



**Deliverable 6.8:  
Demonstration on plant testing, compiling of  
simulation and hardware results**

# **CO<sub>2</sub>-based Electrosynthesis of Ethylene oXIDE**

**Grant Agreement Number: 768789**

**H2020-SPIRE-2017**

**DELIVERABLE REPORT**

## DOCUMENT INFORMATION

<b>Deliverable Report</b>	<b>D6.8: Demonstration on plant testing, compiling of simulation and hardware results</b>
Date	20.07.2021
Report prepared by	<p><b>Siemens Energy Global GmbH &amp; Co. KG, Munich, Germany</b> Dr. Kerstin Wiesner-Fleischer, Dr. Remigiusz Pastusiak, Dr. Erhard Magori</p> <p><b>Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., Straubing, Germany</b> Dr. Arne Roth, Dr. Lenard Csepei, Ferdinand Vogelgsang</p> <p><b>Axiom angewandte Prozesstechnik GmbH, Ebreichsdorf, Austria</b> Dr. Aleksander Makaruk</p> <p><b>University of Science and Technology, Academic Centre for Materials and Nanotechnology, Kraków, Poland</b> Prof. Dr. Konrad Szacilowski, Dr. Krzysztof Mech</p>
Project	<p><b>CO<sub>2</sub>EXIDE –</b> <b>CO<sub>2</sub>-based electrosynthesis of Ethylene oXIDE</b> Grant Agreement No.: 768789 (H2020-SPIRE-2017)</p>
Project coordinator	<p><b>Fraunhofer-Gesellschaft zur Förderung der angewandten Forschung e.V., Straubing, Germany</b> Dr. Luciana Vieira, Dr. Arne Roth</p>
Type	<b>Deliverable Report   Public</b>

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 768789. The authors would like to express their gratitude to the European Commission for this financial support.

## Table of Contents

<b>Abstract</b> .....	<b>3</b>
<b>1 Introduction and Overview of system design</b> .....	<b>4</b>
<b>2 Operation of the Electrocatalytic Reactor Unit (ERU) at AGH</b> .....	<b>6</b>
2.1 Set-up of ERU with 300 cm <sup>2</sup> cell	6
2.2 Set-up of ERU at AGH lab in Kraków	8
2.3 Set-up of integrated demonstrator: Coupling of Electrocatalytic Reactor Unit (ERU) and Ethylene Enrichment Unit (EEU)	11
2.4 Initial testing of integrated demonstrator with pure commercial CO <sub>2</sub> gas	15
2.5 Operation of demonstrator with CO <sub>2</sub> originating from biogas	17
<b>3 Operation of Demonstrator with optimized Ethylene Enrichment Unit (EEU)</b> ..	<b>20</b>
<b>4 Operation of Ethylene epOxidation Unit (EOU) at Fraunhofer</b> .....	<b>22</b>
<b>5 Summary and Discussion of the Demonstration of the CO<sub>2</sub>EXIDE Process Chain</b> .....	<b>26</b>
<b>6 References</b> .....	<b>28</b>
<b>Acknowledgements</b> .....	<b>28</b>

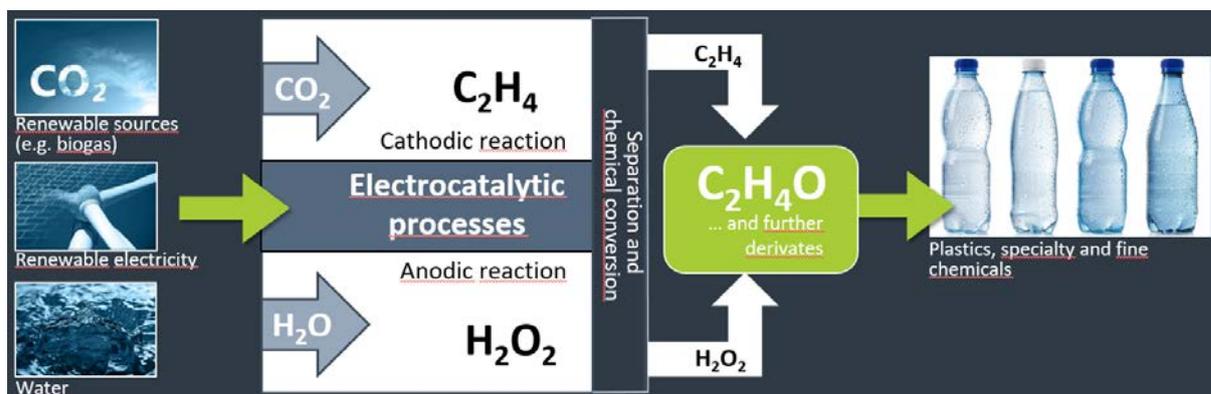
## ABSTRACT

The goal of the H2020-funded project CO2EXIDE is the establishment of an electrochemical energy-efficient and near-to CO<sub>2</sub>-neutral process for the production of the bulk chemical ethylene oxide from CO<sub>2</sub>, water and renewable energy. The CO2EXIDE WP6 “Demonstration in relevant environment” aims at the development of stable operating conditions for the complete CO2EXIDE process chain, based on the coupling of Electrochemical Reduction Unit (ERU), the Ethylene Enrichment Unit (EEU) and the Ethylene epOxidation Unit (EOU) for the synthesis of ethylene oxide as target product. In the final project phase, the CO2EXIDE process chain is demonstrated in a relevant operational environment at AGH laboratory in Kraków (Poland).

The objective of the present report D6.8 is to document the set-up, testing and operation of the CO2EXIDE demonstrator. The reported work comprises set-up and testing of the Electrochemical Reactor Unit (ERU), coupling of the ERU to the Ethylene Enrichment Unit (EEU), operation of the demonstrator with biogenic CO<sub>2</sub> originating from biogas upgrading, and the compilation of the performance data. The Ethylene epOxidation Unit (EOU) for the conversion of the electrochemically generated ethylene and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as final process step could not be transported to Kraków due to COVID-19-related travel restrictions and safety concerns and was operated by Fraunhofer in Straubing (Germany) instead. Material and data was exchanged between the two sites of demonstration to facilitate the highest degree of process integration possible.

## 1 INTRODUCTION AND OVERVIEW OF SYSTEM DESIGN

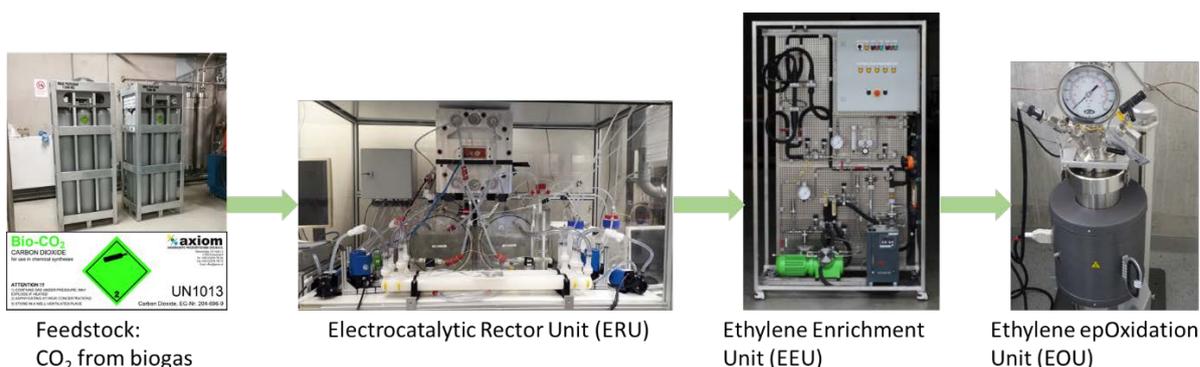
The goal of the H2020-funded project CO2EXIDE is the establishment of an electrochemical, energy efficient and near-to CO<sub>2</sub>-neutral process for the production of the bulk chemical ethylene oxide from CO<sub>2</sub>, water and renewable energy. The CO2EXIDE process chain comprises: i) the supply of raw materials, in particular CO<sub>2</sub> from biogenic sources; ii) the simultaneous electrocatalytic conversion of CO<sub>2</sub> to ethylene (cathode) and of water to hydrogen peroxide H<sub>2</sub>O<sub>2</sub> (anode); iii) the separation and purification of the generated ethylene; and iv) the chemical reaction of the purified ethylene with the anodically generated H<sub>2</sub>O<sub>2</sub> to the platform chemical ethylene oxide (see Figure 1). Ethylene oxide represents a valuable and versatile chemical product used in the chemical industry mainly for the production of tensides and plastic materials, such as polyethylene terephthalate (PET) for plastic bottles.



**Figure 1: The CO2EXIDE process chain.**

In the final phase of the project CO2EXIDE, a demonstrator unit was assembled and tested in the laboratory of the Academic Centre of Materials and Nanotechnology (AGH University of Science and Technology, Kraków, Poland). Figure 2 shows the main hardware components the final demonstrator is composed of, i.e. CO<sub>2</sub> sourced from a biogas upgrading plant, the Electrocatalytic Reactor Unit (ERU), the Ethylene Enrichment Unit (EEU) and the Ethylene epOxidation Unit (EOU).

Prerequisite for assembling the hardware at AGH was thorough planning with simulation and pre-testing. This included drawings of Piping and Instrumentation Diagrams (P&IDs), execution of Hazard and Operability (HAZOP) Analysis and testing of all demonstrator units individually prior to installation in the demonstrator setting at AGH laboratory in Kraków (Poland). Therefore, basic testing and process development of Electrocatalytic Reactor Unit (ERU) has been done at Siemens Energy (Munich, Germany), Ethylene Enrichment Unit (EEU) at AXIOM (Ebreichsdorf, Austria) and Ethylene epOxidation Unit (EOU) at Fraunhofer (Straubing, Germany). Due to COVID-19-related travel restrictions and safety reasons, the EOU could not be transported to and commissioned in Kraków and was operated by Fraunhofer in Straubing (Germany) instead.



**Figure 2: The hardware components to demonstrate the CO2EXIDE process chain.**

The ERU is based on a 3-chamber-cell-design well suited for the combination of the cathodic conversion of CO<sub>2</sub> to ethylene (C<sub>2</sub>H<sub>4</sub>) and the anodic conversion of water (H<sub>2</sub>O) to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). The cathode is built as Gas Diffusion Electrode (GDE) with sputter-deposited copper, whereas the anode is made of boron-doped diamond (BDD). Within the CO2EXIDE project, a small-size PEM cell with an active area of 25 cm<sup>2</sup> and a large-size PEM cell with an active area of 300 cm<sup>2</sup> were developed.

The general purpose of the Ethylene Enrichment Unit (EEU) in the CO2EXIDE process is to separate the undesired by-products in the product gas mixture of the ERU and thus to generate an ethylene-enriched gas stream, suitable for further conversion into ethylene oxide in the EOU. For the ethylene enrichment, the process of gas permeation on polymeric membrane is employed. EEU, which is implemented in the WP6 demonstrator, comprises a compressor, a drying and pretreatment section and a one-stage membrane section equipped with highly selective glassy polyimide fibres.

The last step in the process chain is the EOU, which comprises the ethylene epoxidation to Ethylene Oxide (EO). In this process step, the ethylene-enriched gas stream coming from the cathodic compartment of the ERU via EEU and the anodically generated H<sub>2</sub>O<sub>2</sub> dissolved in the anolyte are reacted in the presence of an MWW-type titanosilicate catalysts. The reaction is carried out in a 2 liter autoclave reactor at mild temperatures and under moderately elevated pressure.

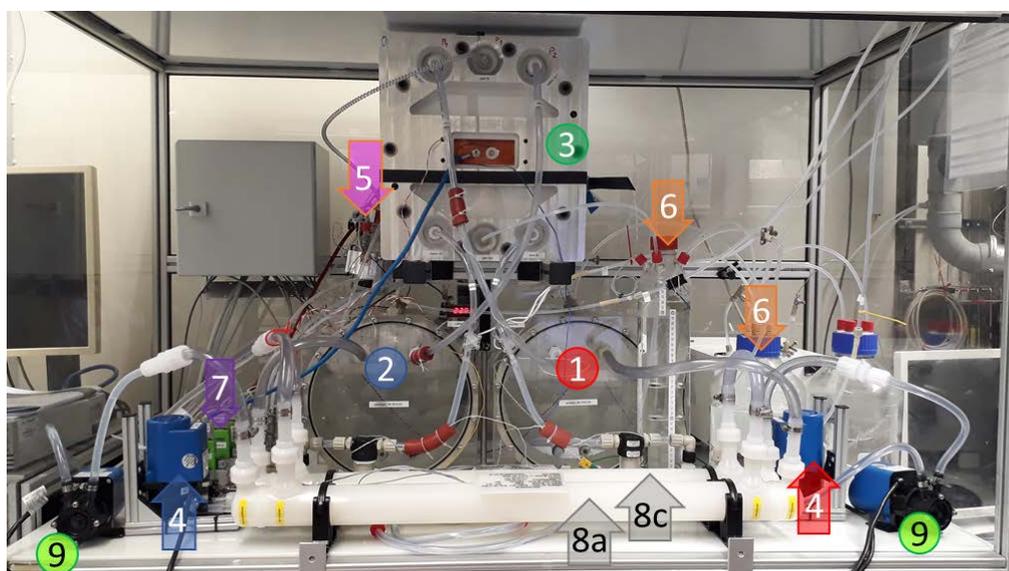
The objective of this deliverable D 6.8 (Demonstration on plant testing, compiling of simulation and hardware results) is to report on all the components the demonstrator is composed of and on the function of the demonstrator.

## 2 OPERATION OF THE ELECTROCATALYTIC REACTOR UNIT (ERU) AT AGH

### 2.1 Set-up of ERU with 300 cm<sup>2</sup> cell

In the phase of scale-up and pre-testing of the individual demonstrator units, first the 25 cm<sup>2</sup> PEM cell and subsequently the Electrocatalytic Reactor Unit ERU with 300 cm<sup>2</sup> cell was set-up and tested at Siemens Energy laboratory in Munich, Germany.

Basic process development and evaluation of peripheral equipment had been performed with the 25 cm<sup>2</sup> cell. For the set-up of the 300 cm<sup>2</sup> cell, upgraded peripheral components have been chosen (e.g. electrolyte reservoirs with inspection glass, heat exchanger) to ensure stable operation (see Figure 3). Measured temperatures of various electrolyser parts during the experiment performed with a properly running cooling system showed that no relevant component of the cell overheated, staying well below 35°C.



**Figure 3: Set-up of 300 cm<sup>2</sup> PEM cell in Siemens Energy laboratory. Test setup and peripheral installations (1 anolyte reservoir, 2 catholyte reservoir, 3 PEM cell, 4 electrolyte flow pump, filter, sensor, 5 humidification of CO<sub>2</sub> feed gas, 6 gas out differential pressure generation, 7 gas supply for CO<sub>2</sub> and purge N<sub>2</sub>, 8a/c heat exchanger/cooling system for anolyte and catholyte, 9 pumps of cooling system).**

In addition, a refined computer-based control system was implemented for automated operation, monitoring of sensors (e.g. pressure, temperature and flow sensors) and data acquisition. The data acquisition platform is based on CompactDAQ (cDAQ-9189, National Instruments). The hardware comprises chassis and 32 channels analog in and 16 channels analog out modules. Sensor data is collected and analyzed using LabVIEW (National Instruments) software. In the standard configuration the data acquisition logs up to 8 mass flow controllers, 8 pressure sensors, 8 temperature sensors and 8 flow sensors.

Operating conditions developed in tests with the 25 cm<sup>2</sup> cell have been scaled up to experiments with 300 cm<sup>2</sup> cell. Minor modifications of operating parameters have been executed. The standard parameters are summarized in Table 1.

**Table 1: Standard operating parameters of experiments in 300 cm<sup>2</sup> PEM cell.**

Electrolysis cell active area	300 cm <sup>2</sup>
Cathode	Cu sputter-deposited on Freudenberg GDL
Anode	BDD/Nb, 2500 ppm boron doping (NeoCoat)
Membrane	Nafion 117
Catholyte	10 L 1M KHCO <sub>3</sub>
Anolyte	10 L 2M KHCO <sub>3</sub>
Electrolyte flow anolyte	~ 1500 mL/min
Electrolyte flow catholyte	~ 500 mL/min
Current density	150 - 200 mA/cm <sup>2</sup>
Gas feed: CO <sub>2</sub> flow	1500 cm <sup>3</sup> /min
Product gas analysis	Gas chromatography
Analysis of anolyte: H <sub>2</sub> O <sub>2</sub> measurement	Macherey-Nagel Quantofix Relax with Peroxide 100 Test stripes

Typical outlet gas composition at the cathode in the experiments performed with the Electro-catalytic Reactor Unit (300 cm<sup>2</sup> cell area) after 1h at a current density of 200mA/cm<sup>2</sup> were: 1,7% C<sub>2</sub>H<sub>4</sub>, 0,2% CH<sub>4</sub>, 0,6% CO, 17% H<sub>2</sub>, rest CO<sub>2</sub>. The C<sub>2</sub>H<sub>4</sub> content of the generated product gas decreases after around 4 h of operation. At the BDD/Nb anode, H<sub>2</sub>O<sub>2</sub> concentration in the anolyte rises to around 30 mmol/L. These results are comparable to those obtained previously in the 25 cm<sup>2</sup> cell, clearly indicating that there is no negative effect of the scale-up on the process performance. This is a promising finding.

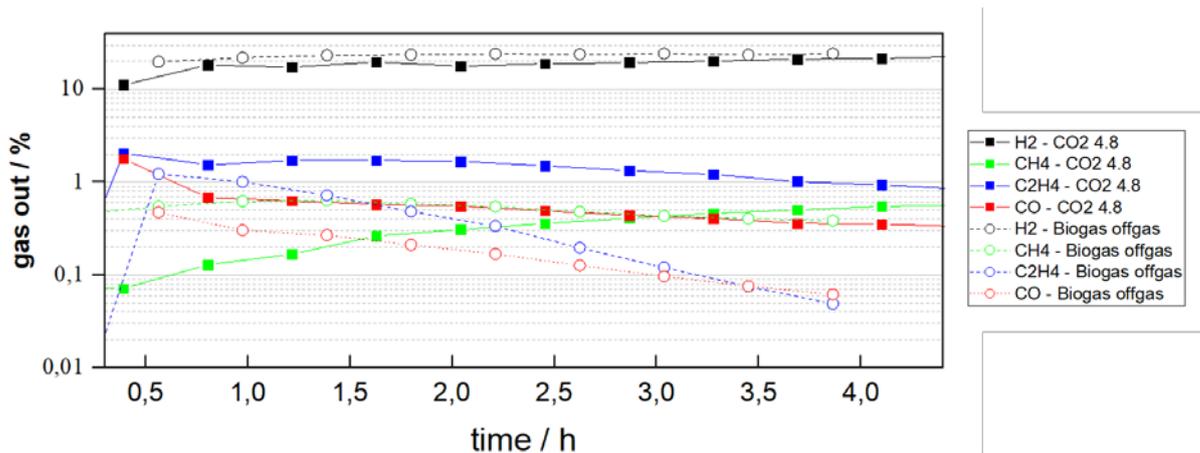
All standard tests in the course of the process development have been performed using gas cylinders filled with CO<sub>2</sub> 4.8 supplied by Linde (purity >=99,998). When the process development was completed, further tests were performed with biogenic carbon dioxide gas from the biogas upgrading delivered by Axiom in May 2019. The bundle of gas cylinders was installed in Siemens Energy laboratory at Munich and the carbon dioxide gas cylinders were connected to the feed-line of the electrolyser to demonstrate the compatibility with CO<sub>2</sub> from biogas upgrading.

The GDE cathode (GDL Freudenberg H23C2, coated with 500 nm Cu, O<sub>2</sub> plasma treatment) was comparable to those used in the previous experiments with commercial CO<sub>2</sub> supplied by Linde. These electrodes were now tested in experiments with carbon dioxide gas originating

from biogas upgrading. However, the experimental results showed that achieved  $C_2H_4$  concentration in the product gas is lower and faster decreasing over the duration of the experiment, when compared to experiments with commercial  $CO_2$  (see Figure 4).

The reason for the lower  $C_2H_4$  production rate and its faster decrease over time is not yet fully understood. It is unclear if the reduced performance is caused by impurities contained in the  $CO_2$  sourced from biogas (e.g. oxygen).

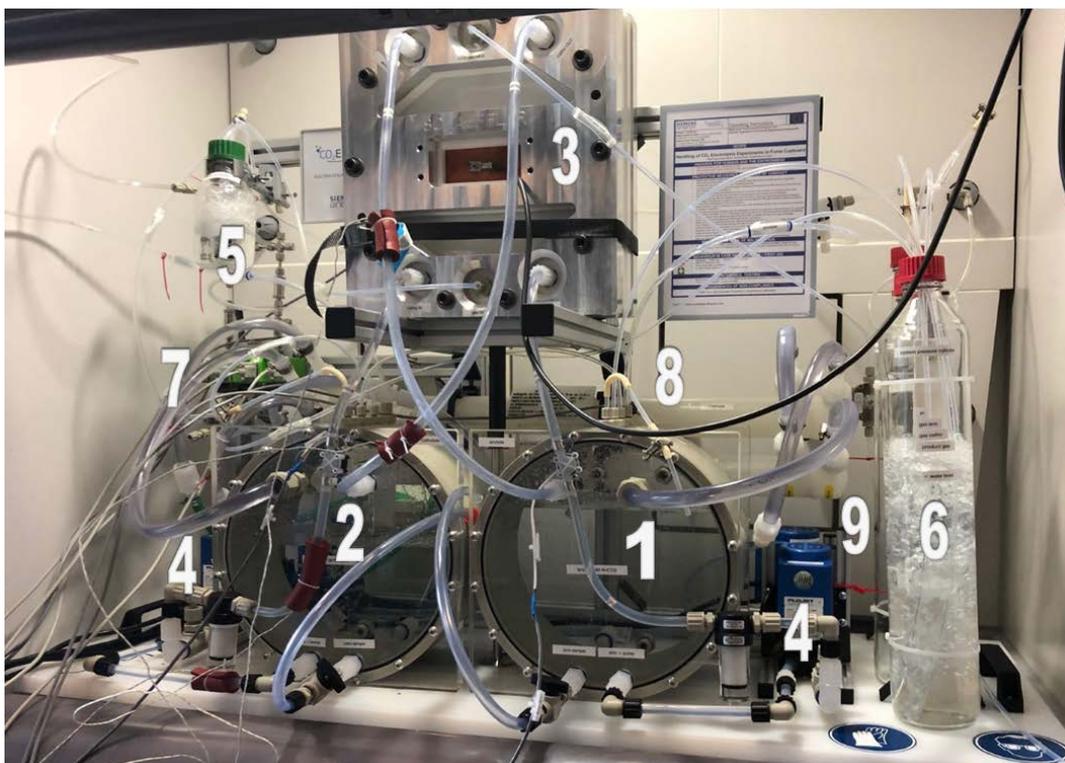
The  $H_2O_2$  production in the anodic cell compartment performed without any problems, as expected. Typical achieved concentration of  $H_2O_2$  were around 30 mmol/L.



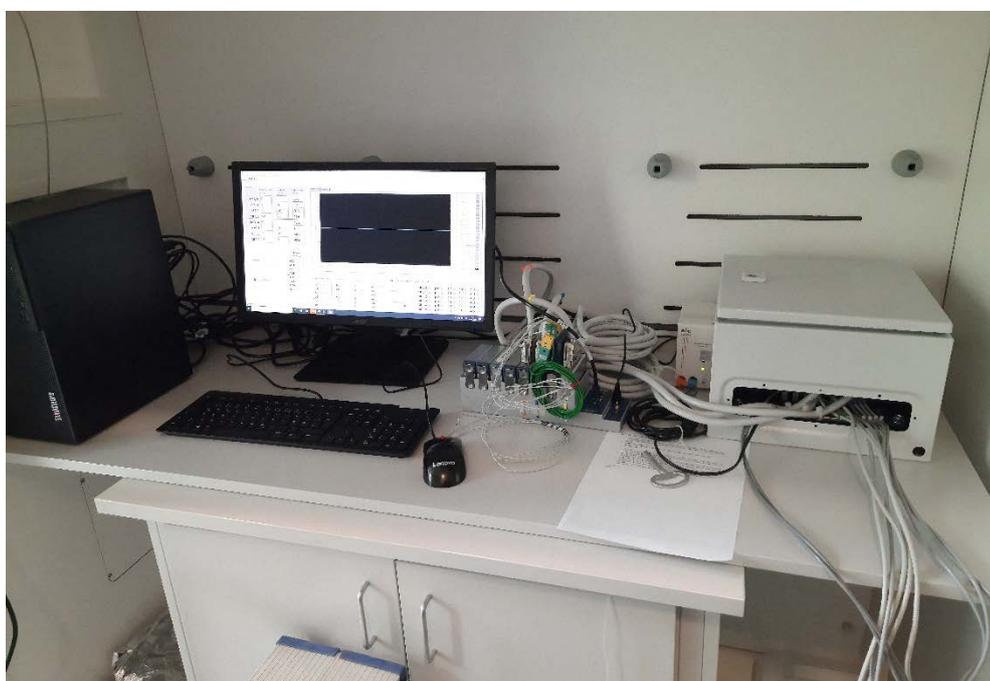
**Figure 4: Experimental results in 300 cm<sup>2</sup> PEM cell. Comparison of feed gas: pure (commercial) CO<sub>2</sub> 4.8 vs. CO<sub>2</sub> sourced from biogas. GDE coated with 500 nm Cu.**

## 2.2 Set-up of ERU at AGH lab in Kraków

The Electrocatalytic Reactor Unit (ERU) has been delivered to AGH as a compact system mounted on a portable board. The complete system has been installed under an efficient fume hood, additionally equipped with carbon monoxide sensor. The laboratory ventilation system was also equipped with a set of gas detectors (carbon monoxide, hydrogen, hydrocarbons). Upon installation of all devices and establishing connections to cooling water, carbon dioxide and nitrogen tanks, the tightness of the system has been carefully checked with electrolyte reservoirs filled with deionized water, and a thick polyethylene foil in place of the GDE cathode and the Nafion membrane. All detected gas and liquid leaks were eliminated. In a subsequent step, all sensors (temperature, gas flow, electrolyte flow and gas pressure) have been tested. After minor adjustments the ERU was ready for electrochemical tests.

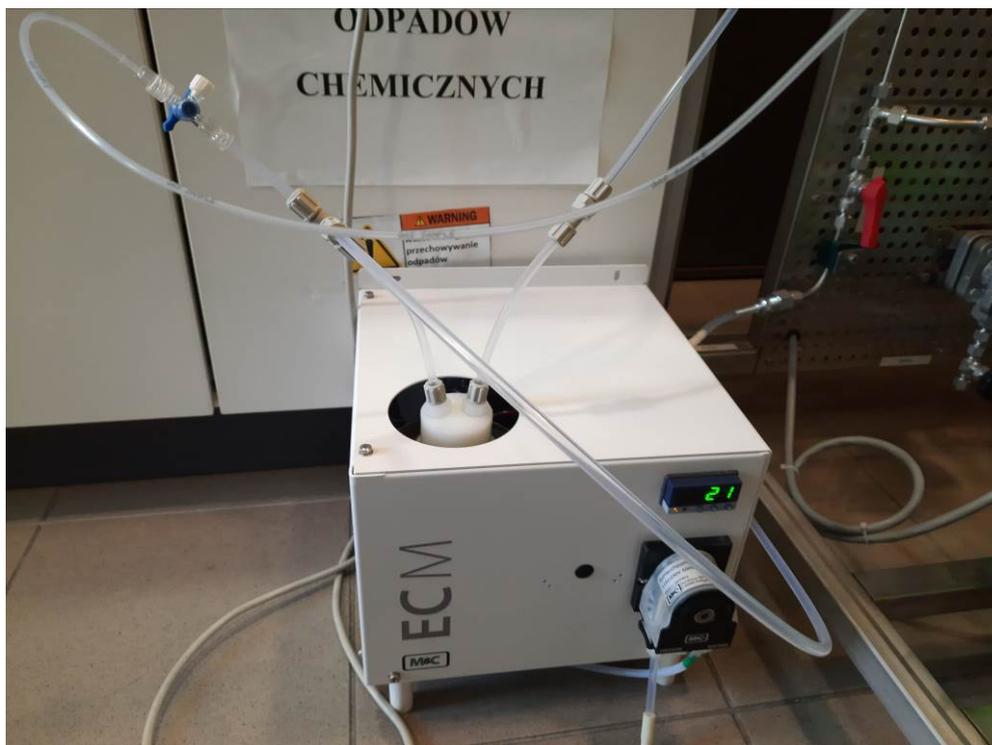


**Figure 5: Set-up of 300 cm<sup>2</sup> PEM cell in AGH laboratory. Test set-up and peripheral installations (1 - anolyte reservoir, 2 - catholyte reservoir, 3 - PEM cell, 4 - electrolyte flow pump, filter, sensor, 5 - humidification of CO<sub>2</sub> feed gas, 6 - gas out differential pressure generation, 7 - gas supply for CO<sub>2</sub> and purge N<sub>2</sub>, 8 - heat exchanger/cooling system for anolyte and catholyte, 9 - pumps of the cooling system).**



**Figure 6: Electronic control system for electrolyser unit.**

The output of ERU was connected to a portable gas dehumidifier and its operation temperature was set to 3°C.



**Figure 7: Detailed view: gas cooler with gas sampling by-pass.**

The qualitative and quantitative analyses of the output gas was performed using GC-MS chromatograph Shimadzu QP2020. An MS line equipped with a column Agilent J&W (0.530 mm diameter, 30 m length) and helium as carrier gas (flow rate of 377.5 mL·min<sup>-1</sup>) was used. A TCD line dedicated for the analysis of hydrogen concentration was based on a column packed with molecular sieve (5 Å). In this case, nitrogen (flow rate 15 mL·min<sup>-1</sup>) was used as carrier gas. The temperature of the oven during measurements was set to 30°C. Before each measurement, both the molecular sieve and chromatographic column were conditioned at 150°C for 600 s.



**Figure 8: Gas chromatograph connected to ERU and EEU.**

The tests of ERU coupled to the demonstrator were performed using a 1200C cathode (Freudenberg H23C2 coated with 500 nm of Cu, O<sub>2</sub> plasma-treated) and boron-doped diamond (BDD/Nb) anode. 1M KHCO<sub>3</sub> was used as catholyte and 2M KHCO<sub>3</sub> as anolyte. Anolyte and catholyte were separated by a Nafion 117 membrane.

### **2.3 Set-up of integrated demonstrator: Coupling of Electrocatalytic Reactor Unit (ERU) and Ethylene Enrichment Unit (EEU)**

ERU and EEU were separately delivered to the Academic Centre of Materials and Nanotechnology (AGH University of Science and Technology, building D-16) and placed in laboratory room 1.07. This room is fully equipped with a highly effective ventilation system, including six fume hoods and special suction lines designed for the removal of potentially hazardous or suffocating heavy gasses. The laboratory is also equipped with sensors for hydrogen, carbon monoxide and flammable hydrocarbon gasses. Access to the room is controlled by a central security system (personalized magnetic cards) and only qualified personnel can enter the room.

Gas cylinders with CO<sub>2</sub> from biogas upgrading, commercial CO<sub>2</sub>, nitrogen and helium have been installed in ventilated gas cylinder cupboards or mounted on safe transport carts.

The electrolyser and all accessories (electrolyte reservoirs, pumps, sensors, pressure equilibration bottles) have been installed inside a fume hood on a specially designed board equipped with a safe rack hosting the electrolytic cell. All accompanying electronics have been placed under the neighbouring fume hood, whereas the Ethylene Enrichment Unit (EEU) was located

CO<sub>2</sub>EXIDE

next to the fume hood hosting the electrolyser system. Electrolyser power supply, equipped with connecting cables designed for currents up to 80 A, was placed on a mobile rack.

All necessary connections are based on hard polyethylene tubes (gasses) or soft PVC hoses (cooling water). The electrolyser is equipped with heat exchangers for independent cooling of the catholyte and anolyte. The heat exchangers are connected to a central cooling system (closed-loop cooling water, average temperature 8°C).

Two gas sampling ports for analysis of gas samples have been established with soft gas sampling tubes terminated with Luer locks and connected to a gas chromatograph sampling loop via a set of three-way valves. One port was located between the gas cooler and the ethylene enrichment unit (EEU), the other at the retentate output of EEU. Connections of exhaust gases (EEU permeate, excess of the EEU retentate, blow-offs from the safety valves) are connected to the central ventilation hub via soft PVC lines.

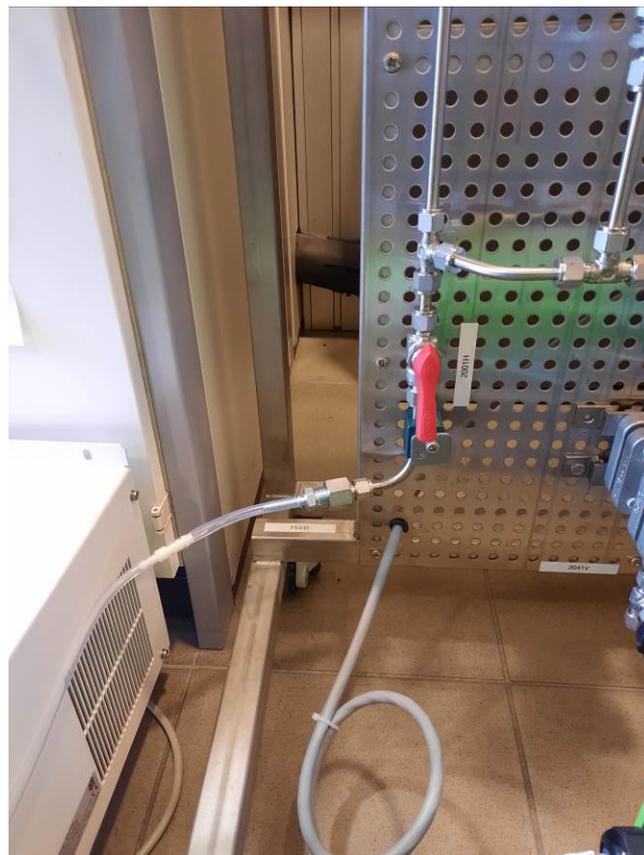
In the following, the assembling of the CO2EXIDE demonstrator is documented through a set of photographs.



**Figure 9: General view of the lab, from left to right: gas cylinders, control electronics for the electrolyser unit, electrolyte unit, primary gas cooling and dehumidification (small box on the floor), EEU, electrolyser power supply.**



**Figure 10: General view of the lab, with the CO2EXIDE demonstrator.**



**Figure 11: Detailed view of the connection between EEU and gas cooler.**



**Figure 12: Detailed view of the electrolyser unit during normal operation at low CO<sub>2</sub> flow (100 cm<sup>3</sup>/min).**



**Figure 13: Detailed view – CO<sub>2</sub> humidifier at high CO<sub>2</sub> flow (500 cm<sup>3</sup>/min).**



**Figure 14: Gas cylinder bundle with purified biogenic CO<sub>2</sub> and auxiliary gas cylinders connected to the system.**

## **2.4 Initial testing of integrated demonstrator with pure commercial CO<sub>2</sub> gas**

Figure 15 presents the results of the experiment with a gas diffusion electrode coated with an oxygen plasma-treated 500 nm copper layer. The test was performed using pure CO<sub>2</sub> at flow of 500 cm<sup>3</sup>/min with ca. 500 mbar overpressure. The electrolyser output gas was monitored on-line and gas samples was probed every 15 min. The ethylene enrichment unit (EEU) was probed every 60 minutes via gas-tight syringes. The maximum observed ethylene concentration in ERU gas output stream amounted to 1.7 %. The observed ethylene concentration in the gas flow was generally stable for the first 3 hours and then decreased. After 3h of operation, an increase of methane concentration in the gas flow was observed. The hydrogen concentration gradually increased as well, by up to 30 % after 6 h of operation. Cell voltage was stable at 12 V for 3.5 h, then increased slightly. Catholyte and anolyte flow rates were stable during the test and amounted to 500 and 1500 ml/min for catholyte and anolyte, respectively. The temperature of the electrolyte was measured on-line at the cell inlet and outlet. The electrolyte temperature in all cases remained below 30°C, but still a moderate temperature increase by 4°C and 2°C of the catholyte and anolyte, respectively, was observed.

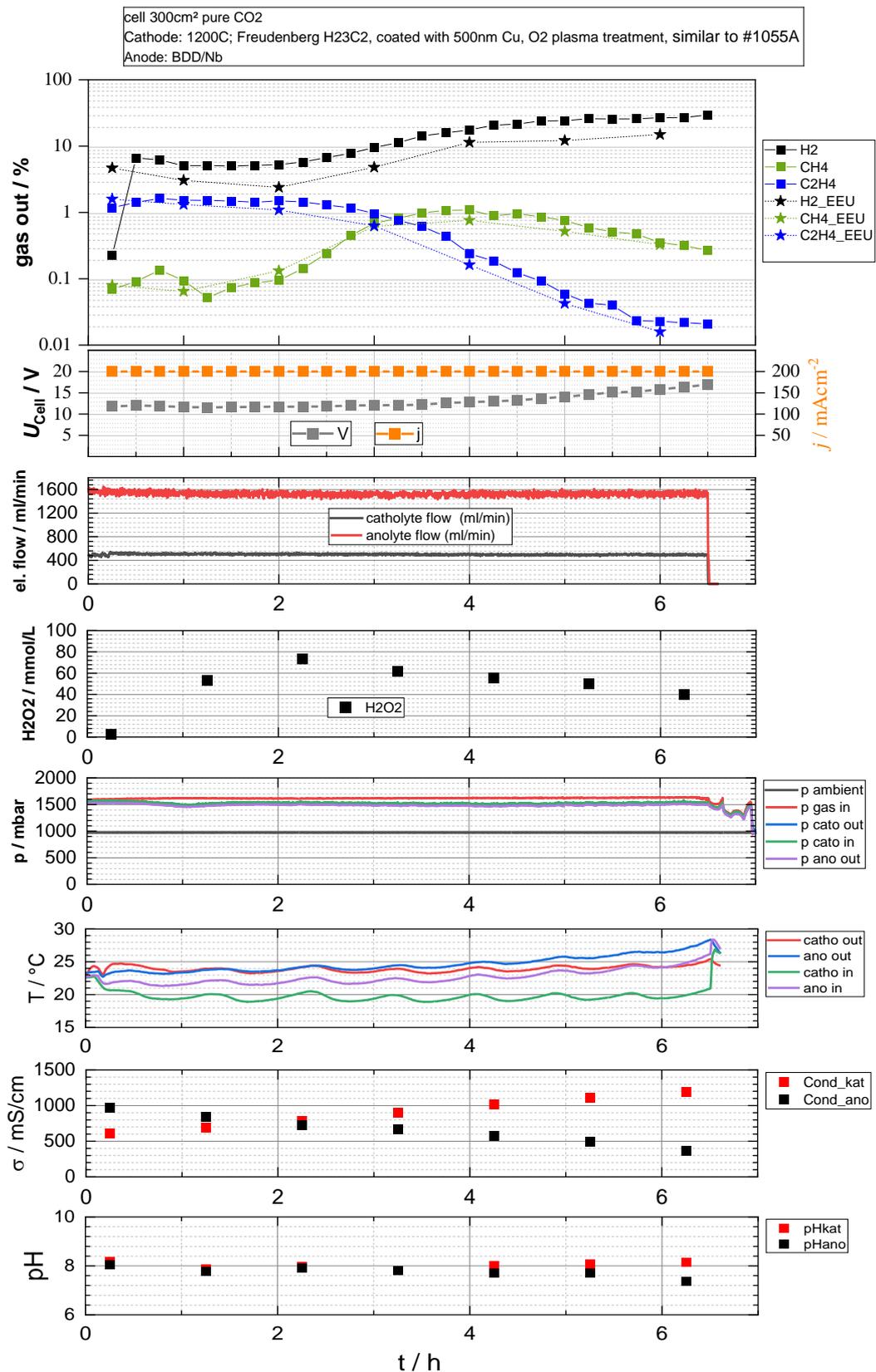


Figure 15: Results of experiment performed using pure CO<sub>2</sub> (EEU not optimized).

Every 60 minutes, 50 ml of anolyte and catholyte samples were taken from reservoirs and probed for pH, peroxide concentration (anolyte only) and conductivity measurements (peroxide concentration was determined immediately after the samples were collected, pH and conductivity were measured after the experiment). It was observed that after 6 hours of operation, the pH of the catholyte slightly increased, while the pH of the anolyte decreased. The conductivity of the anolyte decreased from 1000 to 400 mS/cm, while the conductivity of the catholyte increased from 600 to 1200 mS/cm during 6 hours of electrolysis. Electrolyte and gas pressure measured in several locations of the ERU remained stable during the process. The highest concentration of hydrogen peroxide observed during the experiment amounted to about 80 mmol/L.

The analysis of the EEU output gas flow showed that the concentration of several gas components, such as of ethylene, is slightly lower than in ERU output gas flow. In this context, it should however be noticed that in this test, settings of EEU were not optimized. Results that were obtained for optimized operation of EEU are presented further below in this report.

## 2.5 Operation of demonstrator with CO<sub>2</sub> originating from biogas

Tests have been performed with carbon dioxide gas originating from biogas upgrading delivered by Axiom in May 2019 (as part of WP2). The bundle of gas cylinders was installed in AGH laboratory at Kraków and the carbon dioxide gas cylinders connected to the feed-line of the electrolyser to demonstrate the compatibility with CO<sub>2</sub> from biogas upgrading (see Figure 16) and observe possible negative effects of biogas impurities on the performance of the demonstrator units.



**Figure 16: Bundle of gas cylinders originating from biogas upgrading installed in AGH lab.**

CO2EXIDE

Deliverable 6.8: Demonstration on plant testing, compiling of simulation and hardware results

GA No.: 768789 (H2020-SPIRE-2017)

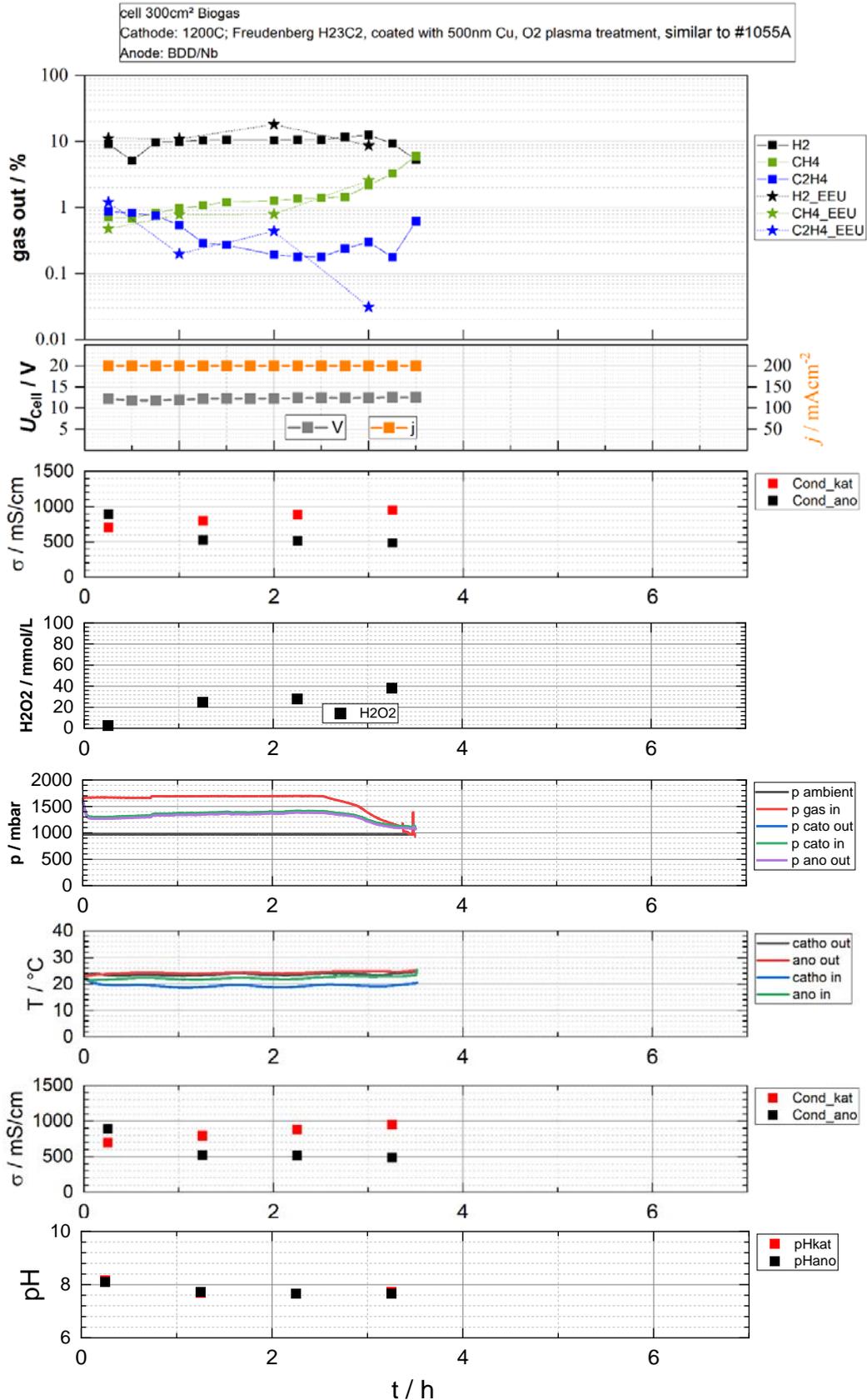
Page 17 of 28

Version 1.0, 20/07/2021

Figure 17 presents the results of the experiment with a gas diffusion electrode coated with oxygen plasma-treated 500 nm copper layer. The electrolyser output gas stream was monitored on-line with data points every 15 min, while a gas sample from the ethylene enrichment unit output stream was probed every 60 minutes by means of gas-tight syringes, similarly to the experiment with pure commercial CO<sub>2</sub>. The highest observed ethylene concentration in ERU output gas stream amounted to 0.88 %. The concentration was stable for the first 1 hour and then decreased over time. In contrast, the methane concentration increased over time, reaching close to 6% after 3.5 h of operation. The hydrogen concentration remained at the level of about 10 %, but then decreased after 3 h of operation.

When considering the composition of the EEU output gas stream, it has to be kept in mind that in this test the settings of EEU had not yet been optimized. We observed that the concentration of several gas components was at a similar level as in the case of ERU output gas. Cell voltage amounted to 12 V and was stable during measurement. Catholyte and anolyte flow rates were stable during the test and amounted to 500 and 1500 ml/min for catholyte and anolyte, respectively. During operation of the demonstrator, on-line temperature monitoring of catholyte and anolyte at the inlet and outlet of the electrochemical cell was performed. The electrolyte temperature in all cases remained below 25°C, but still a moderate temperature increase by 4°C and 2°C of the catholyte and anolyte, respectively, was observed.

Every 60 minutes, 50 ml samples of anolyte and catholyte were taken from reservoirs and probed for pH, peroxide concentration (anolyte only) and conductivity measurements (peroxide concentration was determined immediately after the samples were collected, pH and conductivity were measured after the experiment). Every 60 minutes, 50 ml of anolyte and catholyte were probed for pH and conductivity measurements. It was observed that after 4 hours of test, the pH of the catholyte and anolyte slightly decreased to about pH 7.7. The conductivity of the anolyte decreased from 897 to 500 mS/cm, while the conductivity of the catholyte increased from 700 to 950 mS/cm. Pressure measured in several locations of ERU remained stable for the first 2.5 h and then decreased. It should be underlined that although the electrolyte flows were kept constant, the gas and electrolyte pressures were lower than observed during tests with commercial pure CO<sub>2</sub>. After 2.5 h of operation, the pressure at all monitored cell locations decreased, indicating consumption of the entire volume of biogenic CO<sub>2</sub> in the gas cylinders. The highest concentration of hydrogen peroxide in the anolyte observed during the experiment amounted to about 40 mmol/L.

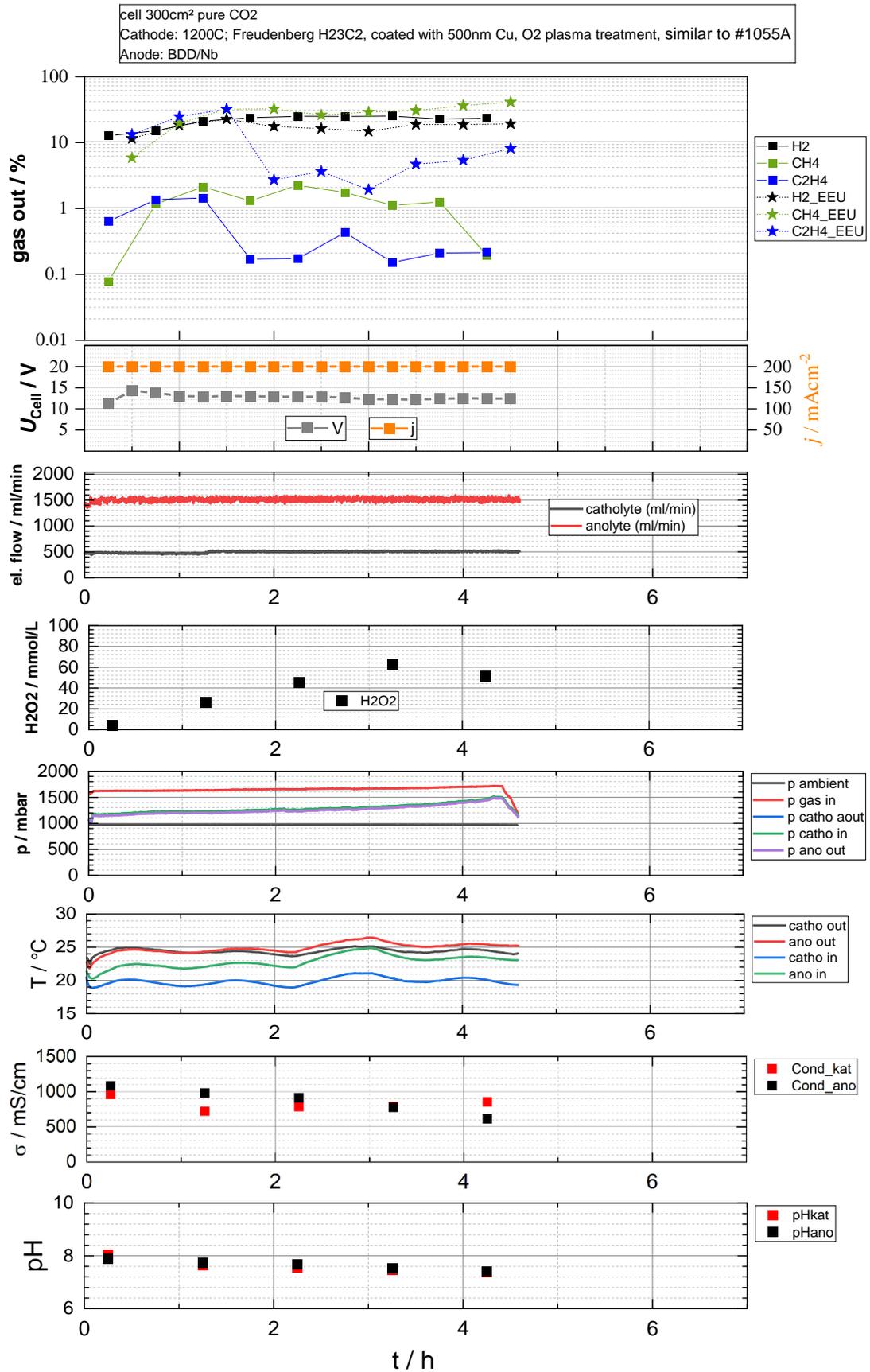


**Figure 17: Results of experiment performed using CO<sub>2</sub> originating from biogas (EEU not optimized).**

### 3 OPERATION OF DEMONSTRATOR WITH OPTIMIZED ETHYLENE ENRICHMENT UNIT (EEU)

Figure 18 presents the results of the experiment with a gas diffusion electrode coated with an oxygen plasma-treated 500 nm copper layer in combination with the optimized EEU (feed pressure equals 9.5 atm, retentate flow rate equals ca. 50 mL/min). The test was performed using commercial pure CO<sub>2</sub>.

The output gas flows of ERU and EEU were monitored on-line with sampling every 30 min. Maximal observed ethylene concentration in ERU output gas amounted to 1.7 %. The concentration was stable for the first 1.5 hours of operation and then decreased. The maximal concentration of ethylene in the retentate channel of EEU output gas was 32.2 % (the other components include methane (32%), hydrogen (22.7%) along with CO, CO<sub>2</sub> and N<sub>2</sub> (ca. 13%)), with an overall ethylene recovery of more than 90%. The achievement of ethylene concentration of >30% indicates adequate operation and effective gas separation function of EEU. Throughout the experiment, concentration of ethylene in the EEU gas output stream was several-fold higher compared to the ERU output stream. As it was observed in previous experiments, concentration of methane in the ERU output gas stream was significantly higher than the ethylene concentration. It was also observed that in the EEU's retentate gas flow, methane is also enriched, in addition to ethylene. This is in agreement with the findings reported previously in deliverables D4.3 and D6.4. The hydrogen concentration in the EEU output gas flow was lower by a few percent than in the ERU output gas flow, with a maximal concentration of 25.2 %. Cell voltage amounted to about 12 V and remained stable during the experiment. Catholyte and anolyte flow rates also remained stable at 500 and 1500 ml/min, respectively. During operation of the demonstrator, on-line temperature monitoring of catholyte and anolyte at the inlet and outlet of the electrochemical cell was performed. The electrolyte temperature remained below 27°C throughout the entire experiment, but still a moderate temperature increase of the catholyte and anolyte by 4°C and 2°C, respectively, was observed. Monitoring of the pH of anolyte and catholyte showed that after 4 h of operation, pH of anolyte and catholyte decreased to about 7.4. The electric conductivity was found to decrease from 1060 to 620 mS/cm after 4h of operation, while the conductivity of the catholyte increased from 950 to 850 mS/cm. Gas and electrolyte pressures continuously increased from 1160 to 1490 mbar. This pressure instability may indicate formation of some obstacles in the ERU, e.g. due to faster degradation of the catalyst as well as formation of solid salt deposits in the cell (for possible degradation mechanisms please confer deliverable D6.6 and recent literature reports: [1, 2]). Faster electrode degradation is a consequence of impurities naturally occurring in the CO<sub>2</sub> sources from biogas. Of these impurities, oxygen is suspected to be the most detrimental one (see deliverable D6.6 for details). The concentration of H<sub>2</sub>O<sub>2</sub> was determined directly after measurement to avoid decomposition of the hydrogen peroxide. The highest concentration of hydrogen peroxide in the anolyte observed during the experiment amounted to about 63 mmol/L.

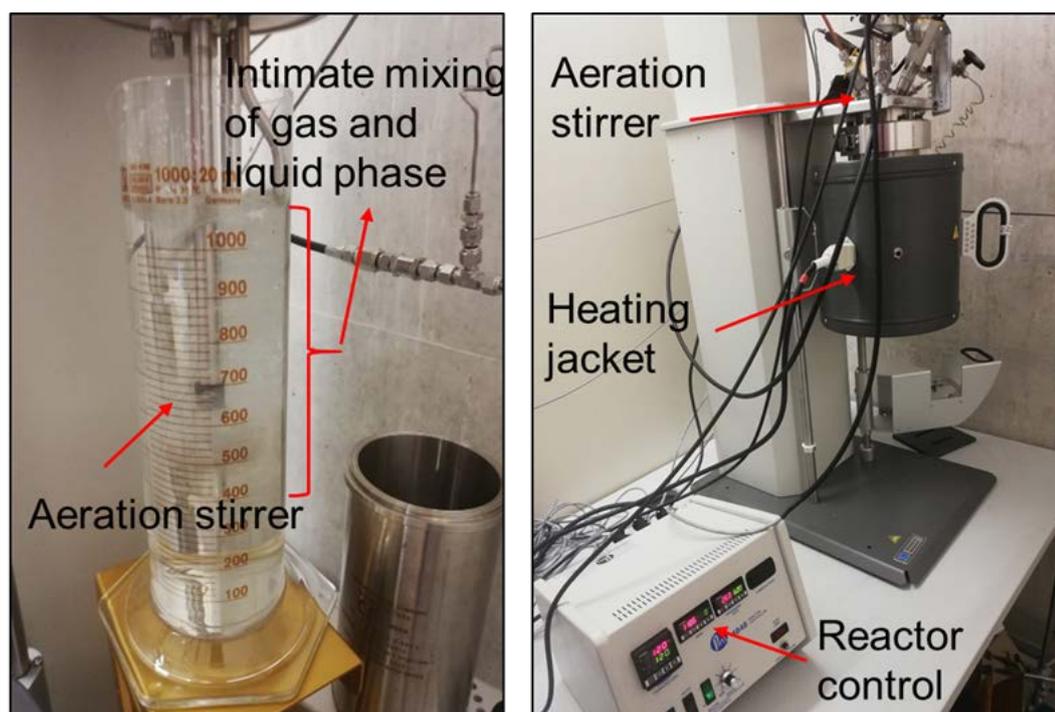


**Figure 18: Results of experiment performed using commercial pure CO<sub>2</sub> (EEU adjusted).**

## 4 OPERATION OF ETHYLENE EPOXIDATION UNIT (EQU) AT FRAUNHOFER

Oxidation of electrochemically produced ethylene to ethylene oxide represents the last chemical conversion step in the CO<sub>2</sub>EXIDE process chain of ethylene oxide production from CO<sub>2</sub>. This reaction step was examined in batch mode at the Fraunhofer site in Straubing, based on the process development and extensive testing of reaction conditions at smaller scale in WP5.

The reaction was carried out in a batch reactor from Parr Instrument Company with a volume of 2 L and operable up to a temperature of 350°C and up to a pressure of 100 bar. Already during the process development at smaller scale in WP5, the introduction of the reactive gas (ethylene) into the liquid (anolyte) was identified to play a critical role. Ethylene solubility in water is rather low at around 0.1 wt.% at 55°C and 15 bar pressure. Hence, the contact between the catalyst present in the liquid, the oxidant H<sub>2</sub>O<sub>2</sub> and the ethylene gas had to be maximized. In order to force more gas into the liquid phase during reaction, an aeration stirrer was installed. Figure 19 shows a picture of the working stirrer and the creation of a high gas-liquid contact area. This effect allowed a high transport of reactant molecules onto the catalyst surface to achieve better conversion rates.



**Figure 19: Left: Experiment demonstrating the effect of the aeration stirrer. A glass cylinder was filled with 1 L of water and the stirring speed set to 800 rpm. Due to safety reasons the speed was not increased to the 1200 rpm as set in a typical experiment in the closed autoclave. However, the high appearance of gas bubbles can be seen in the picture. Right: Batch reactor set-up under working conditions. The gas inlet is controlled by a needle valve, which allows adjusting the pressure with an accuracy of +/- 100 mbar, monitored by a digital and analogue pressure sensor. The temperature was controlled via a heating jacket.**

In a typical experiment the reactor was filled to 2/3 of its volume with a 0.6 molar H<sub>2</sub>O<sub>2</sub> – water or electrolyte mixture and about 6.5 g of Ti-MWW catalyst<sup>1</sup> were placed into the reactor vessel. Then, the system was checked for gas leaks by pressurizing with N<sub>2</sub> to 10 bar above the expected pressure during reaction. After 10 minutes, when the pressure was constant, the reactor was purged three times with N<sub>2</sub> and three times with ethylene gas before adjusting its pressure to 10 bar. While adjusting the pressure, the stirrer was already set to its final speed of 1200 rpm to adjust the equilibrium between gas phase and water solved ethylene. Then, the temperature was set to 50°C and the reaction run for 2.5 hours. After that time the temperature was increased to 120°C. This elevated temperature was set to accelerate the hydrolysis of the generated gaseous ethylene oxide to water-soluble ethylene glycol. For safety reasons, gas phase analytics of the highly toxic reaction product ethylene oxide was not possible, as no sample of the headspace gas could be taken from the autoclave and analyzed. Therefore, measuring ethylene glycol as the product of hydrolysis of ethylene oxide was the only way to indirectly capture the product and analyze it: The presence of ethylene glycol proves the prior formation of ethylene oxide. Finally, the product solution was quantified in a HPLC system “prominence” from Shimadzu equipped with an ODS-2 Hypersil column.

In the following, two experiments serve as demonstration for the epoxidation reaction as an integral part of the complete process cascade. One experiment is the reaction of ethylene and a pure aqueous H<sub>2</sub>O<sub>2</sub> solution without the presence of electrolyte salt from the upstream process (see Table 1). Another experiment is carried under more relevant conditions using the anolyte with KHCO<sub>3</sub> electrolyte salt from the demonstrator unit in Kraków, provided by AGH. The provided anolyte did not contain H<sub>2</sub>O<sub>2</sub> anymore at the time of arrival at Fraunhofer in Straubing as a consequence of the inherent instability of H<sub>2</sub>O<sub>2</sub> and its decomposition into water and oxygen. For the reaction in the EOU, the anolyte was adjusted to a H<sub>2</sub>O<sub>2</sub> concentration of 0.6 M by adding commercial H<sub>2</sub>O<sub>2</sub> solution.

The epoxidation experiment with the anolyte from the demonstrator unit in Kraków represents the final step of the demonstration of the CO<sub>2</sub>EXIDE process chain, combining the Electro-catalytic Reactor Unit (ERU) with the Ethylene epOxidation Unit (EOU) through use of the original anolyte. Originally, it was also planned to use the ethylene-enriched EEU output gas as feed stream. But this could not be realized, as COVID19-related travel restrictions did not allow integration of the EOU into the demonstrator in Kraków. Instead, the EOU unit was operated at Fraunhofer in Straubing, Germany. The results of these experiments are presented in Table 2.

---

<sup>1</sup>Ti-MWW: A titanosilicate with three-dimensional MWW structure. Ti sites are located in the zeolite framework (supercages) as tetrahedral species.

**Table 2: Comparison of two runs in the 2-L batch reactor for the epoxidation of ethylene under mild oxidation conditions. The aqueous liquid phase (1.2 L) was composed of H<sub>2</sub>O<sub>2</sub> solution (0.6 M) and KHCO<sub>3</sub> electrolyte (2 M). About 6.5 g of catalyst (Ti-MWW) was added to the mixture and the system was pressurized with 10 bar of ethylene.**

Parameter	Reaction without presence of electrolyte salt	Reaction with original anolyte from ERU with presence KHCO <sub>3</sub> electrolyte salt
T <sub>Reaction</sub> [°C]	50	50
Reaction time [min]	136	151
Ethylene glycol production [μmol g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> ]	10.85	3.22
T <sub>Hydrolysis</sub> [°C]	120	120
Pressure at 120°C [bar]	18	26

First, the observed ethylene glycol production (and hence the production of ethylene oxide) was found to be much higher (10.85 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) for the 2-L reactor compared to the small batch reactors (100 mL; < 1 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>). This is mainly due to a poor gas introduction in the smaller reactor system, whereas the larger scale reactor showed excellent mixing performance.

Second, by comparing the two columns in Table 2 above, the influence of the electrolyte KHCO<sub>3</sub> becomes obvious. The production rate of ethylene glycol dropped by a factor of 3 from 10.85 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> to 3.22 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>. For the catalytic reaction step, the oxidant has to coordinate with the active Ti centers located in the zeolite framework. A high concentration of CO<sub>3</sub><sup>2-</sup> ions could hinder this coordination through blocking the Ti centers for the oxidant. Formation of peroxohydrogencarbonate may be also responsible for the decreased reactivity of titanium-based catalyst due to decreased effective concentration of hydrogen peroxide [3-5], as described by reaction (1):



Hence, the electrolyte salt inhibits the heterogeneously catalyzed epoxidation reaction and consequently the overall product generation is reduced.

Third, a much more pronounced increase in pressure was observed in the course of the reaction when KHCO<sub>3</sub> electrolyte salt was present in the reaction mixture. The expected increase of pressure due to the thermal expansion of the gas was ~1.32. The final pressure at 120°C is 4 bar higher than the expected 14 bar from gas expansion. This additional gas could be oxygen

as the product of  $\text{H}_2\text{O}_2$  decomposition. More likely for a system containing  $\text{KHCO}_3$ , the additional gas is  $\text{CO}_2$  generated through decomposition of carbonate species. As a result, the final pressure is 8 bar higher.

In conclusion, the following was demonstrated for the EOU:

- A liter-scale (2 L) batch reactor could be successfully operated under mild oxidation conditions for the conversion of ethylene into ethylene oxide.
- The reaction could also be demonstrated for the application of original anolyte from the ERU in Kraków, shipped “as is” and containing  $\text{KHCO}_3$  electrolyte salt and any other species that might have formed during the electrocatalytic process. However, commercial  $\text{H}_2\text{O}_2$  had to be added prior to the epoxidation reaction to reach the required concentration.
- Introduction of reactant gas is a crucial point for this heterogeneously catalyzed reaction. In order to maximize the contact area between the gas phase reactant and the solid catalyst in the liquid phase together with the water-soluble oxidant,  $\text{H}_2\text{O}_2$ , a suitable stirrer, e.g. aeration stirrer, is needed.
- Further, the high concentration of  $\text{KHCO}_3$  (2 M) acting as the electrolyte salt for the upstream electrolysis, appears to inhibit the epoxidation reaction through blocking active Ti sites in the catalyst.
- The experiments have shown, that under relevant reaction conditions, the hydrolysis of ethylene oxide to ethylene glycol is incomplete. Therefore, analytic detection of ethylene glycol as indicator for monitoring ethylene oxide formation is insufficient. Techniques for direct monitoring of ethylene oxide formation are needed instead, but could not be applied here for safety reasons.

## 5 SUMMARY AND DISCUSSION OF THE DEMONSTRATION OF THE CO2EXIDE PROCESS CHAIN

**Process integration:** Electrocatalytic Reactor Unit (ERU) and Ethylene Enrichment Unit (EEU) physically combined and tested in Kraków, also using technical-purity CO<sub>2</sub> sourced from a biogas plant. Combination with downstream chemical processing in the form of the Ethylene epOxidation Unit (EOU) only in a hybrid virtual-physical way possible: COVID19-related travel restrictions did not allow physical integration of the EOU into the demonstrator in Kraków. Instead, the EOU unit was operated at Fraunhofer in Straubing, Germany. Coupling of EOU with the upstream electrocatalytic process step (ERU) was facilitated through transfer of a batch of original ERU anolyte that was used as aqueous phase in the EOU. The reactants ethylene (C<sub>2</sub>H<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) had to be supplied from commercial sources.

**Demonstration of the CO2EXIDE process chain:** The generation of an ethylene-rich gas stream from CO<sub>2</sub> was demonstrated through integration of the electrocatalytic reduction of CO<sub>2</sub> (sourced from a biogas plant) in the ERU with the enrichment of the synthesized ethylene in the product gas stream (EEU). In the EEU, the ethylene concentration was increased from 1-2% in the ERU gas output stream to over 31% at the outlet of the EEU, with an ethylene recovery of over 90%. At the same time, it was demonstrated that H<sub>2</sub>O<sub>2</sub> can be generated in a stable anodic water oxidation process, thus facilitating the simultaneous production of two valuable products, i.e. ethylene and H<sub>2</sub>O<sub>2</sub>, in the same electrochemical process unit. It was also shown that the cathodically synthesized ethylene can be further reacted with the anodically generated H<sub>2</sub>O<sub>2</sub> to yield ethylene oxide and its derivative ethylene glycol.

In summary, it was demonstrated that the CO2EXIDE process enables the conversion of CO<sub>2</sub> into the platform chemical ethylene oxide through combination of an electrochemical and chemical reaction step.

**Limitations of the demonstration and encountered challenges:** It was found that utilization of biogenic CO<sub>2</sub> sourced from a biogas plant leads to lowered electrocatalytic process performance. Specifically, the lower ethylene production rate reduced and the stability of the electrocatalyst decreased. In general, the stability of the catalyst for the electrochemical CO<sub>2</sub> reduction was identified as central technical challenge in the CO2EXIDE process chain.

The achieved H<sub>2</sub>O<sub>2</sub> concentration in the electrocatalytic water oxidation is insufficient for its utilization as oxidant in the subsequent ethylene epoxidation reaction.

The ethylene-enriched gas output stream of the EEU could not be tested in the EOU for the epoxidation of ethylene, as the transfer of gas samples from the EEU in Kraków to the EOU in Straubing could not be realized for logistic reasons. Therefore, only commercial ethylene could be used in the EOU.

The monitoring of the ethylene epoxidation in the EOU was limited: Only the formation of ethylene glycol could be quantitatively monitored by means of HPLC analytics, but not the formation of ethylene oxide. This limitation results from safety reasons: gas samples could not be taken and transferred to a GC due to the high toxicity of ethylene oxide (EO).

The performance of the ethylene epoxidation reaction appears to be negatively affected by the presence of carbonate species. This needs to be verified by qualitative and quantitative reaction monitoring, which could not be realized in the current experimental set-up.

Furthermore, the epoxidation experiments have shown that the reaction performance is strongly enhanced at elevated ethylene pressures of 10-50 bar. Consequently, a pressurization step has to be included between EEU and EOU in future developments.

**Next steps:** The focus of future R&D efforts should be placed on enhancing the stability of the cathodic electrocatalyst, i.e. the catalysts for the electrochemical CO<sub>2</sub> reduction to ethylene.

Attention should be paid to the purity of the CO<sub>2</sub> feed and its effect on the catalyst performance and stability → “real” CO<sub>2</sub> is different from commercial CO<sub>2</sub>. This aspect is highly important for the operation of the process in a relevant environment.

Ethylene epoxidation: The suitability of a “real” ethylene feed stream from the upstream EEU (instead of commercial pure CO<sub>2</sub>) has to be tested; the effect of carbonate species on the catalytic performance has to be clarified.

Process integration has to be progressed to the next level. The focus of the design of individual process units has to be on physical integration, including integrated thermal management and recycling of process streams, such as unreacted CO<sub>2</sub> in the electrochemical reactor (ERU). Another process stream that could be recycled is the anolyte after the epoxidation reaction, i.e. after the H<sub>2</sub>O<sub>2</sub> dissolved in the anolyte is used up in the epoxidation reaction.

The dimensioning of individual process units has to be harmonized so that all process units can operate continuously under optimal conditions. The integration of the units has to be pursued with the clear objective of progressing the CO<sub>2</sub>EXIDE technology further on the road towards an economically feasible process. This is a precondition for any further future scale-up in future.

## 6 REFERENCES

1. Popović, S., et al., *Stability and Degradation Mechanisms of Copper-Based Catalysts for Electrochemical CO<sub>2</sub> Reduction*. *Angewandte Chemie International Edition*, 2020. **59**(35): p. 14736-14746.
2. Bisztyga-Szklarz, M., et al., *In Situ Regeneration of Copper-Coated Gas Diffusion Electrodes for Electroreduction of CO<sub>2</sub> to Ethylene*. *Materials*, 2021. **14**(12).
3. Richardson, D.E., et al., *Equilibria, Kinetics, and Mechanism in the Bicarbonate Activation of Hydrogen Peroxide: Oxidation of Sulfides by Peroxymonocarbonate*. *Journal of the American Chemical Society*, 2000. **122**(8): p. 1729-1739.
4. Bakhmutova-Albert, E.V., et al., *Kinetics and Mechanism of Peroxymonocarbonate Formation*. *Inorganic Chemistry*, 2010. **49**(24): p. 11287-11296.
5. Medinas, D.B., et al., *The carbonate radical and related oxidants derived from bicarbonate buffer*. *IUBMB Life*, 2007. **59**(4-5): p. 255-262.

## ACKNOWLEDGEMENTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 768789. The authors would like to express their gratitude to the European Commission for this financial support.