





Deliverable 4.2:

Report on the overall system design and operational tests of the combined system

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Glossary

Abbreviation / acronym	Description
AC	Alternating current
approx.	Approximately
bara	Bar absolute
BoP	Balance of Plant
DC	Direct current
Del	Deliverable
DoW	Description of Work
ESC	Electrolyte supported cells
HEX	Heat Exchanger
HTE	High-temperature electrolysis
ISM	Integrated Stack Module (sunfire)
NTP	Normal temperature and pressure
OCV	Open circuit voltage
PtG	Power-to-Gas
SOEC	Solid oxide electrolyser cell
SOFC	Solid oxide fuel cell
WP	Work package
SC	Steam Conversion
TRL	Technology Readiness Level

Project partner acronyms	
КІТ	Karlsruhe Institute of Technology
POLITO	Politecnico di Torino
SUNFIRE	sunfire GmbH
ERIC	European Research Institute of Catalysis A.I.S.B.L.
EEI	EthosEnergy Italia
NTUA	National Technical University of Athens
DVGW	DVGW - German Technical and Scientific Association for Gas and Water

1. Executive summary

The objective of the HELMETH project was the proof of concept of a highly efficient Power-to-Gas (PtG) technology with methane as a chemical storage and by thermally integrating high-temperature electrolysis (SOEC technology) with methanation. This thermal integration balancing the exothermal and endothermal processes is an innovation with a high potential for a most energy-efficient storage solution for renewable electricity, without any practical capacity and duration limitation, since it provides SNG (Substitute Natural Gas) as a product, which is fully compatible with the existing pipeline network and storage infrastructure.

The realisation of the PtG technology as proposed within HELMETH needed several development steps and HELMETH focused on two main technical and socio-economic objectives, which have to be met in order to show the feasibility of the technology.

First target was the elaboration of the conditions and scenarios for an economic feasibility of the PtG process towards methane as chemical storage, without significantly deteriorating the $CO_{2^{-}}$ balance of the renewable electricity. Second target was the demonstration of the technical feasibility of a conversion efficiency > 85 % from renewable electricity to methane, which is superior to the efficiency for the generation of hydrogen via conventional water electrolysis.

Within HELMETH the main focus lay in the development of a complete pressurized PtG system consisting of a pressurized steam electrolyser module, which is thermally integrated with an optimized carbon dioxide methanation module. The HELMETH project has proven and demonstrated that the conversion of renewable electricity into a storable hydrocarbon by high-temperature electrolysis (HTE) and methanation is a feasible option. Both units can be coupled and thermally integrated towards highest conversion efficiencies by utilizing the process heat of the exothermal methanation reaction in the high-temperature electrolysis process.

At the sunfire facility in Dresden, the demonstration plant consisting of a 10 kW_{el} pressurized high temperature electrolyser module and the methanation module was assembled and operated. The achieved overall electrical efficiency of the small-scale demonstration plant was > 75 $%_{HHV}$. This value is far higher than any other existing PtG technology. Detailed analysis of the experimental data revealed the deviations between the theoretically expected values and achieved experimental results. Based on a sensitivity analysis, the feasibility of an electrical efficiency > 80 % for a full-scale plant can be projected. This value matches well with the assumptions and simulations from the beginning of the project. As another promising result, the obtained SNG quality was very high (< 2 vol.-% hydrogen and > 97 vol.-% methane), meaning that the produced SNG could be injected to the natural gas grid in Europe without any restrictions. A technological bottleneck identified within HELMETH project, is the need for a sophisticated steam mass flow control at the electrolyser inlet. An instable mass flow control prevented an extended testing of the PtG plant, therefore, the coupling wasn't completely successful.

Thus, the main objective of the project to prove the feasibility of an integrated PtG process for highly efficient storage of renewable energy was achieved. The project showed a successful operation of the world-wide first complete pressured high-temperature electrolyser in coupling with an innovative methanation unit layout.

Finally, the technical and economic feasibility of a pressurized HTE has been evaluated. The results have been used for the evaluation of Sunfire's product development strategy.

2. Introduction

Renewable energy sources such as wind energy and photovoltaic provide electrical power in a volatile manner. This volatility results in several hours and even days of electricity surpluses and deficits. As the share of these sources in power supply increases, long-term or even seasonal storage capacities must be established to ensure a reliable energy supply. Power to Gas (PtG) describes the conversion of electrical power into chemically stored energy by water electrolysis and an optional subsequent methanation with carbon dioxide. Currently the majority of PtG plants are focusing on Power-to-Hydrogen with an injection of the produced hydrogen into the natural gas grid. By doing so, the amount of hydrogen injected is limited by the particular natural gas grid regulations and usually in the range of < 10 vol.-%. With and additional CO_2 -methanation step, synthetic natural gas (SNG) can be produced which is under certain criteria fully compatible with the existing pipeline network and storage infrastructure. Overviews of PtG technologies and plants under operation can be found in (1), (2) and (3).

State of the art Power-to-SNG plants use low-temperature electrolysers like alkaline or PEM (Polymer electrolyte membrane/ Proton exchange membrane) as electrochemical hydrogen source. One of them is the Audi e-gas project/plant in Werlte, Germany. It is the worldwide largest commercial PtG plant and in operation since 2013. For electrolysis 3 pieces 2 MW unpressurized alkaline electrolysers are used, followed by a subsequent one-stage CO_2 -methanation reactor. Before methanation, the produced hydrogen is pressurized. The methanation unit of the plant in Werlte is shown in Figure 2-1.



Figure 2-1: Methanation unit of the Audi e-gas project (3)

The amount of information in literature about process details and operating experience is very limited. The overall Power-to-Gas efficiency is stated with 54 % (2).

In contrast to state of the art operations, the HELMETH project is the worldwide first module combining pressurized high temperature steam electrolysis and CO₂-methanation. It is based on a

thermal integration of the exothermic methanation of carbon dioxide with the heat demanding high temperature steam electrolysis. By providing steam from the methanation modules cooling system to the electrolysis module, both can be thermally integrated. Through directly electrochemically converting steam instead of liquid water (low temperature electrolysis), the amounts of electricity required can be significantly reduced, resulting in a higher overall PtG efficiency. In Figure 2-2 the simplified HELMETH process is shown.



Figure 2-2: Schematic HELMETH Power-to-Gas concept with potential applications.

Starting from (surplus) renewable energy, steam is converted electrochemically into oxygen and hydrogen. After mixing the hydrogen with CO_2 , both are catalytically converted by the exothermic CO_2 -methanation reaction into methane and water. After condensing the produced water, the remaining methane (SNG) can be directly injected in the natural gas grid if certain quality criteria are fulfilled. The heat of reaction from the methanation is used to produce steam for the electrolysis, which in turn produces the required hydrogen. Both units are therefore thermally integrated/coupled.

The objectives of the HELMETH project related to the coupled Power-to-Gas unit are:

- Proof of concept of a highly efficient PtG technology
- Thermal integration of high temperature electrolysis with CO₂-methanation
- Technical feasibility of a conversion efficiency > 85 %

Individual SOEC and methanation unit related objectives are summarized in the dedicated chapters.

While a lot of data and information is available on SOC operation from cell level to full scale systems at ambient pressure (fuel cell and electrolysis operation, e.g. (4), (5)), nearly no literature can be found on pressurized operation. Most of the available literature is based on theoretical analysis and simulations (6), experimental data is only available at cell level (7), (8) and very few on stacks (9).

Generally, the influence of pressure on SOEC performance is low. Advantage is seen at system level in an integrated process at higher pressures, e.g. Power-to-Gas with coupled methanation that operates above 10 bar.

The present deliverable 4.2 "Report on the overall system design and operational tests of the combined system" is part of the work package WP4 "System integration and testing". It is based on the successful completion of development steps performed in the preceding work packages:

- WP1 Conceptual design and simulation
- WP2 SOEC based electrolyser module development
- WP3 Methanation module development

The major outcomes of the previous steps for the coupled prototype are summarized in this Deliverable. For more detailed information, it is referred to the following Deliverables:

- Del. 1.1 Report on the specification of the overall system and main components
- Del. 1.2 Flow sheet and process simulation
- Del. 1.3 Report on the safety concept of the Power-to-Gas system
- Del. 2.1 Report on the pressure vessel design
- Del. 2.2 Report on short stack testing
- Del. 2.5 Report on the stand-alone electrolyser testing
- Del. 3.3 Report on design and characterization of methanation module

3. Power-to-Gas system

The working principle of the HELMETH PtG concept is based on a hydrogen production through SOEC technology and a following CO_2 -methanation unit. The heat release of the exothermic methanation reaction is used to produce steam for the high-temperature electrolysis. By using the heat of reaction for feeding steam into the SOEC, both modules are thermally integrated (see Figure 3-1).



Figure 3-1: Schematic thermal integration of SOEC and methanation unit

Compared to low-temperature electrolysers like Alkali or PEM, an electrolysis of steam offers the benefit of a reduced energy consumption. By energy-balancing the CO₂-methanation reaction:

$$CO_2 + 4H_2 \rightleftharpoons CH_4 + 2H_2O$$
 $\Delta_r H_{298}^0 = -165 \ kJ/mol$
the electrolysis of steam at > 800 °C

$$H_2 O_{(q)} \rightleftharpoons H_2 + \frac{1}{2} O_2 \qquad \Delta_r H_{1073}^0 = -250 \ kJ/mol$$

and the evaporation of water

$$H_2 O_{(l)} \rightleftharpoons H_2 O_{(g)} \qquad \qquad \Delta_{vap} H_{298}^0 = 44 \ kJ/mol$$

it can be seen that the heat of reaction is in the range of being capable to produce the required amount of steam (at 100 % steam conversion).

The PtG efficiency is defined as:

$$\eta_{PtG} = \frac{\dot{n}_{CH4} \cdot HHV_{CH4}}{P_{el}}$$

By using the following very simplified assumptions:

- 100 % steam conversion in SOEC
- 100 % reactant conversion in methanation module
- No electrical consumers beside the electricity demand for a electrochemical steamsplit at 800 °C

an upper efficiency limit can be calculated

$$\eta_{PtG} = \frac{1 \cdot 890.28 \frac{kJ}{mol}}{4 \cdot 250 \frac{kJ}{mol}} = 89 \%$$

In reality the assumptions are not justified and considerations of the following need to be drawn:

- Steam conversion of the SOEC is below 100 % and a surplus of steam is required to produce the designated amount of hydrogen
- Heat release from the exothermic methanation reaction is not sufficient to produce the excess steam, therefore an electrical heater is necessary
- A complete conversion of the CO₂-methanation is not feasible as limitations through chemical equilibrium apply. The real reactant conversion is dependent on factors like reactor concept, operating pressure and temperature, etc.
- Recuperation of heat in both modules is essential and dependent of heat exchanger (HEX) network and performance. E.g. electrolysis products H₂ and O₂ leave the SOEC stack at roughly 850 °C and are used to overheat the saturated steam feed.
- Performance of HEX can be expressed in terms of a pinch-point¹. Pinch-points of 10 °C are often used in literature for very well working HEX. In reality such a low pinch-point requires a very high heat transfer area. Therefore, an additional electrical heater is necessary.
- Pressure levels of produced steam in methanation module and SOEC are not identical. By reducing the pressure of steam adiabatically², condensation may occur at certain points. A re-evaporation of that condensate is not foreseen in the HELMETH prototype resulting in a direct efficiency loss
- As both modules operate at elevated temperatures, heat losses apply even through insulation.
- The system requires an AC/DC conversion step, that has an efficiency in the range of 94...97%.
- Auxiliary devices like air supply, pumps, trace heating, ventilation, control & safety system cause parasitic losses that need to be taken into account.

The above mentioned considerations were in detail investigated in Del 1.2 "Flow sheet and process simulation", resulting in the following extended PtG-efficiency:

$$\eta_{PtG-CH4} = \frac{\dot{n}_{CH4} \cdot HHV_{CH4}}{P_{el,soec} + \dot{Q}_{additional}}$$

By introducing $\dot{Q}_{additional}$ as additional heat source/ electric consumers, a realistic maximum efficiency for large-scale systems of 85 % was calculated, and thus principally confirming the feasibility of the HELMETH concept

¹ Point where temperature difference between hot- and cold-stream in a HEX are minimal

² Adiabatic = Isenthalpic = no transfer

4. Pressurized SOEC

As hydrogen supply for the methanation unit a high-temperature electrolyser (HTE) was selected. The HTE has a remarkable higher electrical efficiency compared to other electrolysis techniques, the advantage is in the range of 15 %. Figure 4-1 shows the energy demand of electrolysis technologies working at the thermodynamic optimum. HTEs typically operate at significantly higher temperatures of about 850 °C compared to PEM and Alkaline electrolysers. Due to the higher temperatures, the specific electric energy demand is lower for HTEs than for the competing technologies. This results in potentially higher electrical system efficiencies of up to 90 % based on the lower heating value, as a significant share of energy input can be provided by heat or waste heat from industrial processes, respectively.

The potential low electrical energy demand, shown in Figure 4-1, and the higher overall electrical efficiencies, respectively, substantially contribute to the target of 40 kWh_{el} per kg hydrogen identified in the "Electrolysis Study" from FCH-JU (10) (see Figure 4-1, dotted line). The study also indicates that SOEC has still a huge potential of further cost reduction compared to other electrolysis technologies operating at lower temperatures, which can eventually result in system costs similar to alkaline electrolysers.



Figure 4-1: Energy demand of electrolysis technologies at the thermodynamic optimum

The main energetic step is the usage of steam instead of liquid water. The exothermic methanation process provides the necessary waste heat for the evaporation process. This is a unique feature for the HELMETH process layout.

A high temperature electrolyser was designed to be operated at high pressure up to 15 bar. At the time of the project, it is the first pressurised high temperature electrolysis system worldwide. So far, only simulations (6) or tests at cell and stack level (7), (8), (9) had been performed.

The reason for this approach is again the increase in total efficiency of the complete system. Hydrogen is used in many industrial applications, most of them require inlet pressure that is higher than ambient pressure. For high temperature electrolysis, so far the common approach is to operate at ambient pressure and add a compression step afterwards. Due to the low density, compression of hydrogen is challenging from the technical point of view and consumes a lot of electrical energy, e.g. compared to the compression of water. The pressurised operation of the high temperature electrolyser allows to save this compression step and instead to generate the hydrogen at the required pressure of the following process step. The usage of steam is beneficial too, because steam has an elevated pressure as well, depending on the temperature. The assumption of the HELMETH concept is the setting of the pressure in the steam supply and operating the whole unit at more or less equal pressure, supplying pressurized hydrogen to the methanation unit.

Details on the system setup and results of the stand-alone operation are described in the previous Deliverable 2.5 'Report on the stand-alone electrolyser testing' and in (11).

4.1. Setup

Sunfire stacks with electrolyte supported cells (ESC) with an active area of 127.8 cm² each were used. In total the electrolyser module consist of 90 cells. The cell has a Ni-GDC (nickel/gadolinium doped ceria oxide) cathode, a 3YSZ (3 mol% yttria stabilized zirconia) electrolyte and a LSCF (lanthanum strontium cobalt ferrite) anode, with several interface layers. Sheet metal interconnects (Crofer 22 APU) with a protective coating are used. Gaskets out of glass ensure a very good gas tightness between anode and cathode side.

The 'hot' BoP unit consists of a heat exchanger and an electrical heater for each, anode and cathode side. Additionally, an electrical evaporator is attached to ensure the stand-alone operation, when no external steam is supplied.

The evaporator, electrical heaters and heat exchangers are developed by sunfire. To heat up the gases, direct electrical heaters with a power of 3.5 kW each are used. The heat exchanger on the hydrogen side has a plate-type design. On the oxygen side, a complex heat exchanger build by additive manufacturing (Direct Metal Laser Sintering - DMSL) developed inside the HELMETH project was integrated in the final operational step.

The electrolyser system was installed in a standard container (20 ft) which is equipped with a full safety system, safety valves and blowouts. The whole system was inspected and approved due to the Pressure Vessel Directive by an approved inspection authority.

The system includes the pressure vessel, media supply, pressure control system, electrical DC power supply for electrolysis and a control cabinet, all installed inside the container. The water supply for stand-alone operation is done with deionized water. The container with the system can be seen in Figure 4-2.



Figure 4-2: SOEC pressure vessel inside container

4.2. Results of the stand-alone operation

Details of the testing results can be found in Deliverable 2.5 'Report on the stand-alone electrolyser testing' and in (11). The pressurized HTE system has been operated for more than 500 hours. The main focus and complexity was the control of the pressure difference between hydrogen side and oxygen side of the stack at different conditions. The differential pressure could be controlled in a way that it did not exceed \pm 100 mbar in all operation points, even in the transient states. Nevertheless, a control deviation can lead to pressure fluctuations that might damage the stacks irreversibly. During the project lifetime, several stacks needed to be replaced.



Figure 4-3: Complete test run in pSOEC mode

An example of the system operation under variation of stack pressure, steam flow and temperature are shown in Figure 4-3. Different trials have been made for maximizing the steam conversion and increasing the pressure. A steam conversion of up to 90 % could be achieved even under pressurized conditions.

4.3. Efficiency of the high temperature electrolyser

In terms of possible business models, the efficiency of an electrolysis system is of high importance. The reason is that the overwhelming part of the total operation costs (OPEX) comes from the required electrical energy. To justify higher investment costs (CAPEX) for a high temperature electrolyser, it has to have higher efficiencies than the competing technologies.

The efficiency can be calculated at different levels. First is the stack efficiency itself, only taken into account the produced amount of hydrogen and electrical DC power input:

$$\eta_{Stack} = \frac{\dot{V}_{H2_Output} \cdot HHV_{H2}}{P_{el_DC_Stack}} = \frac{c}{U_{Stack}}$$

The HHV of Hydrogen is 3.54 kWh/Nm³. Next step is to consider the heat losses. The assumption is that the heat losses are balanced by the two electrical heaters. As the AC side of the system is not measured, the power of the electrical heaters is considered as the nominal AC power multiplied with the control signal (PWM – pulse width modulation):

$$\eta_{Heat_Loss} = \frac{\dot{V}_{H2_Output} \cdot HHV_{H2}}{P_{el_DC_Stack} + P_{el_AC_Gas_Heaters}}$$



Figure 4-4: Efficiency of Stack itself and with compensation of heat losses and evaporation

To complete the picture, the electrical evaporation has to be taken into account for this specific system:

$$\eta_{Total} = \frac{\dot{V}_{H2_Output} \cdot HHV_{H2}}{P_{el_DC_Stack} + P_{el_AC_Gas_Heaters} + P_{el_AC_Evaporator}}$$

Figure 4-4 shows the average stack temperature, the total current and the corresponding hydrogen production, average cell voltage and the efficiencies of the stack and the system.

The stack efficiency is independent of the current and the steam conversion. The reason is that η_{Stack} is only indirectly proportional to the stack voltage, while current and hydrogen production are related by a constant factor and HHV is also constant. In case the stack is operated close to the thermoneutral voltage (approx. 1.25 to 1.3 V / cell), the electrical efficiency of the stack is about 110%_{HHV} (peak at the beginning due to measurement inaccuracy at low current). The reason for electrical efficiencies above 100% is that the required energy for the electrolysis is partly coming from the thermal energy of the steam.

When the electrical heaters and the electrical evaporator are taken into account the picture is changing. The efficiency η_{Total} drops to values about 75 ... 80%, because the evaporation enthalpy has to be overcome. For that reason, it is highly recommended that high temperature electrolyser systems are coupled to existing steam supplies.

To operate at higher pressures, the excess steam requires temperatures of above 200°C, which corresponds to a pressure of about 15 bar. These are pressure levels that can be found in PtL and PtG processes like methanation. The coupling of HTE and methanation as in HELMETH shows the potential of a fully integrated process (integrated at temperature and pressure side).



Figure 4-5: Efficiency shares of heat losses and evaporation

To show the influence in case steam can be used instead of water, in Figure 4-5 the share of the efficiency only with the electrical heaters and stack is shown. With increasing hydrogen production (that means increasing current and increasing stack operation temperature) the efficiency of stack and heaters (η_{Heat_Loss}) rises to above 95%_{HHV} close to 105%_{HHV}. As the gas flow rates and the heater output temperatures are kept constant, a higher stack temperature leads to higher heat transfer in the heat exchangers and therefore less requirement of electrical heating. In a real system, it is likely that also in part load conditions the efficiencies will be high, as flow rates and, if required, heater temperatures will be adjusted to the operation point.

The small-scale demonstration system has a couple of limitations that are not present for a full-scale system. In the following, this will be summarized:

- Heat losses (and temperature drops) are much higher at low flow rates compared to a large-scale system
- A laboratory power supply was used which has a low AC/DC conversion efficiency.
- The container equipment (ventilation, auxiliary heaters, control & safety system) has a high specific electricity consumption in a small-scale system.
- The heat exchangers weren't optimized for the given operation conditions. This is also difficult for the low flow rates. A final system would have a much better heat recovery rate.

5. Methanation unit

The major objective of the methanation module was the development of a unit that is capable of producing steam for the SOEC and SNG at qualities for a gas pipeline feed-in. A summary of objectives for the methanation module and SNG feed-in quality criteria can be found in Table 5-1.

Item	Value	Document/ source
Multi-step methanation module		DoW
Stable and pressurized steam s	upply	DoW
Modulation	20-100 % load	DoW
Stand-by operation	DoW	
SNG feed-in quality		DoW/ Del 1.2
CH ₄	≥ 92.5 Vol%	Del. 1.2
CO ₂	≤ 2.5 Vol%	Del. 1.2
H ₂ ≤ 5 Vol%		Del. 1.2
Feed-in pressure range > 10 bar		Del. 1.2
Max. SNG production 30-60 kW (based on HHV)		Del. 1.2

Table 5-1: Methanation module objectives

For the actual development several reactor concepts were investigated in detail in Del. 1.2 "Flow sheet and process simulation". The use of adiabatic reactors with and without recirculation of product gases was diminished quickly as a realization proofed to be too challenging.

In order to develop a cost- and performance optimized concept, cooled reactors with boiling water cooling were chosen. A simplified rector concept is shown in Figure 5-1.



Figure 5-1: Simplified final HELMETH CO2-methanation reactor design

A detailed description of the module can be found in Del.3.3 "Report on design and characterization of methanation module".

Key results of the methanation module development and test can be summarized as follows:

• For the operation of the methanation module, an optimal boiling water temperature of 250 °C was found.

- For stand-by operation, a hot standby at 250 °C proved to be the most effective mode. Heat losses at 250 °C with no gas flow through the unit are 760 W, with several options to reduce them drastically in future plants
- The operation of the boiling water system was extremely stable resulting in a control range of plus/minus 0.05 °C (see Figure 5-2)





- Start-up time of the reaction was in the range of minutes (< 3 minutes) and for the prototype limited by the operator, as no complete automation was established
- The temperature control within the fixed beds limited the maximum temperature below the allowable catalyst specifications. Temperature profiles within the fixed beds were collected for multiple operating points and showing clear tendencies and influences (see Figure 5-3).



Figure 5-3: Influence of mass flow on the Temperature in R1 at 20 bar

• The produced SNG quality was finally always exceeding the HELMETH quality criteria. As a main indicator of SNG composition, the hydrogen content is used in Table 5-2.

CH4 output duty	6.6	12	20	24	30	36	40	60	kW
10 bar	1.65		1.17		1.7		3.5		vol%
20 bar	High	n quali	ity eas	y to	1.02		1.46		vol%
30 bar	i	achiev	e (τ↓)					1.56	vol%

Table 5-2: SNG quality results in terms of H2 concentration

Additionally a modulation from 20 - 100 % of the design point can be achieved, with the option of even increasing the highest load (not possible within tests, as limited by BoP component size). Operation at 10 - 30 bar posed no problems, with beneficial effects on SNG-quality at the highest operating pressure.

• For future plants the low boiling water temperature of 250 °C and the corresponding steam pressure of 40 bar offers the potential of significantly reducing the size of the pressure vessels. With this reduced pressure compared to the current maximum of 87 bar (300°C), vessel thicknesses can be reduced and therefore the size of the vessels, resulting in even lower heat losses at hot stand-by.

6. Operational tests of the combined system

6.1. Set up and operational results

The demonstration plant was assembled at the sunfire facility in Dresden. Therefore, the CO_2 methanation unit, developed and built by KIT in Karlsruhe, was set up inside a container and after the extensive stand-alone testing transported to sunfire to perform the coupling and combined operational tests.

The methanation container was installed as close as possible to the electrolyser container (Figure 6-1). For the coupling, it was planned to have as less interfaces as possible, from the fluidic as well as from the electrical and signal point of view. The minimum number of fluidic connections is two: the steam outlet from the methanation cooling circuit to the electrolyser and vice versa the hydrogen output from the electrolyser to the methanation unit. The steam was converted to hydrogen in the electrolyser.

No control loops or signals were exchanged, as both units can react on their own to changes on the inlet flows. Even no safety signals were exchanged, because the previous stand-alone operation required an intrinsically safety of each of the units. So, besides the two fluidic connections, only an Ethernet connection for remote access was built.



Figure 6-1: Coupled PtG plant (left container: methanation; right container: electrolyser)

For the combined operational tests, the methanation module was operated at a stable operating point with a gas feed-in pressure of 10 bar. The required hydrogen was drawn from a line that included the SOEC outlet and bottled hydrogen. From a methanation point of view the main focus was on a stable steam supply for the electrolysis. Steam from the methanation module cooling system was generated at 250 °C (40 bar) and then reduced in pressure down to 12.7 bar as shown in Figure 6-2.



Figure 6-2: Stability of steam supply from methanation unit to electrolyser

The generation of steam was very stable with a minor emergency event due to SNG-burner blowoff (strong winds) at around the time 15:10.

Operational data from the electrolyser in the coupled mode are given as an example in Figure 6-3.



Figure 6-3: part load operation of electrolyser in coupled PtG plant

Steam pressure from the methanation module was set by using a pressure relief valve at a higher pressure than the electrolyser operational pressure, in order to allow flowrate control by control valves in the electrolyser unit.

However, the steam flow control in the electrolyser showed unexpected and strong fluctuations (Figure 6-3). Thus, overvoltages occurred suddenly and the safety system of the electrolyser

switched off the power supply to protect the stack. A stable operation was hardly achievable or for very short duration. As a consequence, only part load operation could be achieved for a short time in the coupled mode. Full load would have required a longer and voltage stable operation in the exothermal mode to obtain higher temperatures and therefore lower resistance with the possibility for higher current density.

While in the stand-alone operation of the electrolyser the steam flow rate was controlled by the liquid water flow rate feed to an electrically driven evaporator within the electrolyser unit, in the coupled operation, this flowrate control has to take place in the steam line. It was identified, that there is the need for new technical solutions for accurate steam mass flow control at extremely low steam volume flow rates at the electrolyser inlet. Since the electrolyser module operates at pressures in the range of up to 15 bar, while differential pressure between the not communicating anode and cathode side should remain well below 100 mbar to avoid stack damage, even small fluctuations in the steam volume flow rate are critical.

Because of these circumstances and since stable operation could not be maintained over a reasonably sufficient duration, a reliable measurement of the efficiency of the pilot plant could not be done in the coupled operation. However, since both modules were reliably characterized over longer operational time in stand-alone stable operation, efficiencies were calculated by the results of the stand-alone operation of both modules.

6.2. Efficiency calculation based on stand-alone module tests

Based on the steam amounts produced from the methanation module cooling system (see Figure 6-4) and with the results from the stand-alone electrolyser tests, the efficiency of the combined modules was calculated. The basis of these calculations is solid, as only the steam transport line heat losses are neglected.

The derivation of the PtG efficiency equation will be conducted in detail along the scheme from Figure 6-4.



Figure 6-4: Schematic sketch of streams and enthalpies

As in previous deliverables shown, the PtG efficiency is the higher heating value of the produced methane (without remaining H_2) per electrical energy consumed.

$$\eta_{PtG-CH4} = \frac{\dot{n}_{CH4} \cdot HHV_{CH4}}{P_{el,soec} + \dot{Q}_{additional}}$$

1

The molar flow of produced methane is one forth (stoichiometry) of the fed hydrogen times the conversion

$$\dot{n}_{CH4} = 0.25 \cdot \dot{n}_{H2} \cdot X \tag{2}$$

Using the ideal gas law, the molar flow can be written in terms of volume flow (NTP)

$$\dot{n}_{H2} = \frac{p_n \cdot \dot{V}_{H2,n}}{R \cdot T_n}$$

Inserting 3 in $1 = 1^*$

$$\eta_{PtG-CH4} = \frac{0.25 \cdot \frac{p_n \cdot \dot{V}_{H2,n}}{R \cdot T_n} \cdot X \cdot HHV_{CH4}}{P_{el,soec} + \dot{Q}_{additional}}$$
1*

The electricity consumption of the SOEC can be derived from its "heat loss" efficiency. This is including all electrical consumers in the SOEC system without the built in evaporator.

$$\eta_{Heat-loss} = \frac{\dot{V}_{H2,n} \cdot HHV_{H2}}{P_{el,soec}}$$

$$4$$

Inserting 4 in $1^* = 1^{**}$

$$\eta_{PtG-CH4} = \frac{0.25 \cdot \frac{p_n \cdot V_{H2,n}}{R \cdot T_n} \cdot X \cdot HHV_{CH4}}{\frac{\dot{V}_{H2,n} \cdot HHV_{H2}}{\eta_{Heat-loss}} + \dot{Q}_{additional}}$$
1**

The additional heat demand is due to additional steam that is needed for the SOEC. A main reason for the imbalance is the steam conversion of the SOEC which is below 1. Therefore the heat of reaction is not sufficient to produce the required steam amount.

$$\dot{Q}_{additional} = (\dot{V}_{steam,n,required} - \dot{V}_{steam,n,meth}) \cdot \Delta h_{steam}$$
 5

The required amount of steam is defined by the H₂ consumption and steam conversion

$$\dot{V}_{steam,n,required} = \frac{\dot{V}_{H2,n}}{SC}$$

 Δh_{steam} is the volumetric enthalpy difference from water to steam at the desired temperature/pressure level. T_{water} is the feed in temperature of the additional water into the methanation reactor and is defined by the HEX and their performance

$$\Delta h_{steam} = h''(250^{\circ}C) - h(T_{water})$$

6 and 7 in 5 = 5*

$$\dot{Q}_{additional} = \left(\frac{\dot{V}_{H2,n}}{SC} - \dot{V}_{steam,n,meth}\right) \cdot \left(h''(250^{\circ}C) - h(T_{water})\right)$$
5'

5* in 1** results in the final equation for the efficiency calculation

$$\eta_{PtG-CH4} = \frac{0.25 \cdot \frac{p_n \cdot V_{H2,n}}{R \cdot T_n} \cdot X \cdot HHV_{CH4}}{\frac{\dot{V}_{H2,n} \cdot HHV_{H2}}{\eta_{Heat-loss}} + \left(\frac{\dot{V}_{H2,n}}{SC} - \dot{V}_{steam,n,meth}\right) \cdot \left(h^{\prime\prime}(250^{\circ}C) - h(T_{water})\right)}$$

$$1^{***}$$

The values used for the calculation are summarized in Table 6-1 and chosen very conservative.

7

Symbol	Explanation	Value
p_n	Pressure (NTP)	1.013 bar
<i>V</i> _{H2,n}	Hydrogen consumption of methanation module at operating point	See Del. 3.3
R	Universal Gas constant	8.31425 J/(mol·K)
T _n	Temperature (NTP)	273.15 K
Х	Conversion	0.98958 ¹
HHV _{CH4}	Higher Heating Value CH4	890280 J/mol
HHV _{H2}	Higher Heating Value H2	12744000 J/m^3
$\eta_{Heat-loss}$	Stack efficiency including heat losses (DC-stack, gas overheating, <u>no</u> evaporator)	1.05 ²
$\dot{Q}_{additional}$	Additional heating due to missing steam/ low SC	See eq. 5
$\dot{V}_{steam,n,required}$	Required steam amount for a hydrogen production $\dot{V}_{H2,n}$	See eq. 6
$\dot{V}_{steam,n,meth}$	Steam production from Methanation module	See eq.5
SC	Steam Conversion SOEC	0.7 ³
h''(250°C)	Enthalpy of saturated steam at 250 °C	2801 kJ/kg
T _{water}	Reactor inlet temperature of additional Water	100 °C ⁴
$h(T_{water})$	Enthalpy of liquid Water at T _{water}	422.78 kJ/kg
Remarks:		
1	A mean of measured values (= 95 Vol% CH4)	(Underestimated)
2	Mean of sunfire values.	
3	Sunfire value.	Underestimated
4	Estimation from measurements	

Table 6-1: Glossary and values of efficiency calculation

The calculations and resulting values are summarized in Figure 6-5.

60





Figure 6-5: Calculated PtG efficiency

The PtG efficiency is ranging between 75.4 and 76.1 % depending on the measurement point. As mentioned before the used parameters are very conservative. In Figure 6-6 the methane output duty measurement point (76.1 %) was used for a parametric study. An increase of the steam conversion rate from 0.7 to 0.9 would increase the efficiency by 4 %. Improvement of the thermal insulation, resulting in lower heat losses, can lead to an improvement of efficiency by 2.5 %.



Figure 6-6: Major influences on PtG efficiency

The main increase for efficiency can be received from a higher SOEC steam conversion. Here, 70% a currently a standard value for operational safety, however, it was tested that steam conversions of up to 90% can be achieved.

Comparison with Deliverable 1.2

Results from Del 1.2 indicate the posibility to reach an efficiency of 85 %. In order to evaluate the actual value, the calculations from Del. 1.2 have to be recapitulated.

Assumptions for Del 1.2 calculation

- SNG quality from equilibrium reactors .
- Steam Conversion in SOEC = 0.8
- Thermoneutral voltage + external gas over heating = Exothermal voltage

$$\eta_{PtG-CH4} = \frac{\dot{n}_{CH4} \cdot HHV_{CH4}}{P_{el,SOEC} + [\dot{Q}] + heat \ loss} = \frac{0.0672 \frac{mol}{s} \cdot 890280 \frac{J}{mol}}{67023 \ W + [1325 + 963]W + 1000 \ W} = 85.1 \ \%$$

1325 = additional heating in SOEC due to HEX network 963 = additional heating in methanation due to $\underline{SC} = 0.8$ 1000 = heat losses for <u>both</u> modules

Standard case with measured values

Using the values from Table 6-1 results in the following numbers

 $\eta_{PtG-CH4} = \frac{0.06669 \cdot HHV_{CH4}}{66981 + 6379 + 4647} = 0.7612$

66981 = Electricity consumption of SOEC stack

6379 = Electrical heater of SOEC feeds and heat losses of SOEC

4647 = Additional heating for required amount of steam

NOTE: Heat losses of the methanation module are already included in the produced steam amount

From the equations above, it can be concluded, that the SOEC stack is operated in thermoneutral mode and the SNG composition is close to chemical equilibrium. The highest deviations are from the SOEC heater and the additional steam generation required due to the SOEC steam conversion of only 70 %. Additionally it hast to be mentioned that a lower steam conversion also requires a higher SOEC heater duty due to the higher mass flow of steam.

7. Exploitation of results

7.1. Market potentials and business cases for high-temperature electrolyzers and power-to-gas applications

Overview

The key objective of the project is an optimized methanation process in combination with SUNFIRE's high-temperature electrolysis (HTE) for the storage of fluctuating renewable electricity. HTE allows superior efficiencies of more than 90 $%_{LHV}$ if steam is provided from external sources compared to low-temperature variants (alkaline / PEM based electrolysers. Within the HELMETH project, coupling of HTE with exothermal methanation for the production of synthetic natural gas (SNG) is investigated. This has the potential of reaching conversion efficiencies in the range of $85\%_{HHV}$. These high conversion efficiencies allow an economic storage of renewable electricity. Storage of SNG is preferred compared to pure hydrogen: Due to its specific density, an existing infrastructure, and regulatory requirements; the Power to Gas method might be a technically and economic feasible way for load balancing without government subsidy.

In order to achieve a viable business case, new business models need to be elaborated that take into account the interests of different players in the electricity field like wind park operators and owners of thermal power stations. It is evident, that PtG won't be economical in small power classes, but at power levels > 5 MW due to specific cost of the processing plants. Several steps of upscaling will be necessary to reach this target. The highest cost saving potential lies in the HTE itself. Here, viable business cases need to be addressed at smaller scale in order to increase the production volume and with it decrease the production costs. Therefore, further products have been defined in the fields of hydrogen and syngas production.

The following business cases will be investigated in detail:

- 1. High-temperature electrolyzes Hydrogen supply to:
 - Industrial H₂ users (iron & steel, glass, semiconductor)
 - Refineries
- 2. Compact pressurized electrolysers with integrated methanation: PtG process
- 3. Syngas generation by co-electrolysis of steam and carbon dioxide for: PtG / PtL / PtX (X means any hydrocarbon) processes

Hydrogen production for industry & mobility

Globally, the refining, chemical and industrial gas industries use approximately 7.2 EJ (Exajoule) of hydrogen per year according to IEA (12). About one third of total hydrogen production is used for fertilizers (ammonia production). The second largest share is the hydrogen supply to refinery processes followed by chemical production, food processing, metallurgy, glass production, generator cooling and semi-conductor manufacturing.

Today the majority (48 %) of produced hydrogen comes from reforming of natural gas and refinery gas, as a by-product from chemicals production (30 %) and from coal gasification (18 %). Only about 4 % of global hydrogen production (65 million tons) comes from electrolysis (see IEA (12)). However, industrial hydrogen from electrolysis is not destined for specific industry segments but used where it is cost-effective.

It is expected that the global hydrogen usage will substantially grow in the coming years due to the extension of (fluctuating) renewables in the grid or the decarbonization of the transport sector. Hydrogen generated from electricity and water can be stored in large quantities over long periods and retransformed to electricity. It can be converted to synthetic natural gas or sold as fuel for fuel cell vehicles in the transport sectors. Hydrogen can fulfil renewable quotas in refineries if the legal framework is adapted.

Hydrogen or SNG for energy storage require large units at MW-scale and very low electricity prices to become competitive. Hydrogen in industrial applications has a much higher cost tolerance if it competes with logistic H_2 . Sunfire has estimated potential business numbers for three markets:

Germany, UK and California (due to larger amount of renewables). Results for the period 2015 to 2020 are shown in Figure 7-1.



Hydrogen Electrolysis in Germany, the UK and California: 2015 - 2020

Figure 7-1: Market prospective of hydrogen produces by electrolysis

If electrolysers are used to compensate fluctuations from renewable electricity, state-of-the art technologies are PEM and alkaline based electrolysers. A detailed analysis of this technologies is performed in the 'Electrolysis Study' from FCH-JU (13). This study identifies an efficiency target of 40 kWh_{el} per kg hydrogen to be competitive in special hydrogen markets. Only SOEC technology has today the potential to reach this level.

Electricity costs of 50 €ct/MWh, 100 €ct/MWh and 150 €ct/MWh (large industry with high electricity consumption, medium-sized industry and SME) are assumed to calculate hydrogen production costs. It can be seen in Figure 7-2 that 60 to 80 % of total costs are related to the electricity prices indicating the significance of high conversion efficiencies. Also shown are target markets for hydrogen: Industrial hydrogen that is today delivered via gas bottles or trailers is the lowest hanging fruit, followed by hydrogen for refineries (including renewable quotas). In all cases, the SOEC lowers hydrogen production costs by about 12 to 22 %.



Figure 7-2: Cost comparison and target markets for 2025 between SOEC (HTE), PEM, and alkaline based electrolysers (13)

Power to Gas applications

Synthetic (substitute) natural gas (SNG) that is produced by the coupled high-temperature electrolysis and methanation, so-called Power to Gas (PtG) applications, will be the key outcome of the HELMETH project. SNG can be used either for storage of surplus renewable electricity in the natural gas grid or direct usage of compressed natural gas (CNG) for transport applications. The business case PtG is challenging for the following reasons:

- Using surplus renewable electricity allows only a limited number of operation hours (<2000) during the year. This results in very long amortization times; alternatively models of using base load need to be applied.
- Taking an electricity price of 4-5 €ct/kWh results in a SNG price of 5.7-7.1 €ct/kWh (70% efficiency assumed) if only operational costs are considered. The market price of natural gas is in the range of 2-3 €ct/kWh. Thereby, SNG is not directly competitive.
- Surplus wind power and photovoltaics are, at least in Germany, also recompensed if the units are idling due to a low demand in the grid. The EEG (German Renewable Energy Act) prevents alternative usage of surplus electricity. If this compensation would be stopped, it's not clear which market price will establish for surplus electricity.
- SNG production needs a coupling with CO₂ sources and should preferably be close to the location of the renewable power generator. The different possibilities for CO₂ sources are evaluated within HELMETH, as shown in Del.5.1. "Initial LCA results on the "base case HELMETH concept system" and Del. 5.2 "The final LCA report".
- SNG quality criteria for grid injection need to be considered. This makes the unit complex and increases costs.
- Power-to-power efficiencies in a combination of PtG and SOFC reach maximal 50%. This is much lower than electricity storage using batteries. On the other hand, costs of storage capacities (per kWh) are much lower since the natural gas grid is already available. Batteries are no option for long-term storage of fluctuating renewable electricity.

PtG needs sophisticated business concepts in order to be viable. Legislation in Germany (Renewable Energy Act) forces currently a monetary compensation of the renewable energy

producers, even if the electricity cannot be supplied to the grid. On the other hand, natural gas is currently cheap and there is an overabundance of gas in the market, which results in a low incentive of buying 'green' gas. Results of the project will therefore be the investigation of business cases, where PtG could work and to elaborate legislative or similar measures that needs to be taken in future, if the technology is available.

Sunfire has performed different studies for methanation business concepts in the 5 ... 25 MW range (14). The economic feasibility of PtG is mainly determined by the electricity price and the investment cost of the electrolyser and methanation modules. Most critical for the business cases is the production of hydrogen. Results of an economic evaluation are shown in Figure 7-3. The results are based on an electricity price of about 4.5 €ct/kWh which corresponds to current market prices for base-load electricity. It can be seen that the electricity takes about 50 % of the total costs (related to 1 kWh of natural gas). It is therefore the main leverage to improve the economics by increasing the conversion efficiency or buy surplus renewable electricity at lower costs. Investment costs amounts at about 25 % of total costs. Here, the electrolyser is assumed to have a range of 8.2 to 15.2 m€ (for 6.6 MW power it leads to1240 ... 2300 €/kW_{el}). Methanation is estimated to 7.3 m€ and gas processing costs are about 1.6 m€.

Investment costs are lower if the system size is increased. Here, lower stack production costs are assumed but also the specific costs of the methanation unit will be lower. The main revenues are expected to come from the bio fuels share. Subsidies will play a major role in potential business cases.



Figure 7-3: Economic evaluation of PtG concepts

Syngas generation by co-electrolysis of steam and carbon dioxide

Hydrogen could be used in large amounts to synthetize gas and liquid hydrocarbons, whose systems of storage and distribution are well established. Co-electrolysis of steam and CO_2 to produce H_2 and CO is one of the most promising ways to convert electricity into a syngas. Steam plus CO_2 co-electrolysis constitutes the corner point of power to chemicals and power to fuel strategies, for green chemicals, CO_2 recovery and electricity storage at large scale. Indicatively, Power to Gas, by means of the methane as energetic carrier, is a good example and the co-electrolysis process to produce hydrogen and CO as hydrocarbon precursors, is a very promising way on that, resulting in higher conversion efficiencies and lower system complexity (14).

The main challenge is to store excess renewable electricity in the form of hydrogen and CO. By producing syngas, co-electrolysis would enable various storage options like methanation and storage in liquid organic carriers. Co-electrolysis could become a more efficient way of producing hydrogen from electricity. This topic will contribute to hydrogen carriers, using CO₂. The produced syngas, CO plus hydrogen, is again in the scope for multiple ways of conversion, including filtration and utilization of hydrogen for transport and combustion / conversion of CO for stationary applications.

Specifically, co-electrolysis towards liquid fuels offers advantages over an electrolysis plus methanation process, in case where hydrocarbon fuels are the desired final products. Moreover, co-electrolysis can be fed with recycled CO_2 from power generation or industrial processes towards the progressive reduction of GHG emissions. The produced syngas is used for the synthesis of light hydrocarbons as H₂ carriers. The commercialization of co-electrolysis will provide a simpler and cost-efficient way for the production of light-fuels compared to the mainstream technologies, whereas it is advantageous that the expected technology development can be based on the on the existing status of Solid Oxide Cells.

To commercialize this technology improved component design and system optimization are required to increase efficiency, as well as a clear understanding of the integration of the technology in the energy system. Some technological hurdles need to be overcome like long-term stability issues of co-electrolysis or carbon formation risks if the product gas is recuperated.

7.2. Exploitation of project results

High-temperature electrolysers

Sunfire has a high interest of commercializing the HTE for industrial applications, due to costcompetitiveness at small and medium scale (H₂ production 50 ... 400 Nm³/h). This is paving the way for future MW-scale applications in refineries, SNG (power-to-gas) or power-to-liquids. SOEC technology starts from Technology Readiness Level (TRL) of 4 to 5. Field test sales will require at least a TRL of 7, before market entry can be started with TRL 8. The main focus of the economical exploitation will be on the realisation of further demonstrations of system prototypes in different operational environments paid for by third party customers. Potential interest already exists from oil refineries, chemical parks, photovoltaic and wind industry, automotive industry and others in case of a successful realization of the proposed project. The practical results from the proposed project will be used to support the business development of the HTE technology. The involvement of industrial customers will enable the up-scaling to TRL 8 seeing a complete system qualified for different market segments. In a last step, the realisation of actual systems proven in operational environments will be performed. It will be important to identify niche markets were the HTE presents an economic advantage to advance to TRL 9 in order to be a marketable product. The full commercial roll out will happen in 2020-21 latest, seeing first mover customers investing into commercially attractive, unsubsidized projects.

SNG applications

SNG applications require system sizes of at least 5 MW to become competitive. The results of the HELMETH techno-economic analysis show, that currently a subsidy scheme is required in order to realize SNG projects. It is therefore expected, that a further upscaling step will be required and that the regulatory conditions must be in favour of SNG from renewable electricity. A potential market entry of SNG applications won't be before 2021/22.

Syngas generation by co-electrolysis of steam and carbon dioxide

Syngas generation by co-electrolysis of steam and carbon dioxide is currently at TRL 2. First stack tests show the technical feasibility of the concept. However, long-term operation hasn't been tested yet. It has been revealed that recuperative cooling of synthesis gas, which is required for high system efficiencies, bear the risk of carbon formation. Carbon formation limits and prevention strategies have been investigated by sunfire and KIT.

The definition of target markets and cost expectations are currently performed together with a partner from Norway (Nordic Blue Crude). In parallel, the technical feasibility is investigated in the

framework of the German project Kopernikus. The exploitation plan will be developed if the technoeconomic feasibility is proven.

8. Summary and conclusion

The current deliverable 'Report on the overall system design and operational tests of the combined system' summarizes the main findings of the HELMETH project. In a first step, a detailed theoretical analysis of an integrated pressurized high-temperature electrolyser and methanation unit has been performed. It has been shown that the upper efficiency limit is 89 $%_{HHV}$, where a practical efficiency limit is at about 85 %. These results can be obtained from Del. 1.2.

In a next step, Sunfire optimized and operated the worldwide first pressurized high-temperature electrolyser system. The system works at pressure levels up to 15 bar with a stack operation at 850 °C and an input power of up to 10 kW_{el}. It could be shown that the stack performance at elevated pressure is the same like at ambient pressure and that high steam conversion rates up to 90 % can be achieved. Electrolyser efficiencies above 100 $%_{HHV}$ have been proven to be easily possible for a full-scale system. As a drawback it was shown, that the pressure vessel and pressure control are costly and risky. Even if a constant operation regime at different pressure levels could be achieved, small disturbances of the flow or pressure control can result in differential pressure spikes that might damage the stack. Therefore, it was decided within sunfire to favor the ambient pressure operation for a faster scale-up and market introduction of the HTE technology. The pressurized operation requires further R&D activities in order to increase the Technology Readiness Level (TRL).

Parallel to the SOEC related work, KIT developed and built a multistep CO₂-methanation module working with a boiling water cooling. Extensive tests in stand-alone mode were performed in order to characterize the methanation module performance. The gas pressure was varied from 10 to 30 bar and a load modulation from 20 to 100%. Boiling water cooling that can be operated at up to 300 °C (87 bar) showed an extremely stable and effective heat removal capability, while being able to control the temperature in a range of plus/minus 0.05 °C. Based on considerations of high SNG quality, heat removal from the exothermic reaction, steam pressure reduction and others, an optimal boiling water temperature of 250 °C was determined. These 250 °C are equivalent to only 40 bar steam pressure, which is less than half of the maximum design pressure of 87 bar and therefore offering the chance for vessel thickness reduction in future HELMETH plants. For stand-by operation a hot stand-by at 250 °C proved to be most effective, resulting in heat losses of around 760 W with no gas flow. Start-up time of the reaction was in the range of minutes with the chance of significant reduction in fully automatic controlled plants. At the end of the test campaigns the methanation module produced SNG with hydrogen contents below 2 vol.-% and therefore excelling the quality target by far.

Finally, both systems were coupled and installed within the Sunfire premises. This process was quite straightforward since both systems can be operated independently and are only coupled via steam and hydrogen. It turned out that the coupled operation was limited by the challenges in the steam mass flow control at the electrolyser inlet, resulting in large pressure fluctuations and unstable steam conversion rates. Therefore, the coupling wasn't completely successful. By analysing the efficiencies of both systems, an efficiency for the PtG process as high as 76 $%_{HHV}$ could be achieved which is a very good value for a first prototype at small scale. The efficiency of a scaled up plant with the HELMETH technology would be realistically > 80 % due to reduced relative heat losses. An important outcome of HELMETH was also the identification of technical obstacles, which should be in focus in future developments towards reaching technological maturity, namely the accurate flow and pressure control of steam at high pressures and the thermal insulation at high pressures

It has been shown that the market of hydrogen generation for industrial applications is very promising in terms of market size but also business models. An economic feasibility is given provided that the costs of the electrolyser system can be reduced to below $2000 \notin kW$, which seems to be possible by 2020. In parallel, HTE based products must reach a technological maturity which is not given yet. Long-term stability of cells and stacks, dynamic operation, RSOC cycling and H₂ polishing are identified as main obstacles before market penetration can be started.

SUNFIRE has elaborated an exploitation plan, where these technological challenges are addressed. A detailed analysis of required R&D efforts and capital is ongoing.

It has been shown that the PtG this market is challenging due to low natural gas prices as competing fuel and limited yearly hours where surplus renewable electricity is available. In order to bring PtG into the market, the regulatory framework needs to be adjusted. It has been shown that HTE is the only electrolyser technology that has the potential to be competitive with natural gas due to its high conversion efficiencies. Nevertheless, cost reduction targets are ambitious and require large installations in a MW scale and established products. The exploitation of early markets is therefore of very high significance.

The third addressed product is the generation of syngas with co-electrolysis of steam and CO₂. This technology is still in its infancies, so that fundamental questions like long-term durability of cells or carbon formation risks during recuperative the cool-down of product gas need to be answered. Part of this work will be done in the HELMETH framework. A next step is then the investigation of market potentials and business cases. The latter is part of SUNFIRE's company strategy, where co-electrolysis has been identified as key technology for Power to Liquid (PtL) applications.

Bibliography

1. Rönsch, Stefan, et al., et al. Review on methanation – From fundamentals to current projects. *Fuel.* 2016, 166.

2. Bailera, Manuel, et al., et al. Power to Gas projects review: Lab, pilot and demo plants for storing renewable energy and CO2. *Renewable and Sustainable Energy Reviews.* 2017, 69.

3. van Basshuysen, Richard. *Natural Gas and Renewable Methane for Powertrains.* Wiesbaden : Springer Fachmedien, 2015.

4. A. Brisse, J. Schefold, A. Glauche. Long-Term Operation of Electrolyte Supported Solid-Oxide Cells in the Steam Electrolyser Mode. *Proceedings 11th European SOFC Forum, Lucerne, Switzerland.* B1302, 2014.

5. D. Schimanke, C. Walter. SOEC Development Status at sunfire. *Proceedings 11th European* SOFC Forum, Lucerne, Switzerland. A0804, 2014.

6. M. Henke, et al. Theoretical study on pressurized operation of solid. *International Journal of Hydrogen Energy.* 2014.

7. S. H. Jensen, et al. Hydrogen and synthetic fuel production using pressurized solid oxide electrolysis cells. *International Journal of Hydrogen Energy.* 2010, 35.

8. X. Sun, et al. Performance characterization of solid oxide cells under high pressure. *Proceedings of 11th European SOFC & SOE Forum.* 2014, Vol. Chapter 16.

9. M. Riedel, et al. Pressurized Operation of a 10 Layer. *Proceedings of 12th European SOFC* & *SOE Forum.* 2016, Vol. Chapter 03.

10. Undertaking, Fuel Cells and Hydrogen Joint. *Study on development of water electrolysis in the European Union.* **2014**.

11. Brabandt, Jörg and Posdziech, Oliver. System Approach of a Pressurized High-Temperature Electrolysis. ECS Transactions. 2017, Vol. 78, 1.

12. IEA. Technology Roadmap Hydrogen and Fuel Cells. [Online] 2015. http://www.iea.org/publications/freepublications/publication/TechnologyRoadmapHydrogen andFuelCells.pdf.

13. Fuel Cells & Hydrogen Joint Undertaking. *Study on development of water electrolysis in the EU.* 2014.

14. Deliverable 1.1. *Report on the Specification of the Overall System and Main Components.* s.l. : HELMETH, 2015.

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