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Introduction

Aim of the document

This document is intended to present and illustrate the construction of the two different bench-scale pilot installations for direct power-to-X technologies. The decision to build two bench scale installations was taken by the consortium at the beginning of the project in order to be able to explore two reaction concepts within the project: (1) the direct production of formate and (2) the direct production of formate with in situ separation of formic acid.

For the direct formation of formate, a two compartment electrochemical reactor was constructed by VITO, and for the integrated direct formation of formate with in-situ separation of formic acid, a three compartment electrolysis bench-scale installation was constructed by TNO.

This document will provide the construction specifications of both set-ups.

Connecting objectives, results, outputs and activities

As part of Work Package 1: *Enabling research,* and more specifically as part of the activity 1.4: *Technology screening for direct conversion of CO_2*, two highly flexible feasibility systems have been constructed. The lab-scale set-ups are intended for the validation of new catalyst materials, novel electrode configurations, diverse electrolyte compositions and innovative system concepts at TRL 4.

Different partners of the consortium will provide input for the validation of the several system concepts. Antwerp University will provide an efficient catalyst material for the conversion of CO_2 to formate, which will be used by VITO to manufacture the gas diffusion electrodes (GDE) to be used in the electrochemical reactor. Delft University of Technology (TU Delft) will provide data with respect to the electrolyte nature and composition to be used in the electrochemical system. All the different components of the electrochemical system will be tested using the two different set-ups constructed at VITO (2-compartment system for formate production) and at TNO (3-compartment system for formate production with in-situ separation of formic acid).

The experimental testing of these lab-scale set-ups and the results obtained will be used for the design of the pilot demonstrator for direct electrochemical conversion of CO_2 which will be constructed and tested in Work Package 3: *Demonstration systems*.

System requirements

The key targets for the final showcase were determined and reported in the Interreg E2C deliverable D1.1.1: *Report on user requirements and key performance indicators for direct and indirect CO_2 conversion*:

1. Production rate of formate or formic acid of up to 1 kg per hour
2. Current density: **I >100 mA/cm^2.**
3. Selectivity / faradaic efficiency towards desired product: **FE > 80%**
4. Stability: **1 week (170h) with a decrease of less than 10% FE towards formic acid/formate**
5. Total cell voltage: **ΔE < 3.0 V**

Moreover, the following boundary conditions have been formulated in D1.1.1:

- Electrolyte: $KHCO_3$ saturated with CO_2 as standard electrolyte
- Electrochemical cell: flow by vs. flow through
- Membranes: Nafion 117 (standard); anion exchange membranes; bipolar membranes
- Pressure: 1 atm.
- Temperature: room T (standard); up to 50°C
- The bench scale installations described in the present document are designed to comply to the target requirements and boundary conditions listed above.

VITO Two compartment Electrochemical Reactor (VITO EC reactor)

VITO Two compartment Electrochemical Reactor (VITO EC reactor)

Basics of design

The design of the VITO EC reactor, as described in D1.4.1: *Design documentation for the feasibility system*, is visualized in Figure 1. The catholyte and anolyte will be pumped through the cathodic and anodic chamber respectively. This will be carried out continuously, either with or without recirculation of the electrolyte (not shown). The reactant, a CO_2 gas stream, will flow through the gas diffusion electrode on the cathode side. The VITO EC reactor will consist of electrodes with a surface area of around 400 cm^2.

CO_2 will be reduced to formate which will be produced in the catholyte. A complex system of valves, flow controllers and pumps ensures the continuous operation of the reactor and provides the possibility for sampling and analysis of the various streams.

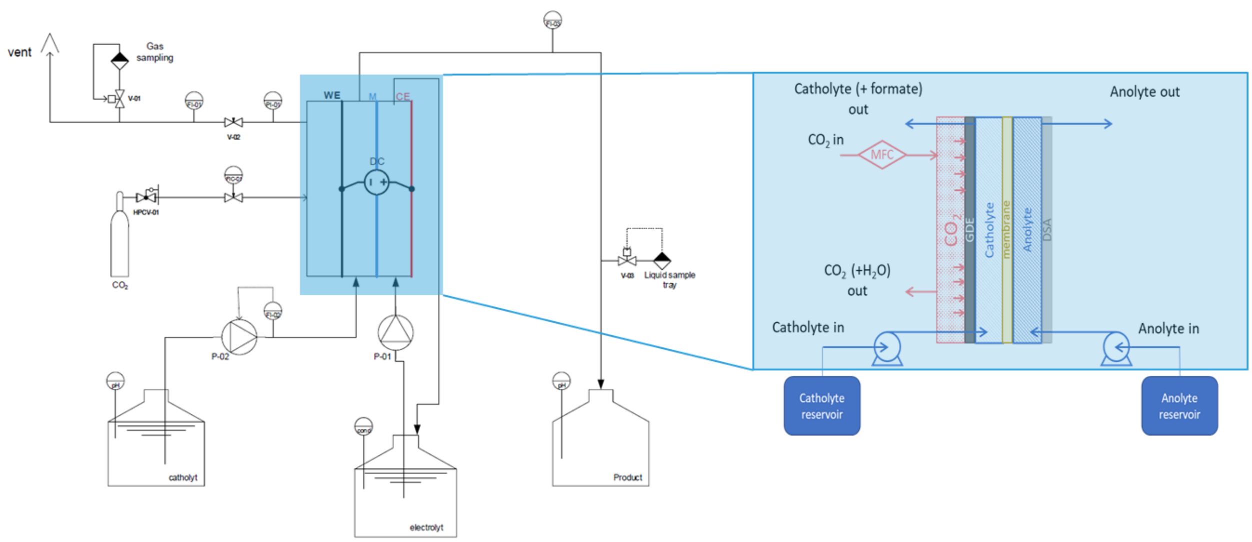


Figure 1 Schematic of VITO EC reactor

Building, commissioning and safety aspects of the VITO EC reactor

In the following figures, various components of the VITO EC reactor and its peripherals are visualized and described.

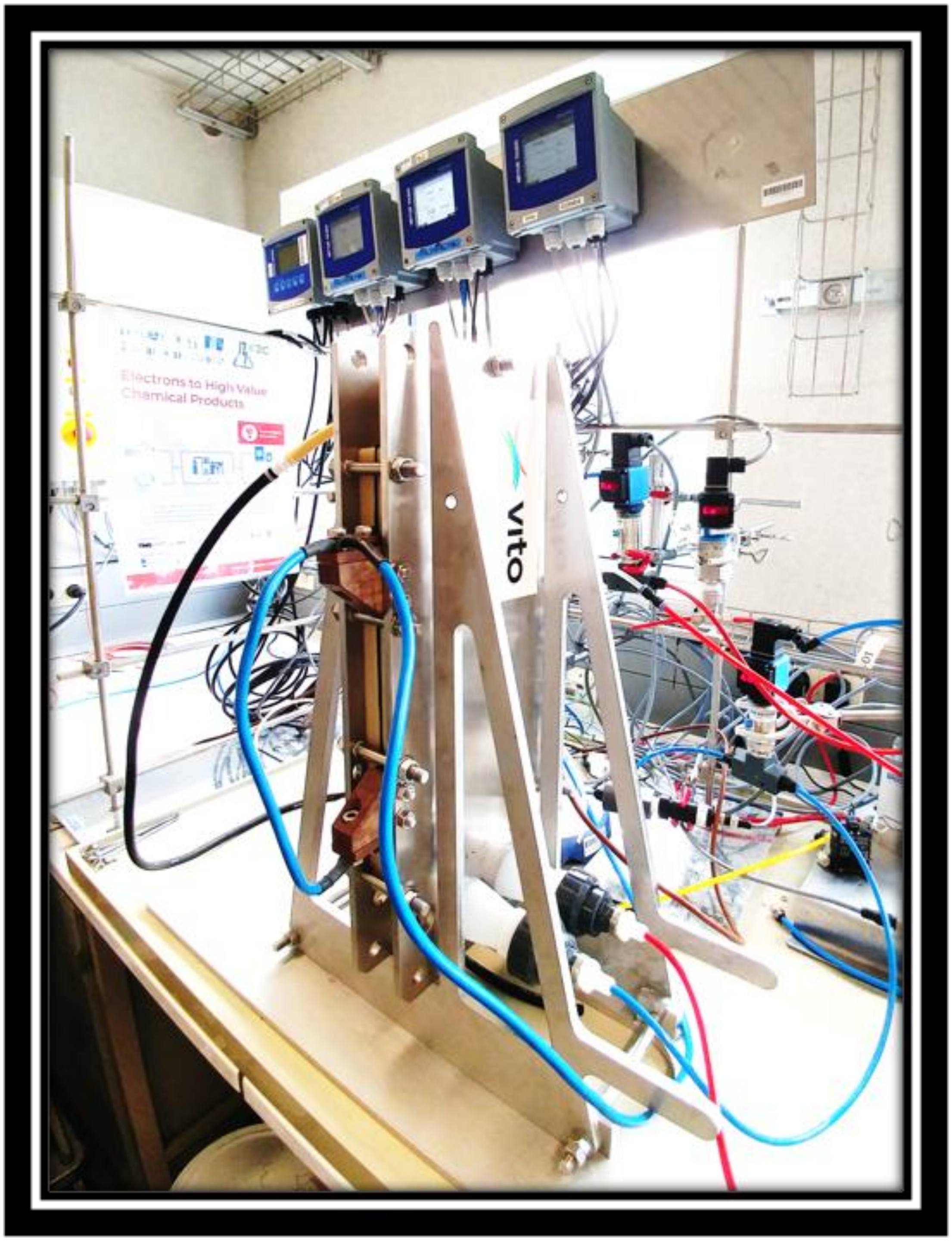


Figure 2. Overview of the VITO EC reactor and its peripherals

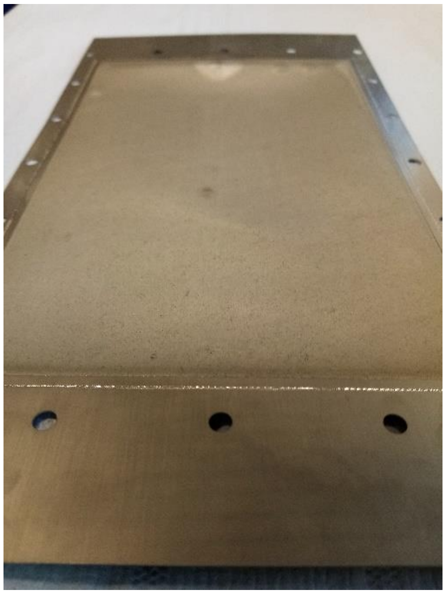


Figure 3 Gas diffusion electrode (catalyst side)

Figure 4 Gas diffusion electrode (gas side)

The gas diffusion electrode used as cathode is shown in Figure 3 and Figure 4. The gas diffusion electrode is prepared via the patented VITO technology. To be compatible with the VITO EC Reactor, the GDE is welded into a stainless steel housing.

Figure 5. Peripherals of the bench scale feasibility system, from left to right, GC gas analyzer, HPLC, liquid sample analyzer, high power power supply and online process control and monitoring system.

The complete system has been tested to ensure proper operation. Next steps are further optimization of the electrode and its connection with the housing. Moreover, several tests will be carried out in order to provide experimental data for the show case pilot as foreseen in WP3. The obtained data will be part of deliverable D1.4.2: *Report on the operation of the feasibility system and showcase test results*.

TNO Three compartment electrolysis bench-scale installation: ELEKTRA

Basic engineering

In Deliverable D1.4.1: *Design documentation for the feasibility system,* the methodology for the design of ELEKTRA, the systems requirements, the system description and the interfaces between the different balance of plant components were presented.

The construction of the bench-scale set-up was carried out following the system requirements defined in D1.4.1: *Design documentation for the feasibility system,* which were formulated based on the Interreg E2C proposal text.

After the formulation of the project requirements, the ELEKTRA system breakdown, the formulation of the ELEKTRA set-up requirements, the conceptual design and the definition of the system interfaces (All of them reported in deliverable D1.4.1), the detailed engineering design of the bench-scale system was carried out and it is presented in this document.

The engineering designed served as input for the safety study (HAZOP) which led to the installation of alarms in the set-up and the description of dedicated operating procedures to ensure the safe operation of the set-up.

After the approval of the safety evaluation, the bench-scale installation was built and commissioned to ensure that all the design functionalities are operative and all the safety measures are met.

ELEKTRA engineering design

Based on the project requirements and on the conceptual design described in deliverable D1.4.1: *Design documentation for the feasibility system*, the engineering design of ELEKTRA was carried out.

Figure 6 shows the schematic process flow diagram for ELEKTRA. The bench-scale set-up consist of five sections:

- S.001: Feeding system
- S.002: Recirculation system
- S.003: Control system
- S.004: Sampling system
- S.005: Ventilation system

The feeding section comprises the feeding of the liquid electrolytes and the gaseous reactants and all the components needed for it such as feeding pumps, gas reducer valves, humidifier system, etc.

The recirculation system comprises all the components needed (e.g. vessel, pumps, flow controllers, etc.) to recirculate the three different electrolytes (anolyte (A), catholyte (C) and middlelyte (M)) from the collection vessel, to the electrochemical reactor and back to the collection vessels. The design of the electrochemical reactor is described in more detailed in the section *Reactor design configurations and use cases.*

The control system consist of three different subsystems: pressure controller, temperature controller, and power supply. The pressure of the overall system is controlled by a set of back pressure regulators which ensure the same pressure in each compartment of the electrochemical cell. The temperature of the system is regulated with a water bath connected to the main three vessels (C, M and A). The power supply is connected to the cathode and anode of the electrochemical cell and is able to operate in galvanostatic (constant current) or potentiostatic mode (constant potential).

The sampling system comprises the liquid sampling and the gaseous sampling. For the liquid sampling, a set of valves was engineer in a way that allows sampling during operation. Liquid samples from the anolyte (A), catholyte (C) and middlelyte (M) can be taken simultaneously and they can be analyzed with a high pressure liquid chromatographer (HPLC). For the gaseous sampling system, a set of valves stablished the possibility of in-line gas detection by a gas chromatographer (GC) of either the gaseous stream from the C-gas compartment of the reactor, or from the gas stream in the collection vessel C.

The ventilation system ensures that the whole set-up has sufficient ventilation to operate in a safe manner, by diluting the gaseous stream that are vented out of the inner system. The set-up is built in a sealed box with sufficient ventilation.

Importantly, the overall system was designed in a highly flexible manner in agreement with one of the project requirements. Therefore, different reactor configurations can be accommodated in the set-up in order to research what configuration is the optimal in terms of energy efficiency, faradaic efficiency and productivity of the desired product. The different reactor configurations are explained in more detail in section *Reactor design, configuration and uses cases*. By using a smart design of valves, the different sections of the process can be enabled or disenabled based on the reactor configuration in use. The numbers (1,2,3,4) in each of the components of the process flow diagram designate which of the components will be enabled depending on the use case.

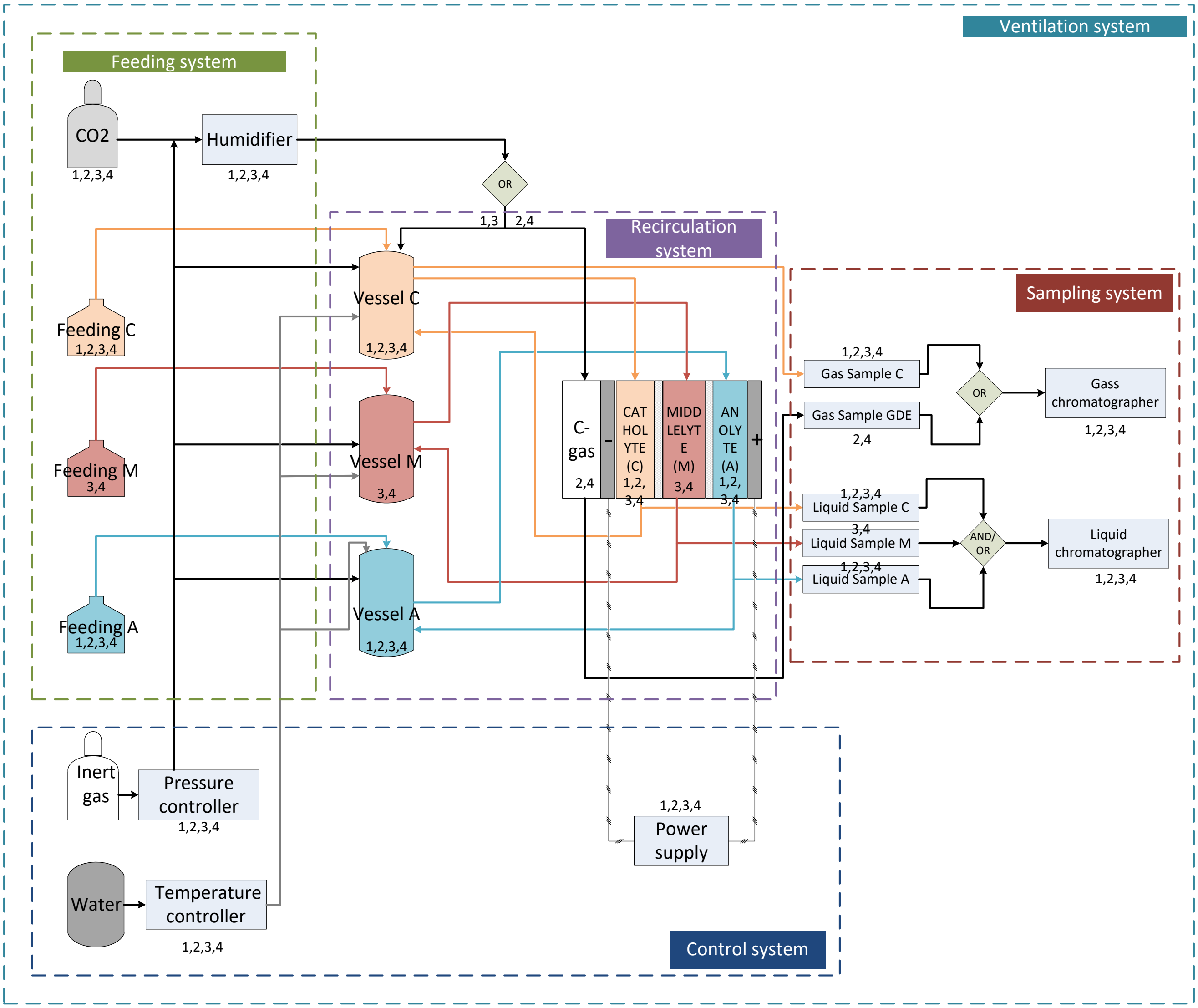


Figure 6. Schematic process flow diagram ELEKTRA

The components were selected based on the requirements described in Deliverable D1.4.1: *Design documentation for the feasibility system,* which allow to operate with the following conditions:

- Pressure : 1-30 barg
- Temperature : 10-80 °C
- pH electrolyte: 2-13
- Liquid flow range: 1-60 L/h
- CO_2 gas flow range: 0-500 NL/h
- Dilution gas flow rate: 10-500 l/h

All the components used in the construction of the set-up have chemical compatibility with the following compounds: CO_2, CO, O_2, H_2, Formic acid, Water, NaOH/KOH, Na_2CO_3/K_2CO_3, $NaHCO_3$/$KHCO_3$, Na_2SO_4/K_2SO_4, Methanol, Ethanol, Isopropanol, Propylene carbonate, Acetonitrile, Formaldehyde, Dimethyl carbonate.

Reactor design, configurations and use cases

The electrochemical reactor was design and constructed in a close collaboration of TNO with Hydron B.V. Due to the confidentiality agreement of TNO with Hydron B. V. this document only shows schematic representations of the reactor and not the detailed drawings of the internal parts. A picture of the house casing of the reactor can be found in section *Building of ELEKTRA*.

The electrochemical reactor was design and constructed following requirements:

- Reactor must accommodate one GDE or one plate as cathode and one plate as anode
- Reactor must ensure homogeneous distribution of gases and liquids
- Reactor must be flexible to construct different reactor configurations (at least the four use cases described in Figure 9)
- Reactor must be able to operate at 30 bar and withstand pressures up to 40 bar
- Reactor must have sufficient corrosion resistance
- Reactor must be able to operate at temperatures between 10-80 °C
- Reactor must be gas-tight and leak-tight
- Reactor must ensure a minimal interelectrode distance
- Reactor must be able to ensure a good mechanical stability of the GDE and the different membranes used
- Reactor cannot have metallic parts in contact with the liquid electrolytes
- Reactor must have 2 current collectors to ensure good electrical conductivity between electrodes
- Reactor must have sufficient inlet and outlet connections for all the gaseous and liquid streams

The conceptual design of the 3 liquid compartment electrochemical reactor (base case) is shown in Figure 7.

The reactor comprises 3 liquid compartments an one gas compartment. As for electrodes, it comprises one plate as anode and one gas diffusion electrode (GDE) as cathode. Briefly, the CO_2 gas is introduced in the gas compartment (back side of the GDE) where it diffuses through the porous layer of the GDE to reach the catalyst layer. In the boundary layer between the liquid catholyte and the catalyst layer, the CO_2 reacts with 2 electrons to form formate ($HCOO^-$). The formate formed crosses the anionic exchange membrane (AEM) to the middle compartment, where it recombines with protons (H+) to form formic acid (HCOOH). The protons which are formed in the anodic reaction (during water oxidation) cross to the middle compartment through the cation exchange membrane (CEM).

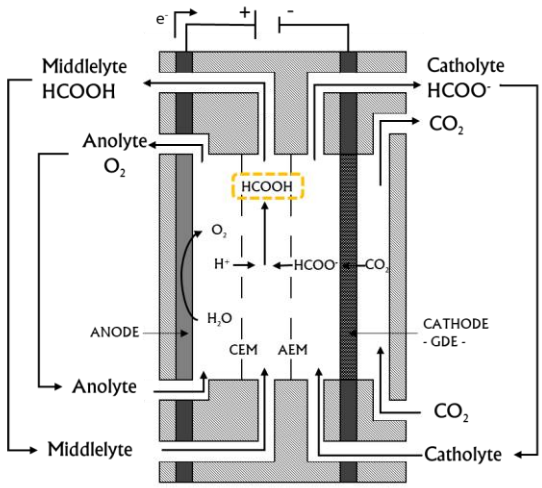


Figure 7. Schematic representation of the 3 liquid compartment reactor design for direct electrochemical conversion of CO_2 to formate with in-situ separation of formic acid (base case).

The flexible design of the reactor and the system allows for testing in different configurations.

The different configurations of the reactor depend on the number of liquid and gas compartments and they can be formed by recombining the different components of the reactor. Figure 8 shows all the configurations that possible to operate with the designed reactor. However, four use cases were selected for the testing of the bench-scale set-up. The use cases are shown in Figure 9.

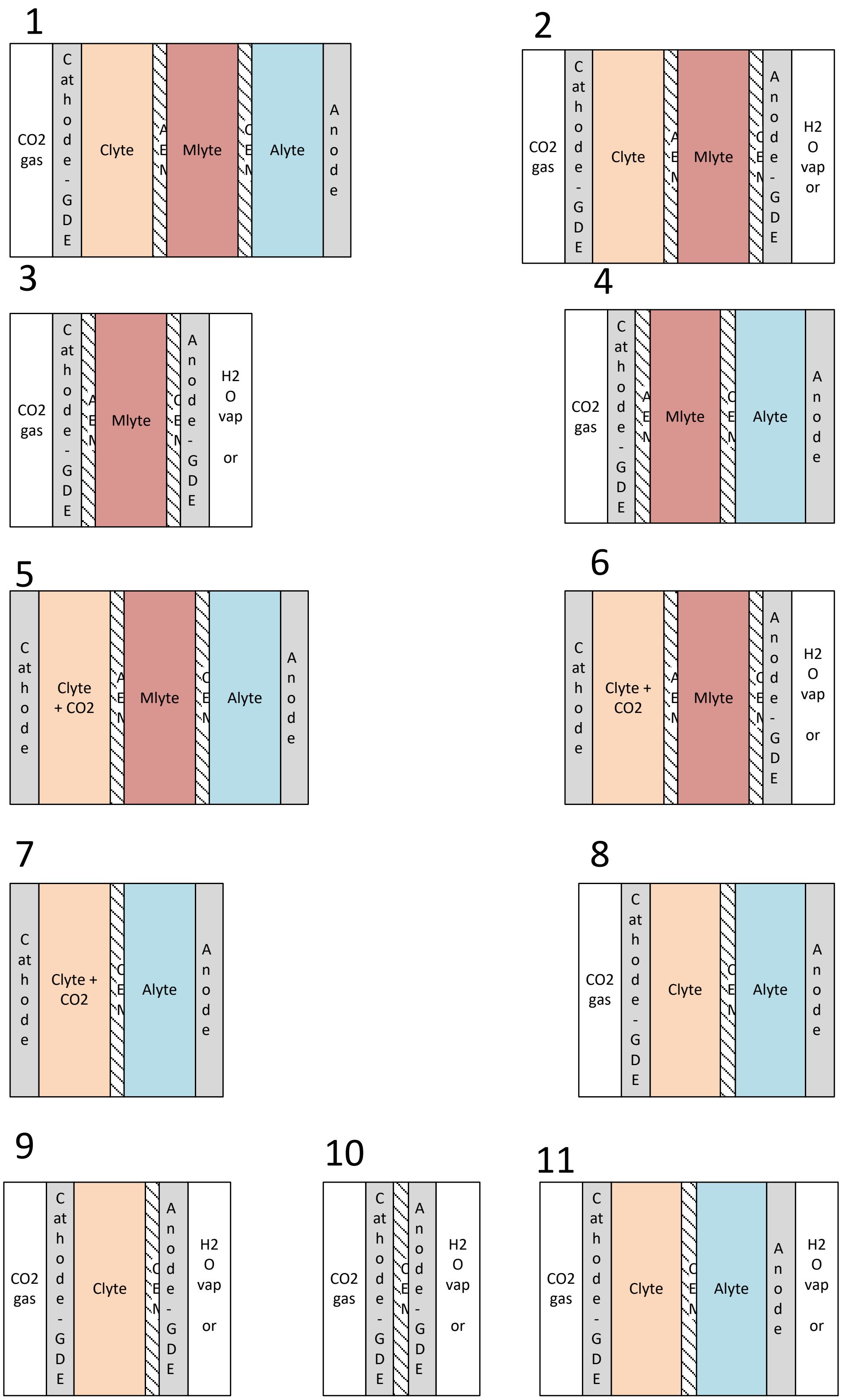
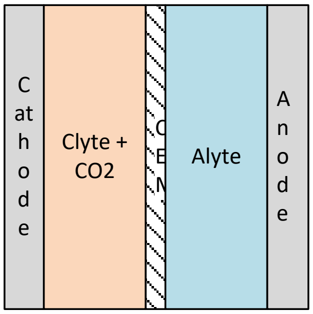
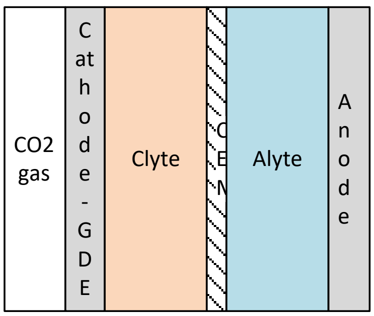


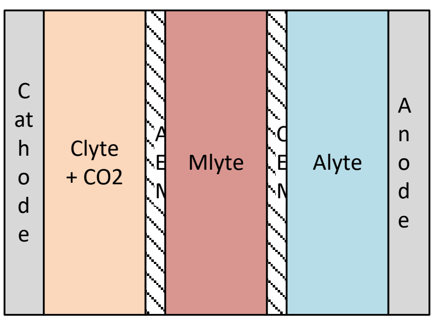
Figure 8. Possible reactor configurations based on number of liquid and gaseous compartment



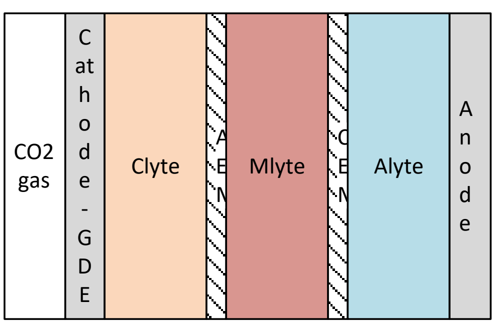
Use case #1
2 liquid compartments (catholyte and anolyte)
Gas CO_2 dissolved in catholyte
2 plate electrodes (anode and cathode)
1 CEM



Use case #2
2 liquid compartments (catholyte and anolyte)
1 gas (CO_2) compartment
1 plate electrode (anode) and 1 GDE (cathode)
1 CEM



Use case #3
3 liquid compartments (catholyte, middlelyte and anolyte)
Gas CO_2 dissolved in catholyte
2 plate electrodes (anode and cathode)
1 CEM and 1 AEM



Use case #4
3 liquid compartments (catholyte, middlelyte and anolyte)
1 gas (CO_2) compartment
1 plate electrode (anode) and 1 GDE (cathode)
1 CEM and 1 AEM

Figure 9. Use cases selected for testing in ELEKTRA

Building of ELEKTRA

The bench-scale demonstrator was built according to the engineering design described in ELEKTRA engineering design section and following the safety recommendation derived from the HAZOP evaluation.

The end result of the set-up is shown in Figure 10, Figure 11 and Figure 12.

Figure 10. ELEKTRA – bench-scale demonstrator set-up and automation software

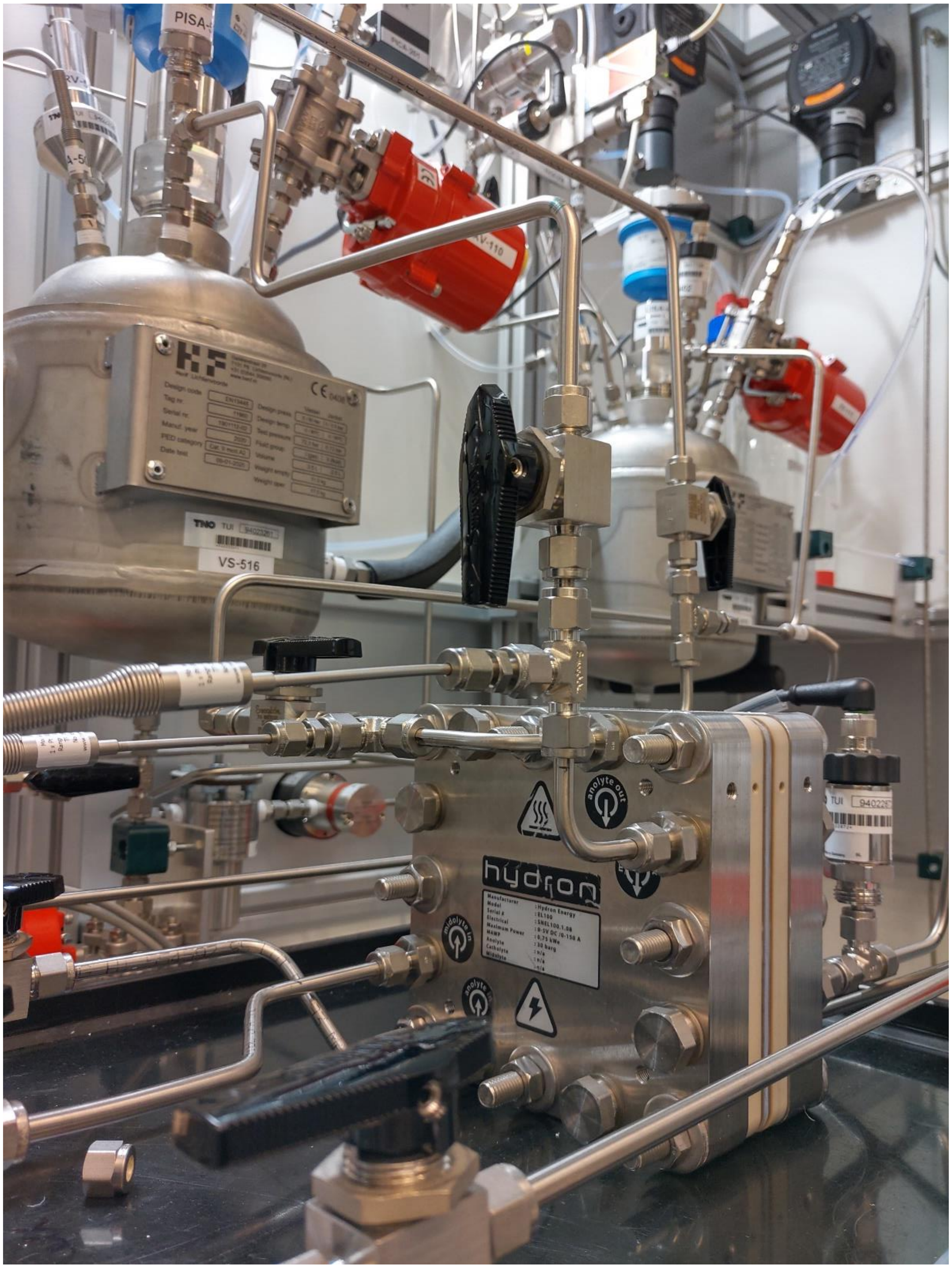


Figure 11. Reactor of bench-scale demonstrator system – designed by TNO and Hydron and constructed by Hydron.

Figure 12. Close view of ELEKTRA