Cost-effective PROton Exchange MEmbrane WaTer Electrolyser for Efficient and Sustainable Power-to-H2 Technology

Grant No. 862253

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***Project Coordinator**: Daniel García-Sánchez - DLR*

Task 5.2 Definition of test plan of electrolyser only and coupled system

WP5: System development and Energy Storage

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Document history

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1	31/08/2021	Christina Mennemann, Stéphane Haag (AL)	First Draft Version
2	20.09.2021	Elena Borgardt (iGas)	Revision + Input description electrolyser
3	24.09.2021	Ulrich Rost, Jörg Neumann, Jeffrey Roth	Revision + Input stack description
4	27.09.2021	Christina Mennemann, Stéphane Haag	Revision of methanol part + Formatting
5	28.09.2021	Christina Mennemann	Final Draft
6	29.09.2021	Christina Mennemann	Final version

Table of Content

1. Executive Summary

This document contains the parameters and indicators to be monitored for performance evaluation, as well as for cost modelling (TEA) and Life Cycle Assessment (LCA). By this it aims to ensure that the parameters to be monitored, recorded and analysed during the tests provide the necessary information to check the compliance with the project objectives and that there is an alignment of the expected information between the partners.

Chapter 5.1 defines the Key performance indicators (KPI) necessary for the comparison of the baseline stack system with the system after implementation of the newly developed PROMET-H2 stack. The KPI needed for the evaluation of the PtMeOH process are given in chapter 5.3.

The testing plan covers phases for independent PEMWE validation (not coupled to the methanol production), PEMWE with reference materials (baseline stack) coupled to the CO_2 to methanol pilot plant and finally the validation of the PROMET-H2 stack and system.

The document gives the testing plan based on the knowledge available in month 18 of PROMET-H2. It may be adjusted if necessary, based on new results of stack development and its testing in the plant.

2. Acronyms and Abbreviations

Parameter	Definition
A	Active area of the cell
AC	Alternating current
AL	Air Liquide Forschung und Entwicklung GmbH
BoL	Beginning of life
BoT	Beginning of test
CCM	Catalyst coated membrane
DC	Direct current
EoL	End of life
EoT	End of test
FCR	Frequency containment reserve
FRR	Frequency restoration reserve
H_2	Hydrogen
iGas	iGas energy GmbH
JRC	Joint Research Centre
KPI	Key Performance Indicator
LEL	Lower explosion limit
MeOH	Methanol
PEM	Polymer electrolyte membrane
PEMWE	Polymer Electrolyte Membrane Water Electrolysis
ProPuls	ProPuls GmbH
PtH2	Power to Hydrogen
PtMeOH	Power to Methanol
RR	Replacement reserve
TIP	Test input parameters
TOP	Test output parameters

3. Harmonized Testing Protocols for Electrolyser

The proposed test plan was developed by using experiences from former European projects as well as by using former work done by the EU and JRC on the development of harmonized testing protocols for low-temperature water electrolysis. The goal of this initiative is to ease the comparison of the results from research performed by different groups and entities.

The EU harmonised polarisation curve test method for low-temperature water electrolysis[1] for example will be referred to for the recording of polarisation curves. In the QualyGridS project standardized qualifying tests of electrolysers for grid service have been developed which will also be used within the PROMET-H2 project[2].

Led by the Joint Research Centre (JRC), another technical report on harmonised testing protocols for low temperature electrolysers is currently in progress with the support from European experts and projects. The report is still not finished, however, the draft[3] is available and was used as a source for inspiration for the testing plan in PROMET-H2.

Within this draft document the following instrumentation and sensor position and characteristics for a PEM electrolyser plant are proposed to ensure an accurate control of the operating conditions for the subsequent testing (Fig. 1).

Table 1 shows the reference settings proposed for PEM electrolysis in comparison to the settings defined for the PROMET-H2 electrolyser. As can be seen in direct comparison, nominal stack temperature as well as nominal pressure are higher in the PROMET-H2 settings.

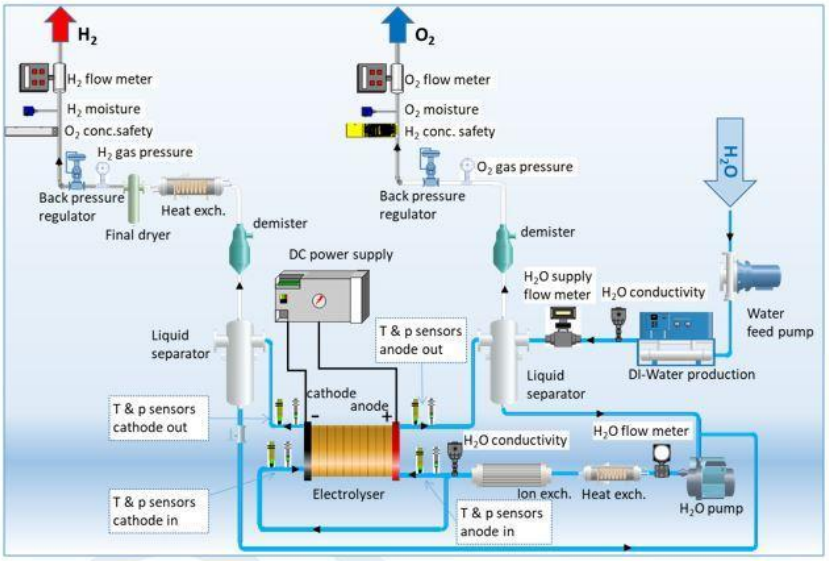

Fig. 1: Scheme of PEM electrolyser including the positions of the monitoring devices.[3]

Table 1: Reference settings for TIPs for PEM single cell and short stack testing[3] in comparison to PROMET-H2 Settings.

TIP	Unit	EU Reference Settings	PROMET-H2 Settings
Cell/ Stack temperature	°C	60	(60 / 70) 80
Water conductivity at the recirculation loop inlet	$\mu S \cdot cm^{-1}$	≤ 1	≤ 1
Anode water inlet temperature	°C	60	60 / 70 / 80
Anode Water inlet pressure	kPa	100	1000
Anode water conductivity in the recirculation loop	$\mu S \cdot cm^{-2}$	≤ 1.0	≤1.0
Anode minimum water inlet flow rate	$ml \cdot min^{-1} \cdot cm^{-2}$	2.0	≤ 1*
Anode absolute oxygen outlet pressure	kPa	100	4000
Cathode water inlet temperature (if applicable)	°C	60	60 / 70 / 80
Cathode minimum water inlet flow rate (if applied)	$ml \cdot min^{-1} \cdot cm^{-2}$	2.0	≤ 1*
Cathode hydrogen outlet pressure	kPa	100	4000

**to be verified by testing*

4. Test setup for electrolyser and methanol synthesis pilot plant

4.1 "Green electrolyser" of iGas

The 25 kW PEM electrolyser of iGas energy GmbH is a containerized solution (Fig. 2) that will be installed at the AL research site in Frankfurt. It comprises the electrolyser stack as the device where actually the reaction takes place (cf. Fig. 3, "Electrolysis") as well as the balance of plant (BOP), which guarantees the efficient functioning of the stack. The combination of the BOP and the stack results in the electrolyser system.

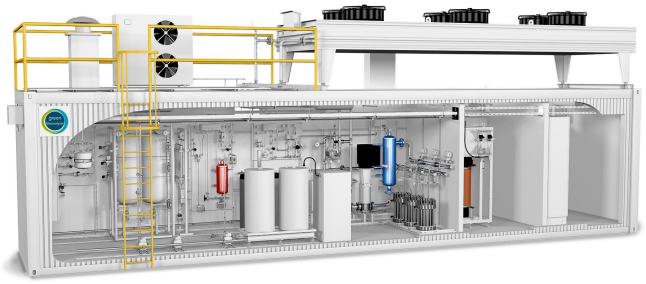

Fig. 2: Green Electrolyser by iGas Energy GmbH.

The functional units referred to as BoP are:

- Water purification unit (H2OC)
- Rectifier (Rec)
- Oxygen circuit (O2C)
- Hydrogen circuit (H2C)
- Cooling water circuit (CWC)
- Refrigeration Circuit (RC)
- Ventilation (VEN)
- Control Center (CC2010)
- Nitrogen supply (N2L)

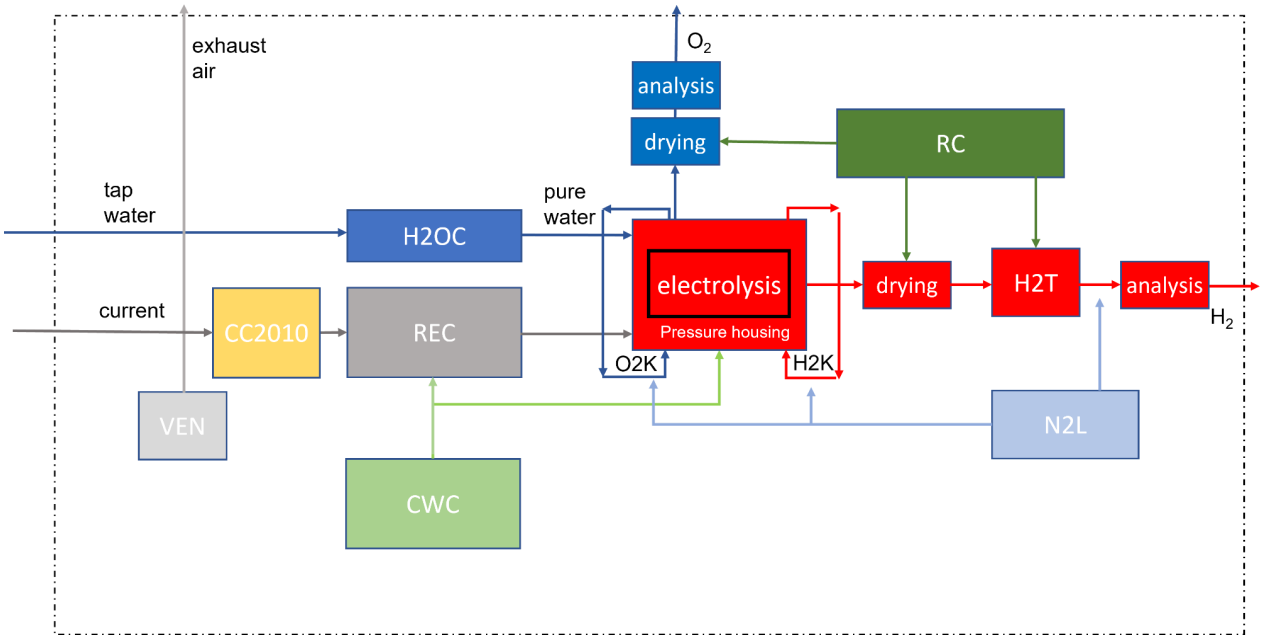

Fig. 3: Schematic representation of the functional units of the green Electrolyser.

Table 2: Specification of the PROMET-H2 PEM electrolyser.

KPI for el. system	Unit	PROMET-H2 system
System manufacturer	-	iGas energy GmbH
Nominal capacity	kW	25 kW
Nominal H2 production	Nm^3/h	5 Nm^3/h
Nominal stack temperature	°C	80°C
Nominal stack pressure	bar	40 bar
Minimum part load	[%]	10 %
Maximum overload capacity	[%]	-
(Rated, guaranteed) System efficiency	kWh/kgH2	64
Rated system lifetime	y	25 y
Hydrogen purity	[%]	99.999% in terms of H_2O and O_2

The electrolyser has a nominal hydrogen production of 5 Nm^3/h and is operating at 80°C and 40 bar in a load range of 10% to 100%. In terms of H_2O and O_2, a hydrogen purity of 99.999% is reached after the purification unit. iGas energy GmbH gives a rated system lifetime of 25 years. (Table 2)

The system supplied by iGas in the frame of PROMET-H2 is based on its standard plant, but has been modified to meet the requirements for research as well as to meet the requirements for this particular stack. For example there are electrolyte cycles both on the anode and cathode side. This option was implemented to have more options and flexibility for the testing of the new material PROMET-H2 stack with its characteristics and properties not yet known. The hydraulic stack concept requires a pressure housing filled with the hydraulic media which is fed by the hydraulic cycle.

Table 3 and 4 summarize the test input and test output parameters in the PROMET-H2 PEM electrolyser.

Table 3: Test input parameters.

Parameter	Unit	Position of sensor
Current	A	Power Supply Module
Temperatures		
Water, anode inlet	°C	As close as possible to stack hardware inlet
Water, cathode inlet	°C	As close as possible to stack hardware inlet
Hydraulic vessel inlet	°C	As close as possible to vessel inlet
Pressures		
H_2 outlet	bar	After liquid and vapour separation
O_2 outlet	bar	After liquid and vapour separation
Hydraulic vessel outlet	bar	As close as possible to vessel inlet
Flow rates		
Water feed to stack	L/min	In anodic and cathodic cycle
Water quality		
Water conductivity	µS/cm	In separators

Table 4: Test output parameters.

Parameter	Unit	Position of sensor
Stack Voltage	V	Voltage terminal, Current collectors
Single Cell Voltage	V	Cell Hardware
Temperatures		
Cell	°C	Not defined yet, preferably at anode and cathode BPPs
Water, anode outlet	°C	As close as possible to stack hardware outlet
Water, cathode outlet	°C	As close as possible to stack hardware outlet
Hydraulic vessel outlet	°C	As close as possible to vessel outlet
Pressures		
Water, anode inlet	bar	Close to the cell stack hardware inlet
Water, anode outlet	bar	Close to the cell stack hardware outlet
Water, cathode inlet	bar	Close to the cell stack hardware inlet
Water, cathode outlet	bar	Close to the cell stack hardware outlet
Hydraulic vessel outlet	bar	As close as possible to vessel outlet
Flow rates		
Hydraulic cycle inlet	L/min	Measurement of the pump speed used for flow calculation
Hydrogen	L/h	After water knockout, measurement by flow meter
Gas safety sensors		
Hydrogen concentration	%	H_2 gas sensor in O_2 outlet
Oxygen concentration	%	O_2 gas sensor in H_2 outlet
Supplemental measurements		
Dew point analysis	°C	H_2 stream, upstream and downstream of DeOxo

The temperatures and pressures at the stack inlet and outlet on both sides as well as at the inlet and outlet pressures of the hydraulic cycle are measured. The water flow rates to the stack as well in the hydraulic cycle and for the water make-up are determined. Also a H_2 flow meter will be installed. The purified feed water as well as the electrolytic water in the separators is monitored by electrical conductivity measurement.

For safety reasons the hydrogen concentration in the gas stream from the oxygen evolution electrode is measured by a hydrogen gas safety sensor as well as the oxygen concentration in the

hydrogen. For example at 0.8 Vol. % H_2 in O_2 (~20% of LEL) the current supply of the stacks will be switched off and the oxygen flow will be diluted with N_2.

Measurement accuracy and sampling rate correspond to the requirements given in the harmonized protocol for polarization curves.

4.2 Baseline and PROMET-H2 Hydraulic Stack Concept

In PROMET-H2 a novel stack concept based on hydraulic cell compression developed by ProPuls GmbH in collaboration with Westfälische Hochschule Gelsenkirchen[4] is used. According to this stack concept, single PEMWE cells are placed into flexible pockets and the hydraulic medium inside a surrounding pressure housing is applied to introduce compression forces. Further, with the optimized stack design developed recently, the hydraulic medium is applied directly to the pole plates of each single cell (Fig. 4, A) and B)) leading to the necessary cell compression and contacting of the different layers inside a cell.[5]

A) *B)*

Fig. 4: A) Schematic drawing of a PEMWE stack based on hydraulic cell compression and B) Spacing for hydraulic medium between individual single cells.

For the PROMET-H2 PEMWE Baseline Stack water is used as a hydraulic medium. During the operation of the stack, water at a pressure level that is always above the inner cell level (ca. 10 bar) surrounds each single cell entirely. With the pressure being uniform anywhere within the pressure housing, a homogeneous compression is achieved independently from the number of cells or the active cell area.[6] Due to a hydraulic cell compression the current density distribution is homogenized which results in minimizing the thermal stress for a cell and helping to avoid hot spots that can lead to accelerated failures. Further, the surrounding water is used to remove waste

heat from the cells of the stack.[7] Less DI water needs to be circulated in the electrolyte cycle and to be fed to the electrolysis cell, as the hydraulic medium not only compresses the stack but also functions as a homogeneous cooling medium, thus leading to the possibility to operate the stack at an elevated temperature level such as e.g. at 90 °C.[8] Finally, due to pressure controls that keep hydraulic media pressure level always 10 bars above the inner stack pressure (balanced anodic and cathodic pressure level) a high-pressure electrolysis can be facilitated with a PEMWE stack based on hydraulic cell compression.[9] In earlier investigations with medium-sized cells it was found that an operation at up to about 100 bars outlet pressure (hydrogen and oxygen) is possible.[10] Table 5 gives the specifications for the baseline stack and the PROMET-H2 stack.

Table 5: Stack specifications.

Parameters	Unit	Baseline stack	PROMET-H2 stack
Stack Manufacturer	-	ProPuls GmbH	ProPuls GmbH
Nominal Capacity	kW	25	25
Nominal H_2 production	Nm^3/h	5	5
Rated current density	A/cm^2	2	1
Nominal Stack Temperature	°C	80	80
Nominal Stack Pressure	bar	40	40
Maximum overload capacity	[%]	100	100
Single cell area	cm^2	500	500
Number of cells	-	14	14 or ~30**
Voltage Efficiency (HHV)	%	67-82	≥70
Voltage at nominal and SOR	V	1.9	to be measured
Voltage at nominal and EOR	V	2.5	to be measured
Rated stack degradation	µV/h	5	≤ 10*

**target from the grant agreement. ** depending on materials selected.*

4.3 Methanol synthesis pilot plant at AL

A new methanol synthesis pilot plant has been built in the frame of another EU project called i3-upgrade. This project has received funding from the Research Fund for Coal and Steel under grant agreement No 800659. The pilot plant has been successfully started in 2020. The entire basic design of the pilot plant including the analytical concept for 16 sample points has been done by AL to optimize the use of carbon dioxide and carbon monoxide emitted by steel plants to transform them into methanol. This plant will be used in the frame of the PROMET-H2 project to convert CO_2 and hydrogen produced by the electrolyser into methanol. The two plants will then work simultaneously during a dedicated test campaign for a duration of about 4000 hours in total.

The key features of this new pilot plant can be described as follows:

- Reactor with 7 reaction tubes
- Several reactor stages
- Various flow schemes possible
- Heat transfer to steam system
- Temperature profile measurement
- Throughput:
    - Feed gas up to 35 m^3_N/h
    - Raw methanol product up to 20 kg/h

Figure 5 presents pictures of the outdoor and indoor parts of the methanol synthesis pilot plant at AL in Frankfurt, Germany.

Fig. 5: Methanol synthesis pilot plant built by AL in Frankfurt/Main in the frame of the EU project i3upgrade.[1]

The methanol synthesis pilot plant allows various configurations of the reaction section (max. of 4 stages with inter-stage condensation, 7 reactor tubes available). The plant concept is optimized for dealing with unconventional gas compositions under once-through conditions or with low recycling. For the planned test campaign about CO_2 to methanol, 4 stages will be filled with commercial methanol catalysts.

The reaction section consists of several stages setup for optimal conversions of CO_2 and H_2. Between each stage there is the possibility to remove the raw methanol (methanol /water mixture) produced and this should allow high overall methanol production and extend the catalyst lifetime. The operation in the new methanol pilot plant using 4 stages filled with catalyst under once-through operation can be described as follows:

- Fresh feed gas is entering stage 1 of the reaction section
- The unconverted gases from stage 1 is feeding stage 2
- The unconverted gases from stage 2 is feeding stage 3
- The unconverted gases from stage 3 is feeding stage 4
- The raw methanol product is removed after each stage and analyzed accordingly.

[1] *This project has received funding from the Research Fund for Coal and Steel under grant agreement No 800659* - https://www.i3upgrade.eu

- The amount of by-products are evaluated for the raw methanol removed between the stages
- The final raw methanol product is gathering all the contributions coming from each stage.

This multi-stage setup will contribute to the development of tailor-made solutions for diverse carbon sources, especially focusing on a circular economy and on the valorization of off-gases and of CO_2 rich streams from industries.

The online analytical concept is based on process gas chromatography. The system was developed and implemented for the analysis of syngas composition, methanol as well as some main by-products in a single gas phase with a broad concentration range and detection limit 0.01 mol% or better.

In particular hotgas streams from reactor outlets, unconverted gases, methanol, water and some oxygenated hydrocarbons under high pressure and temperature can be analyzed online in the gas phase using the special online sample conditioning and analysis system. Moreover, a gas stream dilution system can be applied for hot gas streams, once the chromatography signal is saturated.

Additionally, a continuous evaporation mixture system is integrated as a validation system to monitor the conditioning and analysis system with methanol and water vapor mixture during the operation in a certain time interval.

The online analytical system including a heated conditioning system, a four-channel micro-GC system and a continuous evaporation mixture system is shown in the figure 6 below.

Fig. 6: The online conditioning and analysis system of the methanol synthesis test plant at AL.

The online analyzer with short response time enables the real-time optimization of the process variables and adjustment of feedstock composition in order to control the side reaction and achieve the desired product yield.

5. Test Definition for Power to H_2 / Power to Methanol

The testing plan covers phases for independent PEMWE validation (Power to H_2, PtH_2) as well as tests where the produced H_2 is fed to the methanol synthesis pilot plant (Power to MeOH, PtMeOH). The PtMeOH process will be especially tested using the stack with reference materials (baseline stack) which will be built earlier in the project by the stack manufacturer ProPuls, whereas the newly developed PROMET-H2 stack will only be tested in PtH_2 reaction during the last 3 months of the project period.

KPI´s needed for the evaluation of the electrolyser system and the comparison of the baseline stack based on standard materials with the newly developed PROMET-H2 stack are specified in chapter 5.1, KPI´s needed for the evaluation of the CO_2 to methanol process are defined in chapter 5.3. Chapters 5.2 and 5.4 describe specific tests for the PtH_2 and PtMeOH process.

5.1 Targets and KPI Definition for Power to H_2

The operation of the electrolyser will provide the input for the operational cost estimation and subsequently the calculation of the levelized cost of hydrogen. In example, consumption figures, utility cost as well as the amount of hydrogen produced are important aspects for profitability.

For the performance evaluation a set of KPIs is given in Table 6. First there are a couple of performance indicators targeting the utility consumption (power) as well as the raw material consumption (water) and conversion efficiencies needed to calculate the production capacity later on in the economical evaluation. Although the short period of testing time will not allow us to get meaningful results, the maintenance cost will be monitored.

At the system outlet, O_2 and H_2O content will be determined for calculation of H_2 purity.

Prior to deploying new technologies in industry on a large scale it needs to be demonstrated that they are capable of reaching high availability and reliability values. Overall operational time,

cumulative production of H_2 as well as the availability figures can be named as performance indicators here.

Table 6. KPI´s for electrolyser system and stack performance evaluation during testing.

KPIs electrolyser	Unit	Definition
System specific energy consumption	kWh/kgH_2	Total electricity consumption @ nominal capacity
Stack energy consumption	kWh/kgH_2	Stack electricity consumption @ nominal capacity
Power consumption in warm standby	kWh/h	Power consumption in warm standby
System electrical efficiency [HHV, AC current]	%	H_2 production vs. electricity consumption (AC current)
Current efficiency	%	Ratio of the measured H_2 quantity at the system outlet vs. theoretical hydrogen production based on DC
Water consumption	kgH_2O/kgH_2	Overall water consumption of the PEMWE
Yearly maintenance cost	€/(kW*a)	Maintenance expenses per year
H_2 Purity	%	H_2 purity system outlet considering H_2O and O_2
Cumulative stack operation time	h	Cumulative time the stack has been in operation.
Amount of H2 produced by stack	kgH_2	Cumulative amount of H_2 produced in kg.
Availability 1	%	Percent amount of time the electrolyser was able to operate vs. overall time intended to operate
Availability 2	%	Percent amount of time the electrolyser was operated vs. total time installed.
Cold start ramp time	s	Time required to reach nominal power when starting the electrolyser from a cold state (ambient temperature with no power input or output)
ramp-up & ramp down time	s	Time needed to ramp from min. to max. load and from max. to min. load.
Voltage @ SOR	V	Cell voltages at Start of Run
Degradation rate	µV/h	Hourly degradation rate
Degradation rate	$µV/Nm^3$	Total H_2 production volume based degradation rate
Efficiency degradation	%/y	Efficiency degradation per year
Number of safety incidents	-	Number of incidents relevant for safety.

Another target of this research project is to show that the electrolyser is able to handle fluctuating loads. To assess this parameter, the cold start ramp time as well as the ramp time from minimum to nominal load and vice versa will be determined.

The stack is one key driver for CAPEX. Therefore a high lifetime of the stack is crucial for the overall process to be economically viable. The parameters for the assessment are the degradation rate of the stack based on the overall operation time or on the total amount of H_2 produced. With the voltage at the start of run and the yearly efficiency degradation, the overall lifetime can be easily calculated.

Safety aspects are key and a particular attention has been taken to evaluate the different risks and their mitigations already during the basic engineering phase.

5.2 Test Definition for Power to H_2 Reaction

The pre-testing of the stacks will already be performed at the site of the stack manufacturer including leakage and isolation tests, heat-up and conditioning according to a predefined start-up procedure of the CCM manufacturer. An initial polarization curve (JRC protocol, cf. appendix, 6.1) will be recorded at 80°C and ambient pressure. The baseline stack will be integrated into the electrolyser plant at the systems supplier site and will be started up after the container has been transported to AL in Frankfurt and installed at site. In the last quarter of the PROMET-H2 project the newly developed PROMET-H2 stack will be tested. The exchange of both stacks will be performed by iGas at the AL site.
The tests defined below will take place after start-up and commissioning.

5.2.1 Plant Performance at Nominal Load & Steady State Degradation Test

For a first evaluation of the system and the baseline stack performance the electrolyser will be operated at nominal conditions and the basic KPI´s will be determined. Afterwards a polarisation curve will be recorded. The procedure for polarization curve recording is given in the appendix 6.1 and is consistent with the EU harmonised polarisation curve test method for low-temperature water electrolysis.[1]

A long term test of 2000 to 4000 h TOS under nominal conditions will be performed similarly to the "steady state loading" test protocol for in-situ cell and short stack testing defined in the EU harmonised protocols for testing of LTWE.[3] However, steps 6 to 8 will not be performed, as there is no possibility of applying open circuit voltage conditions in an industrial system. The time considered for determining and calculating voltage increase will exclude the initial conditioning period where the cell voltage may decrease. According to the test protocol proposal it will only start when the average value of $\dot{V}=(\Delta V/\Delta t)$ calculated over the preceding two-hour period is equal or greater than zero. The protocol is reproduced in Appendix, 6.2. Depending on the electrolyser performance the test might also end earlier, for example in the case when the cell voltage increases strongly it will be preferred to perform the other outstanding tests. The TIP´s will be set according to the nominal conditions of the PROMET-H2 system and stack. The H_2 product produced by the baseline stack will be sent to the CO_2 to methanol synthesis pilot plant.
The steady state degradation of the PROMET-H2 stack will be tested for a period of 400 to 1000 h only, as the overall testing period for this stack is 3 months only.

5.2.2 Characterisation of PEMWE for grid service relevant parameters[1]

Electrolysers need to show excellent dynamic behaviour to be able to offer grid-balancing service. The fit for purpose tests described in [3] and developed by the QualygridS project are used to quantify the reactivity and flexibility of the overall system including the stack and to characterize its ability to provide grid service.

The first test proposed is regarding the flexibility or the identification of the system power (SP) range. In the PEMWE specification of iGas a load range of 10% to 100% is given. The goal of the test protocol is to verify, if the power variation at minimum and maximum load is stable with a maximum deviation of ±2%*P_{max} of the system.
5 tests are dedicated to testing the response time for dedicated load changes, e.g. to determine the minimum-maximum setpoint dynamics or the time needed to start up the electrolyser from cold to nominal power.

- Flexibility: Identification of system power (SP) range
- Response time: Determination of ramp-up and ramp down time (Min → Nominal=Max → Min)
- Response time: Cold start time to nominal power
- Response time: Start-Up to nominal power from Standby
- Response time: Nominal Power to Standby

To ensure reliable measurement results, the tests will be repeated 3 times. It will be taken care that the system settings always remain in specification, if not the test will be interrupted. The testing protocols can be found in [2], Annex E.

5.2.3 Testing and degradation at dynamic mode, grid service

In a first test the load of the electrolyser will be repeatedly changed from minimum to maximum load (10%-100%) with a hold time of each step of several hours down to 15 min. In case of the baseline stack the H_2 will be fed to the methanol synthesis pilot plant to evaluate the reactivity of the downstream process, especially the input stoichiometry and the impact on conversion and product selectivity (cf. chapter 3.3.3.).

In a second and third test, the FCR and FRR testing protocols defined by the QualyGridS project will be used for both baseline as well as PROMET-H2 stack to evaluate the system's ability to provide primary and secondary reserve grid service.
The FCR test consists of 10 consecutive steps with overall 3 predefined power levels (low, medium and upper level). The levels will be defined, measured and controlled at the total electrolyser system power input or the electrical power to the rectifier is used for the grid service and the BoP power will be measured in parallel.
The aggregated testing protocols are reproduced in Appendix, 6.3 and 6.4.
The KPI´s used for evaluation of the test results are power stability at the different power levels, the duration of the ramp up and ramp down times as well as the response time.

According to the harmonised protocols for testing of LWTE[3], for electrolyser systems a "Real World Degradation" (RWD) is considered, with a load versus time profile based on actual operating conditions experienced in different electrolysis systems applications. If available, a renewable energy profile from wind or solar power will be used for generating the power input profile for the long term performance evaluation in dynamic mode. Otherwise a dynamic load degradation test protocol will be used. The exact imposed load profile will be defined knowing the outcome of the former tests that have just been described. The degradation test under dynamic load will be performed for 2 to 8 weeks, depending on the measured performance. A polarisation curve will be recorded at least every 2 weeks for comparison.

5.2.4 Sensitivity analysis for pressure and temperature

A sensitivity analysis regarding the operating parameters pressure and temperature will be carried out for the baseline stack. The TIP is given in Table 7. Polarisation curves will be recorded for the different testing conditions.

Table 7: TIP for sensitivity analysis of baseline stack and PROMET-H2 stack.

Test conditions for sensitivity analysis	Nominal	Test 1: Temperature Sensitivity	Test 2: Pressure + Temp. Sensitivity
Operating Temperature [°C]	80	60, 70, 80	60, 80
Operating Pressure [bar]	40	40	15, 20, 25, 30, 35, 40
Load [%]*	100	100	100

**Baseline Stack: 100% load = 2A/cm^2, PROMET-H2 stack: 100% load = 1A/cm^2.*

5.2 Targets and KPI definition for Power to Methanol

The reduction of carbon footprint as well as the valorization of CO_2 rich gases are of in-creasing interest for many industries and methanol is a perfect fit for energy storage. It can be used for producing clean fuels and as a building block for high value chemicals. The production of methanol as an intermediate is an effective way to meet both environmental requirements and economic constraints (see Fig. 7).

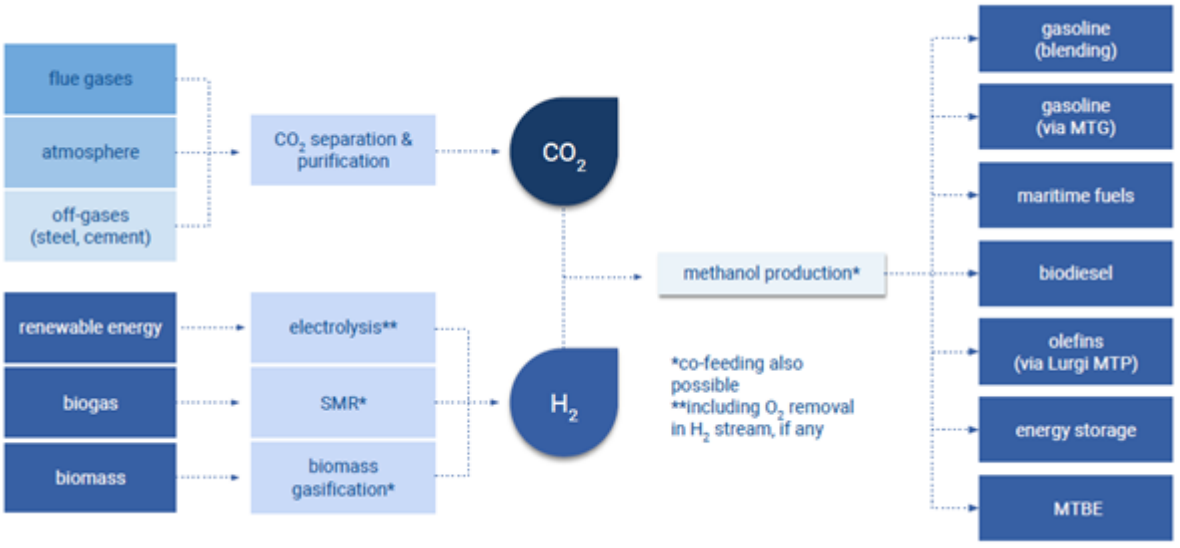

Fig.

Fig. 7: CO_2 and H_2 to methanol and possible methanol downstream processes.

Concepts for methanol synthesis based on CO_2 and hydrogen exist but are not optimized for today's challenges such as smaller capacities, integration into other processes and fluctuating operation. Air Liquide's unique experience with methanol technology sets the basis for an optimized CO_2 based methanol process. First test campaign at AL was done in the late 70's and the first extensive studies of the CO_2-based methanol synthesis were carried out in the mid-90s.

If CO_2 is used as feed gas, both primary reactions, i.e. the CO_2 hydrogenation to methanol and the reverse water-gas shift reaction to CO, are accompanied by a formation of water as described in

the paper from F. Pontzen et al.[2]. Hence, the methanol/water mixture produced from the CO_2-based process shows a significant amount of water (30 to 40%). The amount of CO_2 is not only key for water content but it also impacts the amount of by-products produced during the reaction. The 3 main reactions are described as followed:

CO_2 to methanol:	$CO_2 + 3\ H_2 \rightleftarrows CH_3OH + H_2O$	$\Delta HR0 = -49.6$ kJ/mol
Reverse water-gas shift:	$CO_2 + H_2 \rightleftarrows CO + H_2O$	$\Delta HR0 = +41.3$ kJ/mol
CO to methanol:	$CO + 2\ H_2 \rightleftarrows CH_3OH$	$\Delta HR0 = -90.8$ kJ/mol

When CO_2 is present in the feed gas, both primary reactions, the CO_2 hydrogenation to methanol and the reverse water-gas shift reaction to CO, are accompanied by water formation. Hence, the methanol/water mixture produced from the CO_2-based methanol synthesis process shows a significant amount of water (30 to 40%). It is well-known that H_2O negatively affects the catalyst lifetime, as catalyst degradation increases with high partial pressures of H_2O in the feed. Therefore, high amounts of water lead to challenges regarding faster catalyst aging, as the duration of catalyst lifetime is significantly lower than for CO-rich syngas. The amount of CO_2 is not only key for water content, but it also impacts the amount of by-products produced during the reaction. In this case, the amount of by-products is generally much lower than for CO rich feedstocks.

In the past, methanol plants have been operated under stable and optimized conditions only as there was no need to adapt to fluctuating conditions. With the increase of renewable energy input into the electricity grid the demand for electricity consumers being able to adapt to the current increases.

The goal of the current project is to examine the usage of H_2 from electricity for CO_2 to MeOH reaction under stable conditions to find the best operating point as well as to examine the reactions

[2] F. Pontzen, W. Liebner et al., Catalysis Today, 2011, 171, 242-250

under dynamic operation conditions. In this case dynamics are introduced by the fluctuating energy input to the electrolyser.

The test campaign regarding the methanol synthesis under fluctuating conditions will focus on these Key Performances Indicators:

- Conversions of CO_2 (plant), CO_2 (per pass) and H_2
- Space Time Yield, Weight Time Yield
- Deactivation behaviour of catalyst with time on stream
- Gas compositions at reactor inlet and at reactor outlet
- Methanol production
- By-products
- Water content (%) in methanol
- Mass balances und C,H,O balances
- Temperature profile

5.3 Test Definition for Power to Methanol

The data collected during the 4000 hours of the test campaign will be used for a techno-economical evaluation of the whole process.

In a first step the reactor tubes of the methanol synthesis plant will be filled with fresh catalyst and a reduction of the catalyst will take place. After the reduction phase the catalyst will be ready for the test campaign. A sensitivity analysis will be performed for different test input parameters in the CO_2 to methanol reaction. Afterwards a particular attention will be taken to analyse and to understand the response of the methanol synthesis pilot plant under fluctuating conditions due to the availability of the hydrogen as feedstock.

5.3.1 Catalyst loading and reduction in methanol synthesis pilot plant

The catalyst that will be used for the methanol synthesis will be a proven commercially available catalyst. The new pilot plant will be filled in a 4 stages configuration with catalysts to be able to run the plant effectively in once-through operation. The inner diameter of each reactor tube is 25.6 mm and the height of the catalytic bed is 5 meters for each stage. In the tube center, an additional tube is placed for measurement of the temperature profile. The tube dimensions as well as information about the filled catalyst can be found in Table 8.

Table 8. Key data of the reactor tube and the catalyst bed.

New Pilot Main Information	Unit	WCR
Dimensions reactor tube (ID) in each 4 stages	[mm]	25.6
Dimensions reactor tube for thermocouple (OD)	[mm]	6
Catalyst bed height in each 4 stages	[mm]	5000
Catalyst volume in each 4 stages	[ml]	ca. 2500

The catalyst is usually delivered in its oxide phase and a reduction is needed in order to have an active catalyst during the test campaign. Therefore the catalyst will be reduced according to the following standard conditions. Each step will be held until the concentration of hydrogen in feed and outlet gas will be equal (relative difference less than 1 %):

1 vol% H_2 in N_2, 1000 h^{-1}, 150 °C

1 vol% H_2 in N_2, 1000 h^{-1}, 175 °C

1 vol% H_2 in N_2, 1000 h^{-1}, 200 °C

1 vol% H_2 in N_2, 1000 h^{-1}, 225 °C

1 vol% H_2 in N_2, 1000 h^{-1}, 250 °C

5 vol% H_2 in N_2, 1000 h^{-1}, 250 °C

5.3.2 Methanol reaction condition sensitivity during static PEMWE operation

Regarding the test campaign it is planned to vary the following CO_2 to methanol input parameters and to evaluate the performance regarding the KPI´s mentioned in chapter 3.2, e.g. the educt conversions, byproduct formation etc..

- Temperature (from 210°C to 240°C)
- Pressure (from 40 to 100 bar)
- Gas compositions - Stoichiometric number SN (SN from 0.5 to 8)
- Amount of feed for the methanol synthesis (from 3.3 Nm³/h to 25 Nm³/h)

During this test campaign the electrolyser will be operated at full load and feed the methanol synthesis pilot plant. In case it is needed supplemental hydrogen will be added from the backup tank.

5.3.3 Dynamic PEMWE operation and its influence on PtMeOH reaction

In a first test, the load of the electrolyser will be repeatedly changed from minimum to maximum load (10%-100%) with a hold time of each step of several hours down to 15 min. For every load change, the response of the inlet composition to the methanol synthesis pilot plant, the reaction conditions and the outlet composition will be analysed. This test will be performed at different feed volume flow rates to the methanol synthesis pilot plant to test the response time. (Total feed flow range (CO_2+H_2): 3.3 Nm^3/h for H_2 from electrolysis only up to 25 Nm^3/h total including backup H_2).

In a second test, the electrolyser will be operated by programming the current input according to a renewable energy profile, like for example a wind energy plant or a solar energy plant. During this test the amount and stoichiometry of the gas delivered by the gas mixing station stays constant. Therefore this will lead to a change in overall input stoichiometry and flow rates to the methanol synthesis plant depending on the amount of H_2 produced. It is proposed to test different scenarios in terms of H_2 backup quantity.

6. Appendix

6.1 Polarization curve test procedure

The polarization curve will be determined under nominal conditions (T_{stack} = 80°C, p=40 bar) as well as under different reaction conditions depending on the testing scenarios. The control accuracy and the sampling rate of the static test input parameters will be compliant with the specifications given in the EU harmonised polarisation curve test method. The measurement will be performed under galvanostatic control with a cut-off voltage at beginning of life of 2.0 V. At the end of life a cut-off voltage of 2.5 V will not be exceeded.

For the measurement the stack will be operated at the highest current density (2 A/cm^2) at nominal conditions until a stable voltage, temperature and pressure is established for a duration of 120 minutes. Afterwards the descending part of the polarisation curve will be recorded by measuring from the highest to the lowest current density.

From the highest current density (2 A/cm^2) to 0.5 A/cm^2 the current density will be changed in steps of 0.1 A/cm^2, below smaller steps of 0.05 A/cm^2 will be applied (cf. Table 9). The lowest current density for the measurement will be 0.2 A/cm^2 (10 % of nominal load). The dwell time will be chosen so that the cell voltage does not deviate by more than ± 5 mV over a duration of 30 s and that the stack is in thermal equilibrium. The data acquisition starts at stable conditions and lasts for at least 30 s. As proposed in the harmonized polarization test protocol the pressure may be reduced for the measurement at low current densities in case the measured hydrogen crossover is too high.

Subsequent to the descending part the ascending part can be recorded in the reverse order.

Table 9. Steps for recording a polarization curve.

Setpoint	Current density [A/cm2]	Step duration [s]
1	2.0	
2	1.9	
3	1.8	
4	1.7	
5	1.6	
6	1.5	
7	1.4	
8	1.3	
9	1.2	
10	1.1	
11	1.0	
12	0.9	
13	0.8	
14	0.7	
15	0.6	
16	0.5	
17	0.45	
18	0.4	
19	0.35	
20	0.3	
21	0.25	
22	0.2	

6.2 Steady State Degradation Test Protocol

A steady state degradation test (Table 10) will be performed to get insights about the availability of the electrolyser system as well as the degradation rate. The test protocol was adapted from the "Steady state degradation test protocol for in-situ cell and short stack testing of PEMWE, AWE and AEMWE" that can be found in [3]. However, as in PROMET-H2 WP5 a whole industrial PEM electrolyser system will be tested instead of a single cell or short stack, it is not possible to disconnect the current supply and to leave the testing set-up under OCV conditions. Therefore steps 6-8 from the original protocol have been eliminated for the steady state degradation test protocol in PROMET-H2.

Table 10. Steady state degradation test protocol, adapted from [3].

Step	Description
1	Perform activation and conditioning according to cell / stack manufacturer specifications
2	Set the test input conditions (TIPs) according to reference operating conditions
3	Perform a BoT polarization curve and record voltage at the corresponding current density j, V(t1)
4	Operate the stack at constant TIPs for 500 hours
5	Perform a polarization curve and record voltage at same j, representative of V(t1-Dt1) or V(ti + Dti) for subsequent iterations
6	Repeat steps 4 to 5 to test ends with step 4 after 3000 h (t=2000h, t_{max}=4000 h) hours of steady state operation or when the EoT criterion is reached.

6.3 FCR test protocol

Table 11. FCR test protocol, reproduced from [2].

Step	Test time (s)	Description
1	0	Set the power set point to P_{med}. Measure the system electrical power input and the rectifier electrical power input vs. time.
2	3600	Set the power set point to P_{up}. Measure the system electrical power input and the rectifier electrical power input vs. time.
3	4530	Set the power set point to P_{med}. Measure the system electrical power input and the rectifier electrical power input vs. time
4	5460	Set the power set point to P_{up}. Measure the system electrical power input and the rectifier electrical power input vs. time
5	6390	Set the power set point to P_{med}. Measure the system electrical power input and the rectifier electrical power input vs. time
6	7320	Set the power set point to P_{low}. Measure the system electrical power input and the rectifier electrical power input vs. time
7	8250	Set the power set point to P_{med}. Measure the system electrical power input and the rectifier electrical power input vs. time
8	9180	Set the power set point to P_{low}. Measure the system electrical power input and the rectifier electrical power input vs. time
9	10110	Set the power set point to P_{med}. Measure the system electrical power input and the rectifier electrical power input vs. time
10	20240	End of test.

6.4 mFRR negative control power test protocol

With the mFRR negative control power load profile the electrolyser power increase upon request is tested. The system power is considered stable if the average power of two consecutive intervals of 60 seconds does not differ by more than (±0.05 (P_{up}-P_{low})).

Table 12. mFRR negative control power test protocol, reproduced from [2].

Step	Description
1	Set system at P_{low}
2	Wait for system power to stabilize*
3	Operate at this level for 1 hour
4	At $t=t_1$ initiate power ramp of power (25% (P_{up}-P_{low})) in 15 minutes
5	$t=t_1$+900 seconds: end of ramp
6	Keep set power for 5 minutes
7	Set system at P_{low} (the time the system needs to return to P_{low} is not evaluated)
8	Wait for system power to stabilize*
9	At $t=t_2$, initiate power ramp of power (50% (P_{up}-P_{low})) in 15 minutes
10	$t=t_2$+900 seconds: end of ramp
11	Keep set power for 5 minutes
12	Set system at P_{low} (the time the system needs to return to P_{low} is not evaluated)
13	Wait for system power to stabilize
14	At $t=t_3$, initiate power ramp of power (75% (P_{up}-P_{low})) in 15 minutes
15	$t=t_3$+900 seconds: end of ramp
16	Keep set power for 5 minutes
17	Set system at P_{low} (the time the system needs to return to P_{low} is not evaluated)
18	Wait for system power to stabilize*
19	At $t=t_4$, initiate power ramp of power (100% (P_{up}-P_{low})) in 15 minutes
20	$t=t_4$+900 seconds: end of ramp
21	Keep set power for 15 minutes
22	At $t=t_5$, initiate power ramp of power (-100% (P_{up}-P_{low})) in 15 minutes
23	$t=t_5$+900 seconds: end of ramp
24	Keep set power for 15 minutes
25	At $t=t_6$, initiate power ramp of power (+100% (P_{up}-P_{low})) in 15 minutes
26	$t=t_6$+900 seconds: end of ramp
27	Keep set power for 60 minutes
28	At $t=t_7$, initiate power ramp of power (-100% (P_{up}- P_{low})) in 15 minutes
29	$t=t_7$+900 seconds: end of ramp
30	Wait for system power to stabilize*
31	End of test

6.5 mFRR positive control power test protocol

With the mFRR negative control power load profile the electrolyser power decrease upon request is tested. The system power is considered stable if the average power of two consecutive intervals of 60 seconds does not differ by more than (±0.05 (P_{up}-P_{low})).

Table 13. mFRR positive control power test protocol, reproduced from [2].

Step	Description
1	Set system at P_{low}
2	Wait for system power to stabilize*
3	Operate at this level for 1 hour
4	At t=t_1 initiate power ramp of power (-25% (P_{up}-P_{low})) in 15 minutes
5	t=t_1+900 seconds: end of ramp
6	Keep set power for 5 minutes
7	Set system at P_{low} (the time the system needs to return to Plow is not evaluated)
8	Wait for system power to stabilize*
9	At t=t_2, initiate power ramp of power (-50% (P_{up}-P_{low})) in 15 minutes
10	t=t_2+900 seconds: end of ramp
11	Keep set power for 5 minutes
12	Set system at P_{low} (the time the system needs to return to P_{low} is not evaluated)
13	Wait for system power to stabilize*
14	At t=t_3, initiate power ramp of power (-75% (P_{up}-P_{low})) in 15 minutes
15	t=t_3+900 seconds: end of ramp
16	Keep set power for 5 minutes
17	Set system at P_{low} (the time the system needs to return to Plow is not evaluated)
18	Wait for system power to stabilize*
19	At t=t_4, initiate power ramp of power (-100%(P_{up}-P_{low})) in 15 minutes
20	t=t_4+900 seconds: end of ramp
21	Keep set power for 15 minutes
22	At t=t_5, initiate power ramp of power (+100% (P_{up}-P_{low})) in 15 minutes
23	t=t_5+900 seconds: end of ramp
24	Keep set power for 15 minutes
25	At t=t_6, initiate power ramp of power (-100% (P_{up}-P_{low})) in 15 minutes
26	t=t_6+900 seconds: end of ramp

27	Keep set power for 60 minutes
28	At $t=t_7$, initiate power ramp of power (+100% (P_{up}- P_{low})) in 15 minutes
29	$t=t_7$+900 seconds: end of ramp
30	Wait for system power to stabilize*
31	End of test

6.6 References

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6.6 Figures

6.6 Tables