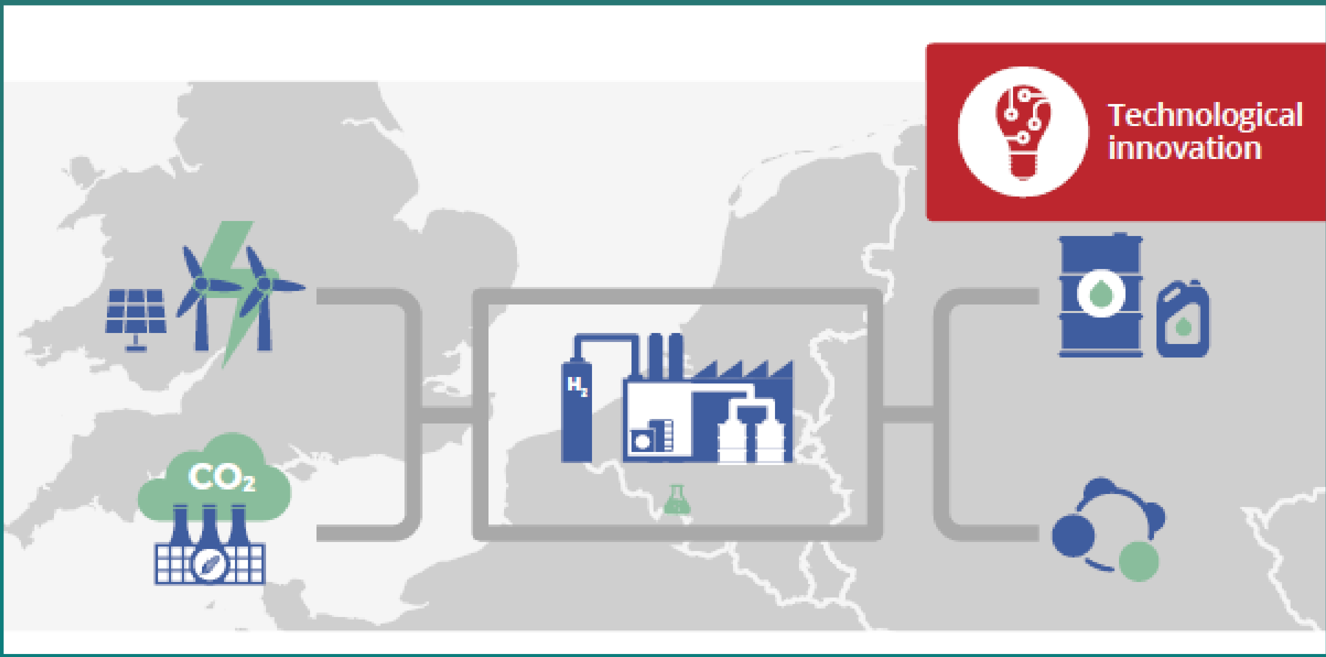

Project Output O1.2

Power-to-X highly flexible pilot demonstrator available for crossborder testing and innovation ZEUS pilot for direct electrolysis of CO2

Anca Anastasopol

Interreg
EUROPEAN UNION
2 Seas Mers Zeeën
European Regional Development Fund
e2C

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1. Introduction

1.1 Project background

The coastal areas of the 2 Seas region combine (future) availability of renewable energy with strong industrial activity. This leads to the common challenge of handling renewable energy surpluses, diversifying feedstocks in the chemical industry, reducing greenhouse gas emissions in energy intensive industry, and meeting societal and regulatory demands on advanced fuels and sustainable chemicals. "Power-to-X" concepts, using (renewable) electricity as a replacement for oil and gas energy sources in the production of chemical products, allow for the combination of a solution to these challenges with the creation of valuable products.

However, several technical and economic hurdles still need to be overcome. These are related to the availability of the renewable electricity, the technological immaturity of novel electrochemical processes and the immaturity of the value chains for electrolysis processes.

In this context, the need for demonstrators and business case calculations to convince industry to invest in further development and implementation of these technologies is undeniable and this is what lead to the creation of the Electrons to Chemicals (E2C) project.

1.2 Output 1.2 pilot demonstrator

One of the main outputs of the Electrons to chemicals project represents the development of a novel technological line for the direct conversion of CO_2 to formic acid.

In order to achieve this goal, the project was structured in two phases, a laboratory and technical feasibility study enabling research, and a technology demonstration phase.

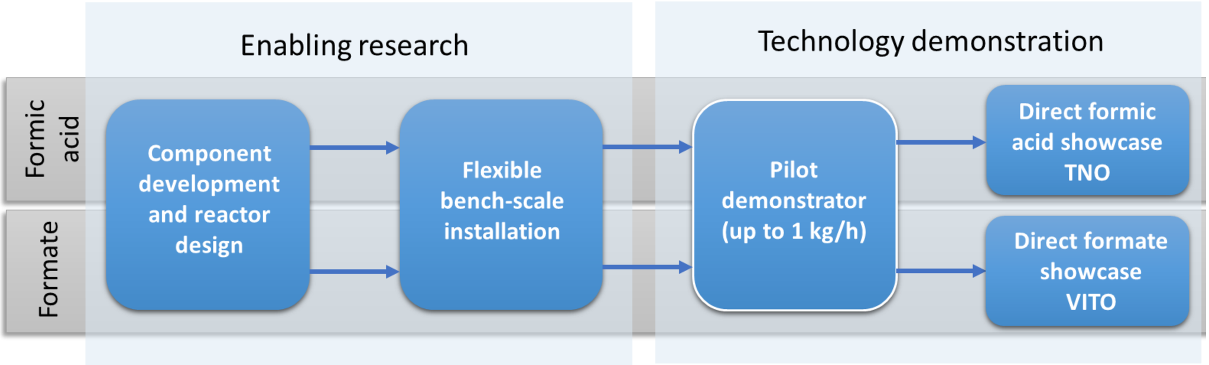

Figure 1. Direct line development phases within the Electrons to Chemicals (E2C) project.

The technology demonstration phase of the project is enabled through the design and construction of a pilot demonstrator. In order to have a relevant scale for testing under relevant conditions (TRL 5-6), the pilot installation is scaled for a production of 1kg/h formic acid.

The formal name of the installation in the context of the Interreg 2 seas project, Electrons to Chemicals is Output 1.2.

The colloquial name of the installation is ZEUS pilot demonstrator. ZEUS is equipped at its core with an electrolysis reactor of 15 cells. The colloquial name for the electrochemical reactor is AHENA reactor.

1.3 Aim of the report

The current report presents the Output O1.2 as built and installed within the framework of the E2C project and it is required as a deliverable in the E2C project. The report may be disseminated to a wide audience via the Interreg 2 Seas communication channels.

The finalization of the construction of this output is also accompanied by a communication workshop on the 15th of March 2023, as well as several communication articles through social media channels.

2. Specifications P2X ZEUS pilot demonstrator

2.1 Scope and execution of the pilot

ZEUS pilot was designed and constructed for the direct electrolysis of CO_2. Figure 2 gives a schematic representation of the direct CO_2 electrolysis. For this purpose, Gas diffusion electrodes developed in the E2C project are employed (Electrodes researched by VITO and TUAntwerp and manufactured by VITO). The gas diffusion electrodes have the unique property of separating the gas supply of CO_2 from the liquid electrolyte which collects the formate resulting from the process. The gas diffusion electrodes are based on porous carbon structure and electrocatalysts coating. The catalyst employed in this case for the formic acid production is based on Sn nanoparticles.

During the project, several synthesis techniques for the catalyst formation were investigated. The electrode assembly procedure was also developed in the early stages in the project.

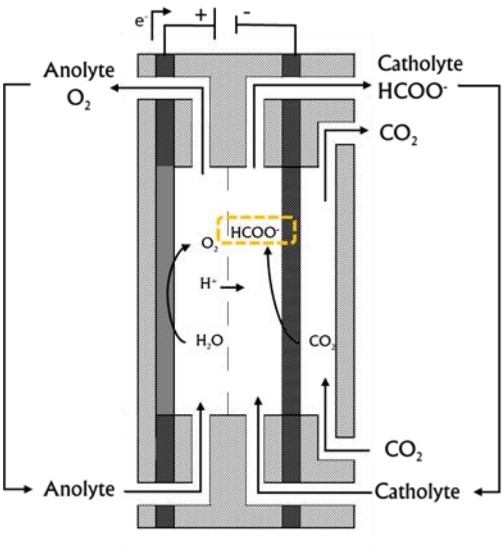

Figure 2. Schematic representation of a single electrochemical cell for direct conversion to formic acid, as applied in the ZEUS installation.

For the current demonstration, the materials and recipes that showed the highest robustness were selected and manufactured.

Besides the gas diffusion electrodes for the electroreduction of CO_2, the reactor also contains ion exchange membranes as well as anodes suitable for the oxygen evolution reaction. The anodes and the membranes are purchased from commercially available sources.

For the electrolytes, aqueous solutions of potassium bicarbonate are used. Due to the high pH of these solutions, the product formed is the formate salt.

The project has also investigated the *in situ* separation of the formate and acidification to formic acid. This was demonstrated using the bench scale feasibility setup ELEKTRA but this functionality is still in the early stages of development and was not included in the design of the ZEUS installation.

The actual electrochemical reactor is composed of 15 electrochemical cells connected in series. Each of the cells has an active geometric area of 20cm x 20cm.

For the safe, continuous and stable operation of the electrochemical reactor, a process installation is needed, also referred to as a balance of plant. With this installation, the suitable reaction conditions of pressure, temperature, electrical current and electrolyte and gas flow are provided and maintained in the electrochemical reactor.

The Output O 1.2 is therefore composed of a balance of plant, colloquially called ZEUS electrolysis installation and the electrochemical stack reactor colloquially called ATHENA reactor.

In Figure 3, a schematic of the process flow diagram for the ZEUS installation is depicted with an accent on the schematic drawing of the electrochemical reactor.

The design and construction of the pilot was outsourced by the responsible project partner, TNO, to an engineering company, MTSA technopower B.V. The contract was awarded as a result of an European tender procedure.

For the design of the ZEUS pilot and the ATHENA reactor, the E2C project has provided input collected from the preparatory phase of the project where bench scale tests were performed.

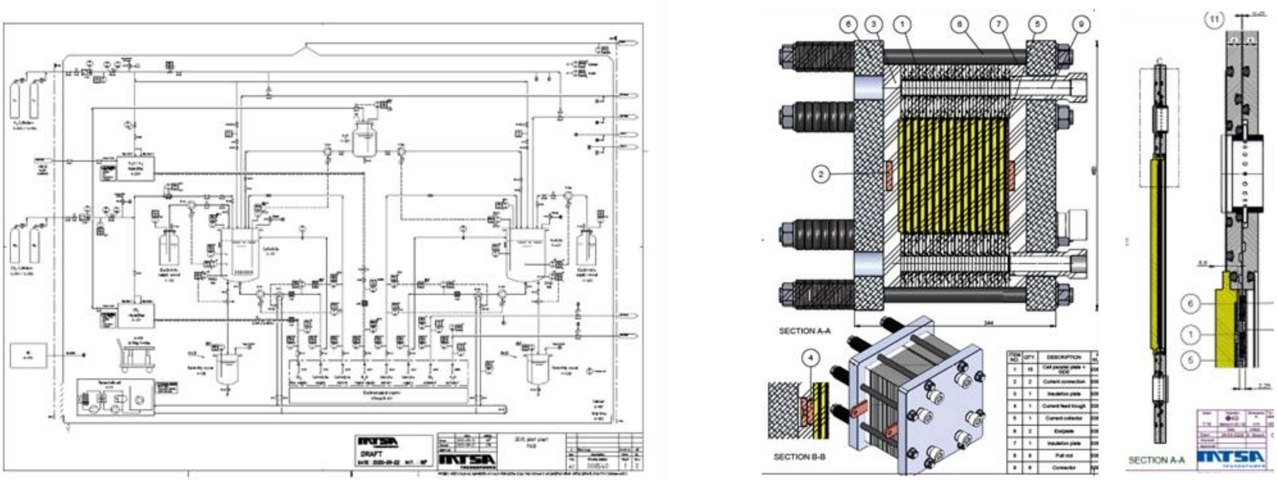

Figure 3. From left to right: schematic representation of the process flow diagram of ZEUS pilot, technical drawings of the Athena reactor.

2.2 Technical specifications of ZEUS installation and ATHENA reactor.

The ZEUS installation has a few unique characteristic and technical specifications. The following sections describe the technical specification of the installation.

2.2.1 Process and mechanical specification

The functionality of ZEUS is to provide the supply and discharge of process flows, the electrical supply, heat management and the control of the entire installation.

The process, mechanical and electrical installation have the following main characteristics:

- The electrochemical reactor can be operated on a pressure up to 20 barg.
- The operating temperature of the installation is between 20˚C and 70 ˚C.
- The design production flow is 1 kg/h formate.

The skid is constructed as an aluminum framework. The sides are closed by means of transparent panels and sliding doors. Construction material of the transparent parts is polycarbonate.

The top of the frame is provided with a cover consisting of aluminum panels. In the top the ventilation connection is incorporated. This is connected on the local ventilation system (utility).

The frame is provided with a leakage tray to contain any unwanted spilled liquid. Entrance of ventilation air is above this tray.

The unit has wheels for an easy maneuverability. It is also provided with height adjustable feet for fixation and a stable horizontal placement during operation.

The lay-out of the skid is such that components and sampling points can be easily reached. This is also important for maintenance and modification purposes.

The skid is a package unit, including own electrical / control system, on which only the utilities need to be connected.

Parts in contact with anolyte and catholyte basically are provided in plastic or with plastic lining. During the basic engineering it was agreed that due to availability and / or cost a number of exceptions will be applied.

The following liquids may be used in the ZEUS installation / ATHENA reactor:

- KHCO3
- KOH
- H2SO4
- HCOO-
- HCOOH
- H2O

Note that the installation is unsuitable for products containing chlorine, both liquids and gases.

2.2.2 Electrical and instrumentation

The installation is defined as a stand-alone unit. This means the skid is provided with an own electro - operating cabinet. This cabinet is placed on the skid, outside the ventilated enclosure. The technical execution of the E/I/A installation meets the applicable European Directives.

The rectifier of ZEUS has a maximum output of 15 kW DC. This with a view to possible capacity expansions in the future.

The ATHENA reactor is designed for 4,8 kW. The dimensioning of other provisions of the Balance of Plant are also based upon this power.

2.2.3 Control and data acquisition

The ZEUS installation has an automated control and monitoring system.

The control consists of a Siemens S1500 PLC for the normal control tasks and a PILZ Pnoz safety PLC or safety I/O cards for the safety tasks.

The gas detectors and the emergency stop are provided as safety inputs. As a safety action, the main power to the pumps and electrolyzer is double-pole switched off. A Siemens touch panel with a screen diagonal of 19 inches is provided as a Human Machine Interface (HMI).

Links with external systems can be realized with Ethernet.

The pumps which are equipped with a frequency regulator and the power supply for the electrolyzer stacks are controlled with Profinet.

The software enables manual start-up of the unit. Once started, the operating mode can be switched to automatic and the unit can continue to run the rest of the test run unmanned. During the test run, in addition to the normal controls, the liquid with formate / formic acid is automatically partly discharged to the product vessel. The raw materials are supplemented automatically.

The installation is capable for running automated for one week. However, some vessels will have to be refilled, emptied or replaced periodically.

The Athena reactor can be operated in different modes.

Depending on the configuration of the Athena reactor, a corresponding process mode can be selected.

Besides process run modes, washing sequences are possible. In this mode the actions are largely manual started and stopped.

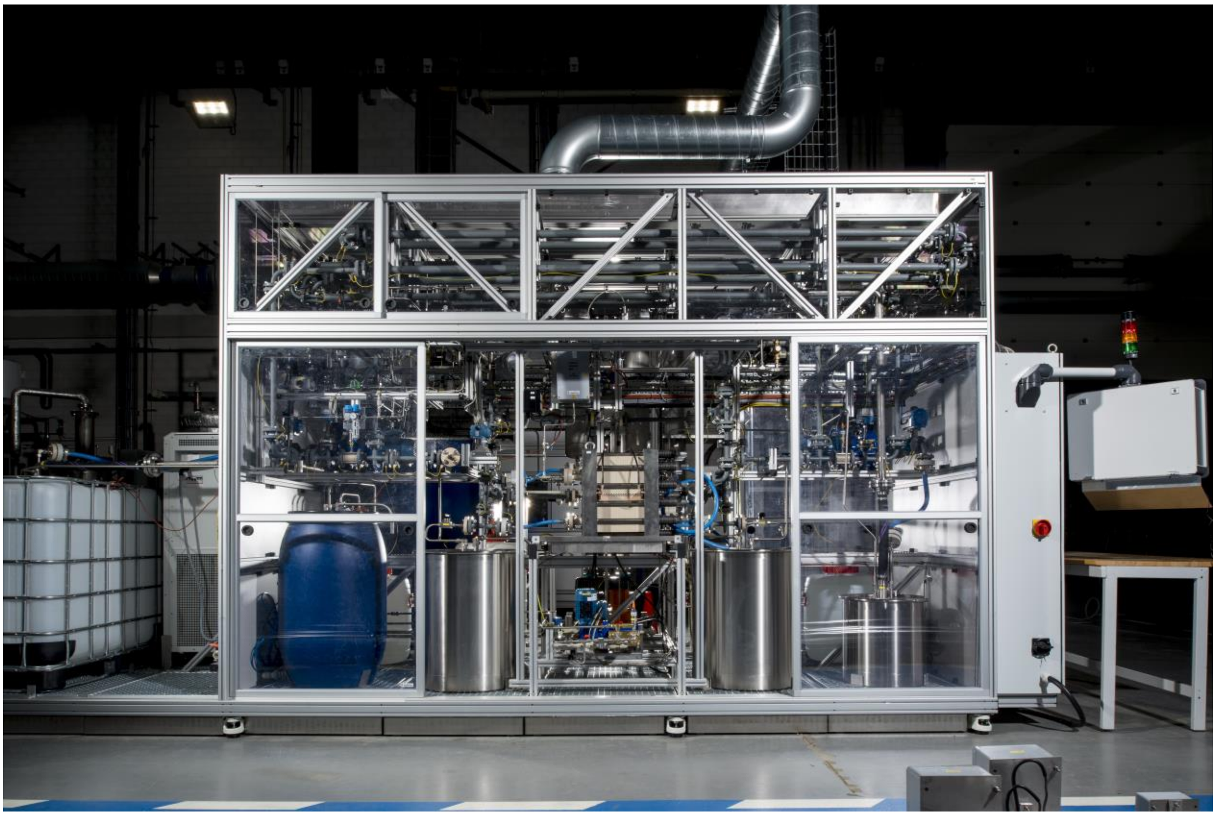

Figure 4. ZEUS pilot installation for the conversion of CO2 to formic acid, as built.

2.2.4 The ATHENA reactor

The main goal from the Athena reactor is to convert carbon dioxide to formic acid.

The electrochemical reactor is an electrolysis stack with a minimum of two cells and maximum of 15 cells and is compatible for use of various types of gas diffusion electrodes for the cathodic reaction.

The principle of the design of the Athena reactor is that it allows two different configurations. The switch over between the different setups is easy and straightforward and requires the minimal amount of modifications in the reactor. The maximum total number of flows from electrolytes and reactants through the reactor is three.

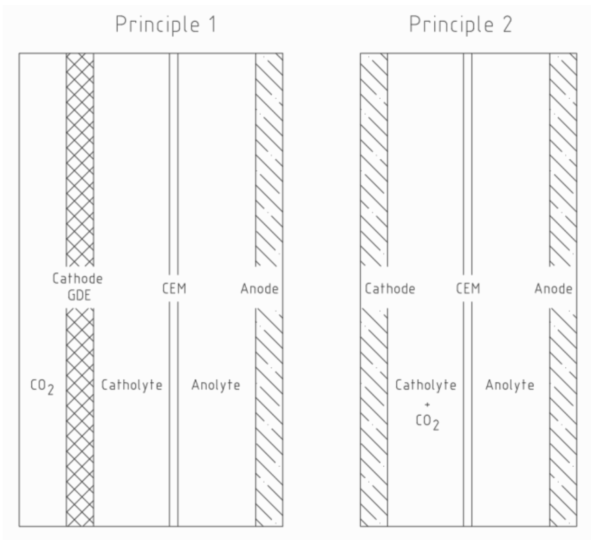

Figure 5. Schematic of the possible configurations of the Athena reactor

Possible reactor setups are: parallel plate + GDE, double GDE and parallel plate anode + cathode.
General material of construction of the cell is plastics and contacting surfaces from electrolytes to metal parts is reduced to a minimum.

There are 2 possible configurations for the electrochemical reactor. See Figure 5. To make the 2 configurations possible, 4 different process flows are required. One flow can be combined. This is the Catholyte flow and the Catholyte flow with extra CO_2 addition.

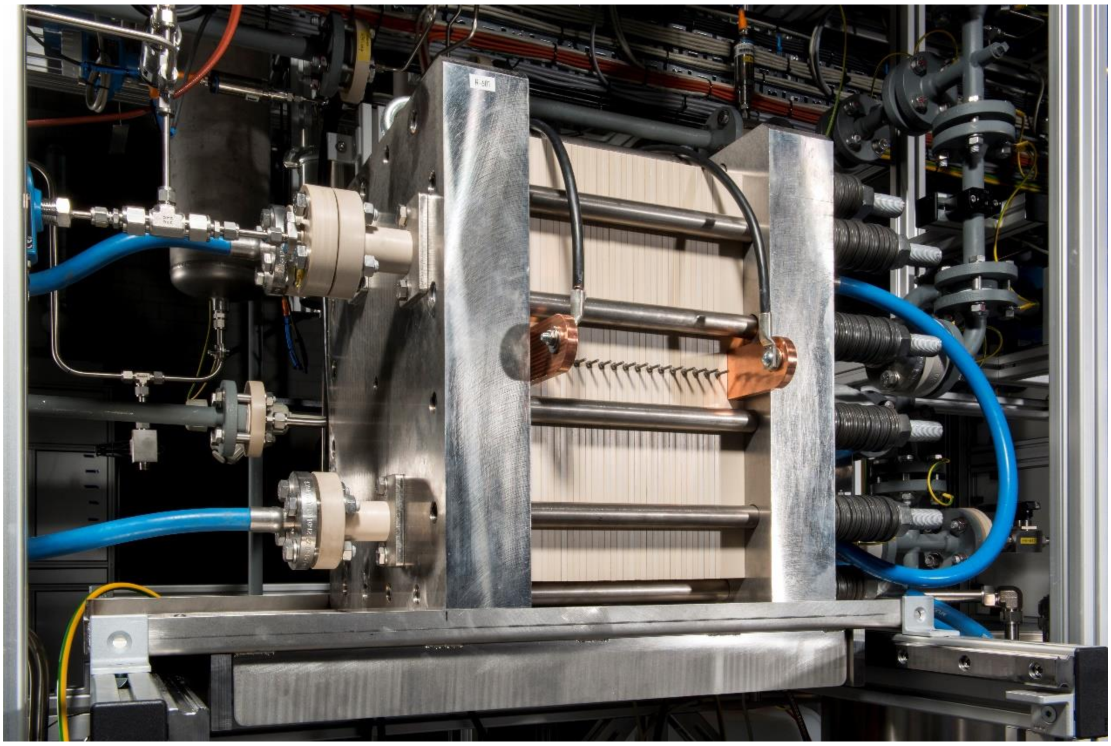

Figure 6. ATHENA electrochemical reactor for the direct electrochemical conversion of CO_2 to formic acid as built.

2.2.5 HSE/ Certification

With regard to safety aspects, a HAZOP / LOPA has been carried out in during the basic engineering phase. The recommendations of this HAZOP are implemented in the design.

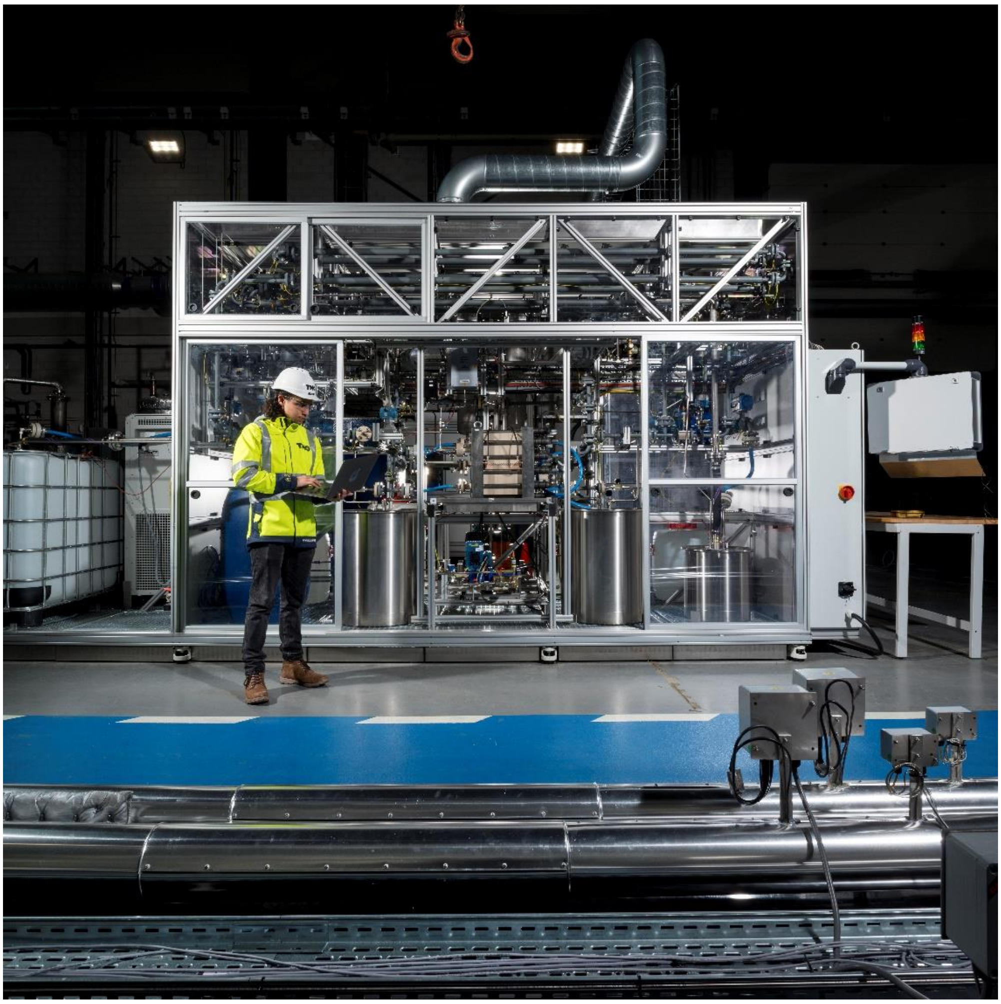

Figure 7. ZEUS installation view in proportion to the human operator.