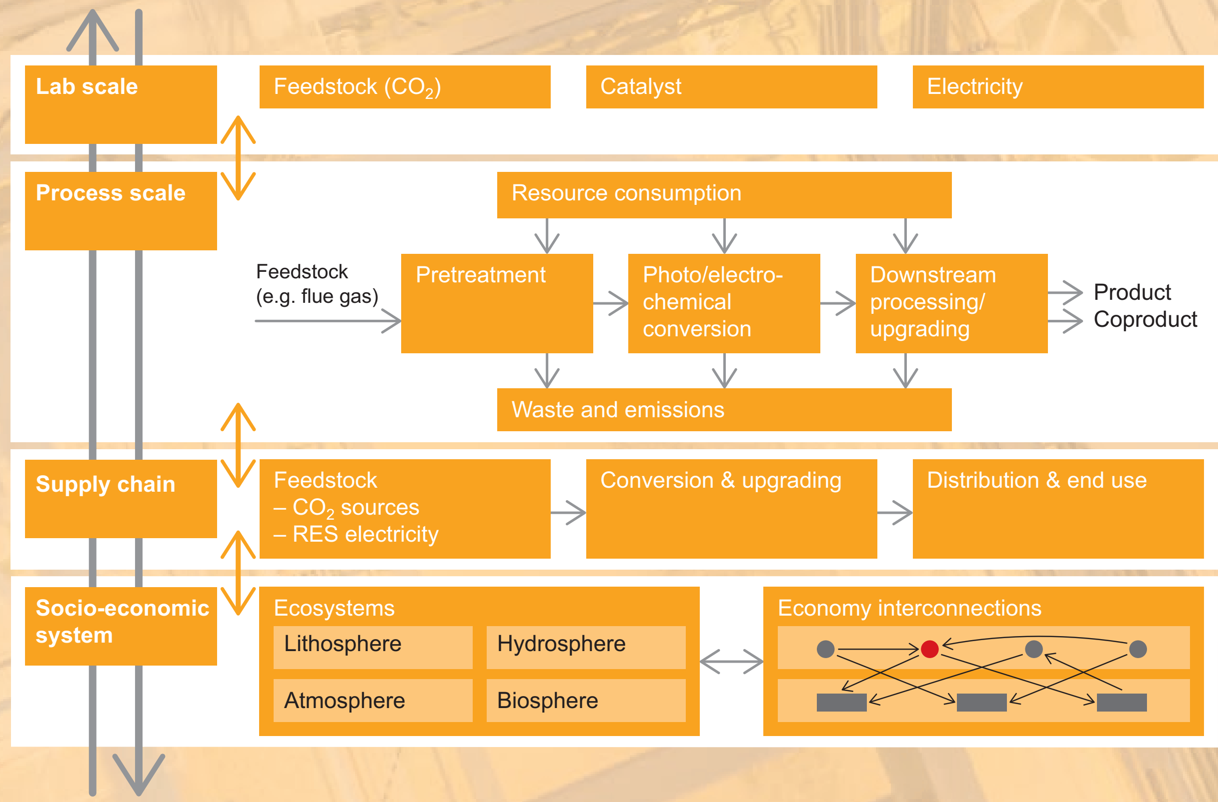
Six partners including TU Delft work together in the Shared Innovation Programme VoltaChem to convert CO_2 with the aid of sustainably produced electricity into large amounts of formic acid. Formic acid can be used as platform (bulk) chemical and intermediate for fuel production. It is well known also as conserving agent in livestock feed. The VoltaChem approach promises lower production costs and less CO_2 emissions, contributing to establishing a sustainable energy system of the future.



Formic acid is currently almost exclusively produced on the basis of fossil fuels. Previously it was demonstrated on a laboratory scale that it is possible to produce formic acid through direct electrochemical conversion of CO_2 at the cathode. Oxygen is produced at the anode.

As water is converted into hydrogen and oxygen with the aid of electricity in this process, formic acid can be considered a liquid and relatively safe hydrogen storage medium.

The consortium now works towards the development of an electrochemical reactor that continuously produces formic acid on a small scale using fluctuating amounts of renewable energy (solar and wind). Next, the challenge is to demonstrate that the process can also be deployed on an industrial scale. For such an activity, CO_2 capture is a pre-requisite. Integration of capture and conversion processes may lead to substantial efficiency gains.



Expertise at TU Delft

Thrust 1

Materials science
- Physical effects of nanostructuring in H, Li, and Na-based battery materials
- Solid-state chemistry
- Characterisation using crystallography, synchrotron and neutron scattering
- Thin-film deposition
- Atomic layer deposition
- Optical properties of thin films
- Scalable production of nanostructured materials
- Si-based thin-film solar cells and device manufacturing
- Chemical vapour deposition

Catalysis
- Redox processes involving enzymes
- Biocatalysts for organic synthesis
- Combination of chemo and enzyme catalysis
- Structured catalysts
- Multifunctional catalysts
- Metal-organic framework-based membranes

Electrochemistry
- Electrochemical cell design
- H_2O splitting, CO_2 reduction
- (Photo)electrochemistry
- Electrocatalytic processes
- Molecular simulations on electrolyte solutions, solid-liquid interfaces, electric double layers
- Corrosion processes
- *In-situ* micro-electrochemical characterisation

Thrust 2

Transport phenomena & membrane technology
- Modelling of mesoscale transport phenomena
- Complex heterogeneous catalysis
- Computational fluid dynamics, microfluidics (flow control) and fluid-structure interaction
- Multiphase flows, experimental characterisation of two-phase flows and measurements in complex flows
- Heat transfer
- Turbulence and mixing
- Coalescence and breakup
- Ion transport in bipolar membranes
- Nanostructures in membrane electrodes
- Molecular transport phenomena
- Simulation of processes at electrodes and membrane transport
- Modelling of heat and mass transport in electrochemical cells

Reactor engineering & process intensification
- Structured multiphase reactors
- Separation-enhanced reaction processes
- Electricity-based processing methods
- Process design and integration
- Microbubble formation and transport in sub-mm channels
- Biofilm reactor modelling
- Bioelectrochemical systems (microbial fuel cells)
- Electrofermentation
- In-situ product recovery

Energy technology & system engineering
- Design and fabrication technology of solar cells
- Devices based on thin semiconductor films
- Scale-out of microdevices
- Systems for integrated microgrids
- Scale-up and systems integration
- Reversible fuel cells
- System thermodynamics
- System engineering & assessment
- Carbon capture technology
- CO_2 conditioning evaluation
- Power input control & optimisation

Thrust 3

System integration, value chain impact and institutional embedding
- System integration
- Environmental assessment
- Life-cycle analysis and sustainability
- Early evaluation of novel low-carbon technologies
- System engineering
- Multiscale modelling of industrial systems: from global scenarios to daily operation
- Sustainable socio-technological systems
- Modelling the evolution of industrial clusters
- Business support and strategy development of integrated industrial networks
- Econometrics
- Institutional economics
- Market design
- Contracting theory
- Game theory
- Complexity science

Open invitation

This document mirrors the collective vision of the scientific community of the TU Delft regarding the large-scale conversion of renewable electricity to molecular bonds. We hope that it will inspire and motivate fellow scientists and stakeholders to come with their views and ideas to enhance and improve this vision. The TU Delft believes that the Netherlands needs an ambitious national R&D programme, encompassing all available top-notch Dutch knowledge, and facilities. We hope that this document helps to fulfil this ambition.

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