



Deliverable 2.2:

Report on short stack testing

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Table of Contents

TABLE OF CONTENTS	3
GLOSSARY	4
1. EXECUTIVE SUMMARY	5
2. INTRODUCTION	6
2.1. DEGRADATION OF HTE STACKS	6
2.2. CO-ELECTROLYSIS	7
3. EXPERIMENTAL	8
3.1. CO-ELECTROLYSIS	8
3.2. LONG TERM TESTING	9
4. RESULTS	11
4.1. CO-ELECTROLYSIS	11
4.1.1 <i>Idle mode</i>	11
4.1.2 <i>Co-electrolysis operation</i>	12
4.2. SHORT STACK DEGRADATION RATE	13
SUMMARY AND CONCLUSION.....	15
BIBLIOGRAPHY	16
TABLE OF FIGURES	17
LIST OF TABLES	18

Glossary

<u>Abbreviation / acronym</u>	<u>Description</u>
approx.	Approximately
bara	Bar absolute
DC	direct current
DoW	Description of Work
GHSV	Gas hourly space velocity
HHV	Higher heating value
HTE	high temperature electrolysis
LHV	Lower heating value
Max.	maximum
OCV	Open circuit voltage
PtG	Power-to-Gas
resp.	respectively
SNG	Substitute/Synthetic Natural Gas
SOEC	Solid oxide electrolyser cell
SOFC	Solid oxide fuel cell
WP	Work package
CO ₂	Carbon dioxide
H ₂	Hydrogen
CO	Carbon monoxide
CH ₄	Methane
H ₂ O	Water

<u>Project partner acronyms</u>	
KIT	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

This deliverable **D2.2 “Report on short stack testing”** is part of the **HELMETH project**, which is devoted to a 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.

The main issues of this report are to show the feasibility of the Sunfire stack for co-electrolysis (beside steam, also carbon dioxide is fed into the stack to obtain a certain amount of carbon monoxide in the product gas) and that the degradation rate targets can be reached.

The results of the co-electrolysis and the degradation rate test are satisfying, although the long term degradation tests could not be completed in the short stack with the originally planned operation hours, due to technical problems of the testing facility. However, on the basis of the achieved results and previous long term tests on cell elements from the same material it can be concluded that the Milestone 3 “Short stack operation confirms degradation rate targets and co-electrolysis feasibility” of the HELMETH project is achieved.

2. Introduction

2.1. Degradation of HTE stacks

The performance of the electrolysis is a key feature for an efficient and economic PtG process. Therefore it is required that the HTE stacks show a stable long term performance, which means to have a low degradation rate.

Degradation inside a stack can take place at different places and has a couple of different reasons. An overview of possible reasons for degradation and the resulting effects is given in Table 1:

Table 1: causes of degradation

Component	Cause of Degradation	Effect
Cathode	Oxidizing atmosphere, Long term operation	Agglomeration of Ni-particles, reduction of active area
Electrolyte	Overvoltage, mechanical stress	Destabilization of ceramic structure, cracking
Anode	Too high oxygen partial pressure	Delamination
Interconnects	Delamination of Cr ₂ O ₃ layer, Cr evaporation,	Increasing contact resistance
Gaskets	Leakages due to mechanical stress or electric effects	Steam conversion too high, destabilization of ceramic layers
Current rods	Oxidation of interfaces	Increasing contact resistance

The degradation can also be influenced by the operation parameters. Temperature, gas composition, current density and steam conversion play a role and make it difficult to compare results (e.g. from different cell manufacturers) if not all values are kept similar.

Additional, the degradation behavior can also change with time. It is especially known from single cell testing that at the beginning the degradation rate can be high, and then is getting lower until a stable rate is reached.

To determine the degradation rate of a SOC stack is a challenge, especially when very low degradation is expected. Usually, the voltage of the stack at a fixed current is observed. As gas composition, current and temperature (temperature dependence of conductivity, especially the electrolyte) also influence the measured voltage even with low fluctuations, these effects can be in a higher range than the real degradation itself.

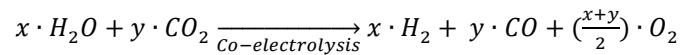
The obvious solution to overcome this issue is to increase the test time to several 1000 h. This is a high effort, as a big amount of test capacity (facility, test stand, personnel) is required, because it is simply not possible to wait until one test ends before a new developed item can be tested.

Furthermore the requirements for the stability of the test equipment are high, and all sensors (flow, temperature, voltage and current sensors) need to be calibrated to consider possible deviations in the interpretation of degradation results.

2.2. Co-electrolysis

Electrolysis of water or steam is well known. For a fuel cell, this process is simply the inversion of the originally supposed reaction, electrochemical oxidation of hydrogen to water. For high temperature fuel cells (SOFC) carbon containing fuels are common too, where carbon monoxide is oxidized to carbon dioxide. It is nearby that the vice versa reaction, carbon dioxide electrolysis producing carbon monoxide and oxygen, would work as well.

For the methanation, besides hydrogen also carbon monoxide (instead of carbon dioxide) is a possible source. So it is of interest to produce hydrogen and carbon monoxide efficiently in one source and in the required stoichiometry:



The main goal of the stack testing is the experimental investigation of this co-electrolysis and, as a proof of concept, the demonstration of a successful operation in the relevant operation range for a following methanation process.

Within this topic, one aim is to understand the role of the water-gas shift reaction during co-electrolysis. With this reaction, an equilibrium between the oxidized and the reduced form of the C and the H-components is formed:

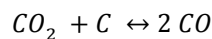


As simulations in the Deliverable 1.1 of the HELMETH project (1) show, the desired feed gas flow for the methanation should fulfill the composition:

$$FEED: \frac{[H_2] - [CO_2]}{[CO] + [CO_2]} = 3$$

During the co-electrolysis tests it will be evaluated if this value can be obtained with sunfire stack technology.

Another main issue one has to handle during CO₂ electrolysis is soot formation. Depending on temperature, gas composition and pressure, the carbon monoxide in the product gas will follow the Boudouard equilibrium:



For the stack operation itself, operation temperature is usually high enough, so that no carbon will be deposited inside the stack. But for further steps in the overall process, the gas has to be cooled down, which increases the tendency of soot formation.

From the electrochemical point of view, no gas on the anode side is required as the formation of oxygen at the electrode does not need a reaction partner beside the oxygen ions coming through the electrolyte. Nevertheless, it is common to have a flow of air or inert gas at the anode side, to flush the oxygen away. This reduces the oxygen partial pressure and should prevent an increased oxidation of the materials like the sheet metal interconnectors.

3. Experimental

For the tests, sunfire short stacks were used. They consist of 10 electrolyte supported cells (ESC) with an active area of 127.8 cm² each. The cells have a Ni-GDC (nickel/gadolinium doped ceria oxide) cathode, a 3YSZ (yttria stabilized zirconia) electrolyte and a LSCF (lanthanum strontium cobalt ferrite) anode, with several interface layers. As interconnects, sheet metal plates (Crofer 22 APU) with a protective coating to reduce oxidation are used. Gaskets out of glass ensure a very good gas tightness between anode and cathode side.



Figure 1: sunfire short stack

The tests were performed in a furnace test stand (FuelCon Evaluator), gases were controlled by mass flow controllers (MFC) and to adjust the water flow a dosing pump was used. A sketch of the test setup is shown in Figure 2.

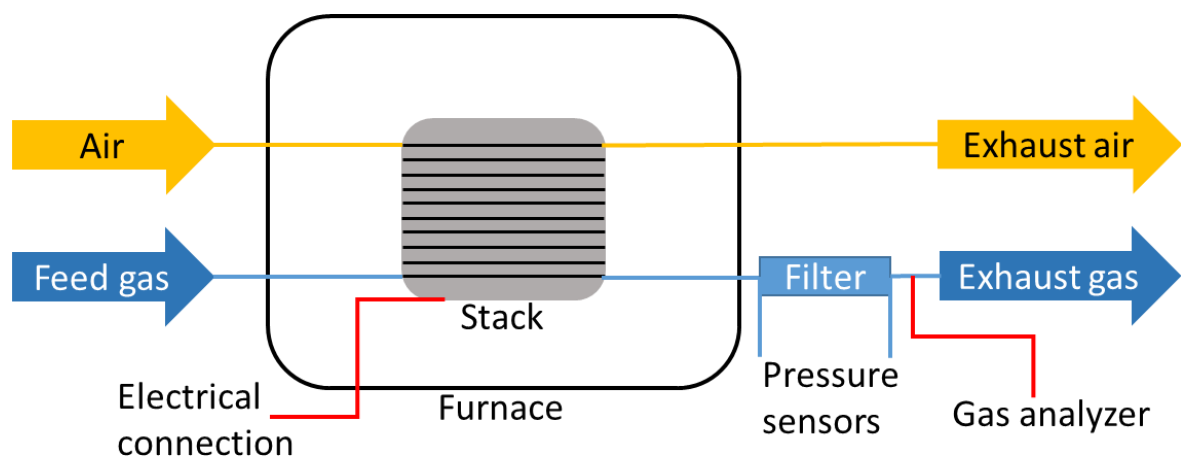


Figure 2: schematic test setup

3.1. Co-electrolysis

During this test, the feed gas composition for the electrolysis was changed stepwise. The amount of steam and hydrogen was reduced, while carbon dioxide and a small amount of carbon monoxide were added. As from the simple electrochemistry it is not possible to distinguish what fraction of steam or carbon dioxide is electrolyzed, samples of the product gas are fed into a gas analyzer (X-Stream XE, Emerson Process Management).

The different feed compositions used during the tests are shown in Table 2. From composition 1 to 6, there is a stepwise increase of the CO_2 / H_2O ratio. In composition 6, the inlet hydrogen, which acts as an oxidation prevention, was substituted by CO.

Before electric operation, the gas was run through the hot stack in idle mode, and the outlet gas composition was analyzed. With this, it is possible to visualize gas reactions not linked to the electrolysis itself. Subsequently, each gas composition was operated in electrolysis mode, with a stepwise increase of the current density from -400 mA/cm^2 to -700 mA/cm^2 (for a better differentiation to fuel cell mode, current densities in electrolysis are marked negative). Gas flows were adjusted in order to reach a gas conversion (GC) of 0.6 at each operation point. The outlet gas was analyzed during all operation points.

Table 2: Inlet compositions for current variations

	Molar fractions in %			
Composition	H_2	H_2O	CO	CO_2
1	5	95	0	0
2	5	75	0	20
3	5	55	0	40
4	5	35	0	60
5	5	15	0	80
6	0	55	5	40

Following to the current variation, an optimum gas composition for HELMETH project was determined, which is shown in Table 3. With this gas composition, a variation of the gas conversion factor was performed. Therefore, the GC was increased stepwise from 0.5 to 0.9, while the current density was kept constant at -500 mA/cm^2 .

Table 3 Inlet composition for GC-variation

	Molar fractions in %			
Composition	H_2	H_2O	CO	CO_2
7	5	80	0	15

3.2. Long term testing

To gain reliable information about the performance of the stack, the stack was characterized in a reference point in fuel cell mode at the beginning and the end of the test. The long term test ran with a gas mixture of 95% steam and 5% hydrogen at the H_2 -side and an air flow at the O_2 side in order to dilute the generated oxygen.

Stack operation is shown in Figure 3. After a short SOFC reference point, the stack was brought to SOEC operation. After 50 h of operation there was a restart of the power supply due to a software error. Within the further operation, the test stand suffered from an increasingly fluctuating water supply. After 400 h operation time, this problem culminated into a complete blackout of the water supply, which also led to an irreversible damage of the stack. Due to this, only a degradation rate within 320 h can be presented here.

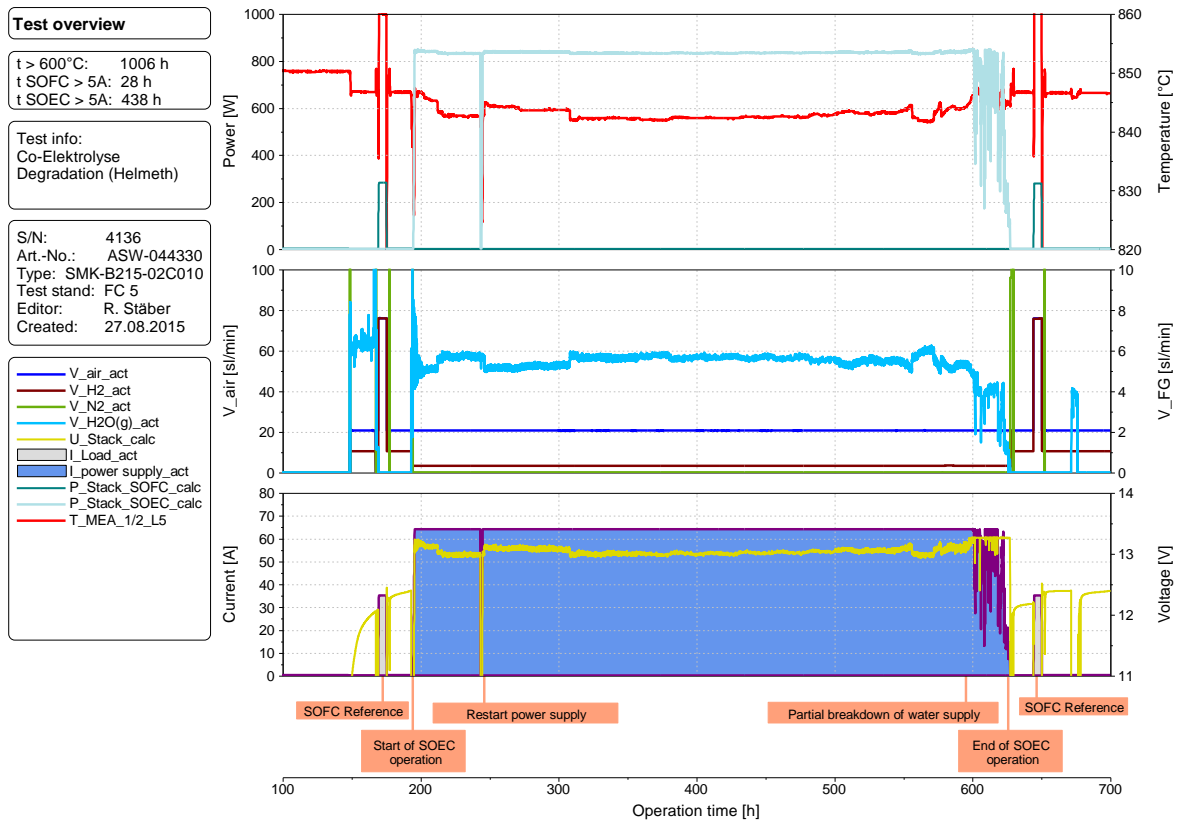


Figure 3: Long term operation stack test

4. Results

4.1. Co-electrolysis

4.1.1 Idle mode

The results of the gas analysis show a clear indication of a gas reaction taking place in idle mode, with no current applied to the stack. Figure 4 shows the exemplary change in gas composition for the inlet composition 5. At this gas composition, the feed gas consists mainly of CO₂, with only a small amount of H₂O left. Analysis of the outlet gas shows a significant increase in H₂O and CO, while the amount of CO₂ and H₂ was reduced.

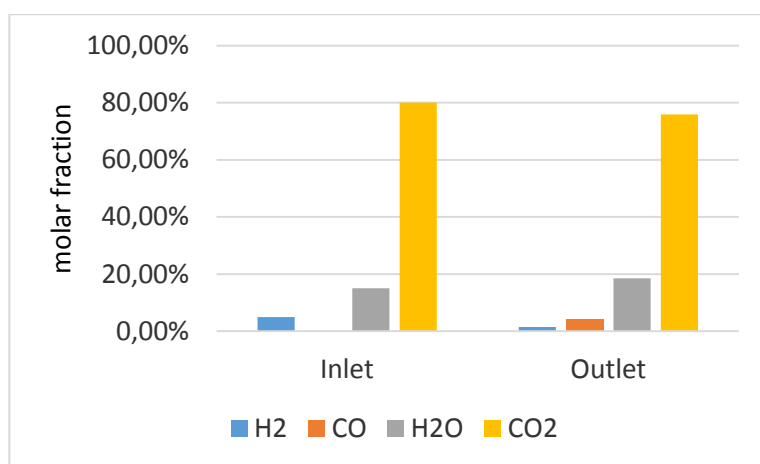


Figure 4: Gas composition change in idle mode for composition 5

The results are a clear evidence for the water-gas shift-reaction taking place inside the stack. With this reaction, an equilibrium between H₂, H₂O, CO and CO₂ is formed:



It is assumed, the H₂-electrode of the stack acts as an efficient catalyst for the water-gas shift reaction at the common operation temperatures above 800°C.

As the free reaction enthalpy is very close to 0 within the stack operation range of 860°C, the equilibrium is expected to be in the middle of both sides of the reaction. This is in good agreement to the obtained gas analysis results.

As the water-gas shift reaction also takes place during co-electrolysis operation, there is the possibility of a direct reduction of CO₂ and H₂O at the electrode, or alternatively only H₂O is reduced while the CO formation is caused by the water-gas shift reaction.

4.1.2 Co-electrolysis operation

Electrolysis operation showed to be possible for all operation points described in chapter 3.1. Figure 5 shows the I-V dependency of the different feed gas compositions during co-electrolysis. It can be seen, that the stack voltage is hardly influenced by the stepwise substitution of H₂O with CO₂. Only for a high CO₂-fraction of 80% (composition 5), there is a more distinct increase of the voltage. The substitution of the 5% inlet H₂ with CO (composition 6) showed the highest stack voltage. However, as the voltages for all compositions are located very close together, no restriction in stack operation is expected within this operation range.

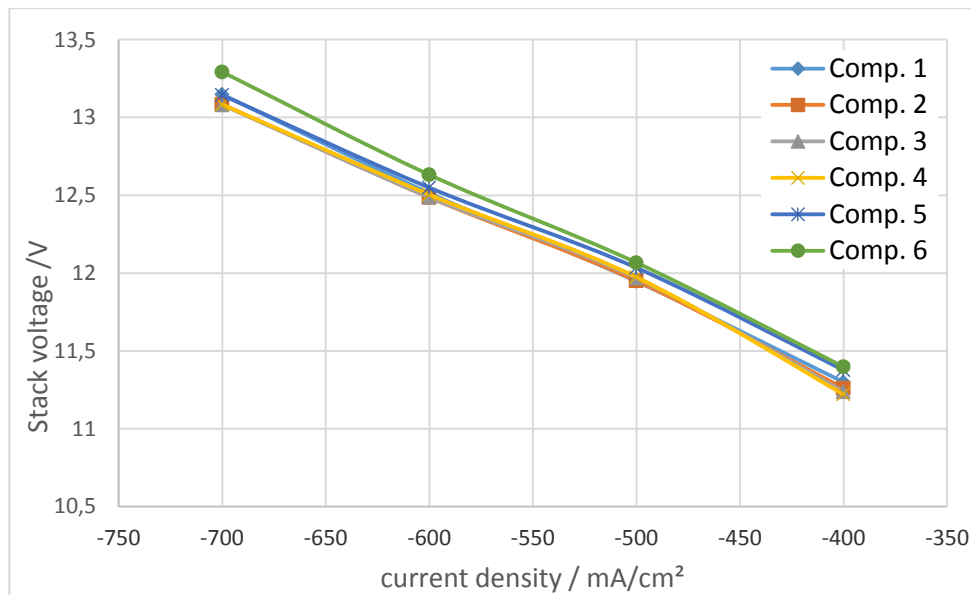


Figure 5: I-V curves for different gas compositions

As the gas analysis of the outlet gas showed, H₂ and CO were generated with roughly the same relation as the inlet gases H₂O and CO₂. As there is already a H₂-amount in the feed gas, the equilibrium is slightly shifted towards the CO side.

As an example, Figure 6 shows the inlet and outlet composition of operation point two. With a H₂ amount of 37.9% and a CO amount of 10.2%, the outlet gas would be suitable for use in a following methanation process.

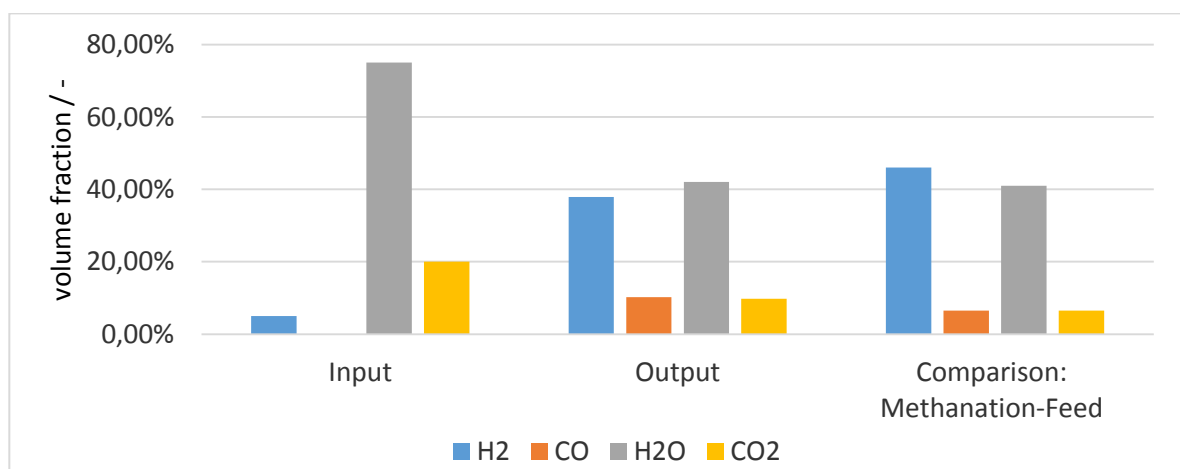


Figure 6: Gas composition change within electrolysis (operation point 2)

As a comparison, Figure 6 shows also the feed composition suitable for methanation, which was calculated by the equation described in chapter 2.2. The composition is very close to operation point 2, and can be reached with a small change of the electrolyser input (more H₂O, less CO₂) compared to operation point 2.

The last step for parameter variation was a stepwise increase of the gas conversion. This was realized by decreasing the inlet flows while keeping the stack current constant. Figure 7 shows that an increase in gas conversion leads to an increasing stack voltage. However, the voltage increase was only moderate, leading to the conclusion that co-electrolysis at high gas conversion factors is possible.

Nevertheless, this statement should be validated in long-term stack tests, in order to see if there is an unwanted impact on degradation rates caused by a high steam conversion.

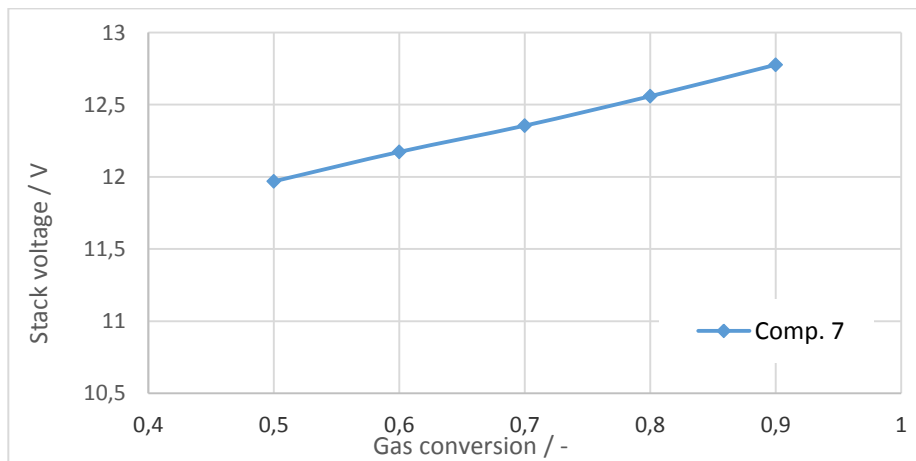


Figure 7: Dependency of the stack voltage on the gas conversion

4.2. Short stack degradation rate

As described in chapter 3.2, evaluation of the stack degradation was only possible within 320 h. As the water fluctuation had a strong impact on the stack voltage, biasing a possibly degradation tendency, it was necessary to evaluate two points in time with exactly the same water supply. Figure 8 shows the single cell voltages, the water supply and the datasets which were used for degradation calculation.

As a measure for degradation, the relative voltage increase was calculated. A voltage degradation of 0.133% was obtained for 320 h. Linear extrapolation leads to a degradation of 0.426% per 1000 h. Degradation tests on cell level for several thousand hours are available and show a reduction of the degradation rate over operation time (2). Exemplary results of these tests are shown in Figure 9. The investigated cells in these previous single cell tests are the same as used by sunfire today (supplied by Kerafol GmbH). Additionally, a 30 cell stack was operated in electrolysis mode for more than 2.300 h. the observed degradation rate was not increasing after 1.500 h in stable operating points (3). The current experimental data on a complete stack basis provide reliable information on degradation only for 320 hours. Due to the previous longer investigations on single cell and short stack level, it seems reasonable to extrapolate these findings in a linear manner, in order to obtain maximum degradation rates, since the previous investigations show a rather decreasing degradation rate over operational time.

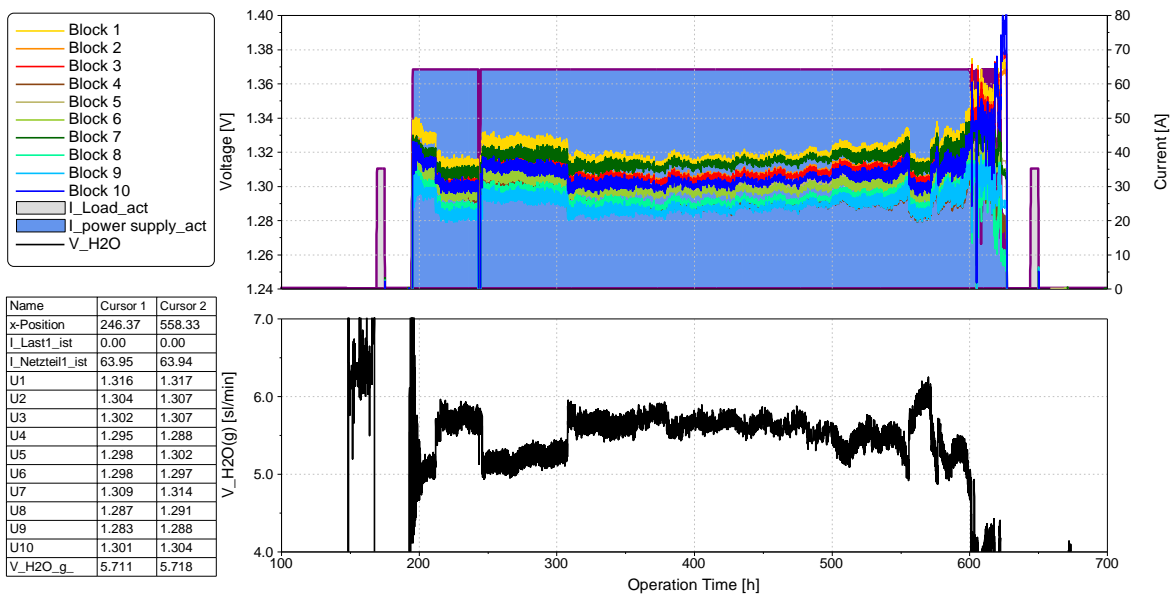


Figure 8: Degradation evaluation on the stationary operation test

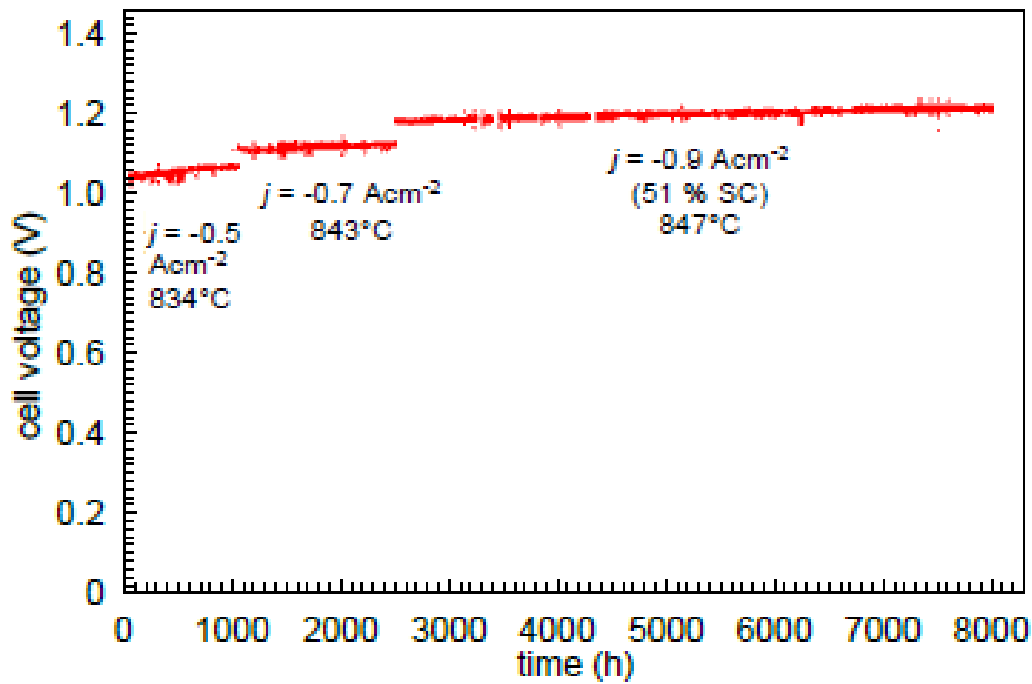


Figure 9: single cell test at EIFER institute with a similar cell as used by sunfire (2)

Summary and conclusion

It has been shown that sunfire HTE stacks are capable of co-electrolysis. The ratio between hydrogen and carbon monoxide in the product gas flow can be tuned in a wide range by changing the inlet gas composition. Water gas shift reaction takes place and influences the result, but compared to the electrolysis it plays a minor role.

The desired outlet gas composition of the co-electrolysis as feed gas for the methanation is within the tested parameter range and is achievable by the available technique.

Soot formation inside the stack can be avoided by choosing a suitable set of parameters of gas composition, temperature and pressure.

The degradation rate of the short stack is in the expected range, the extrapolation of the values shows a rate of $< 0.5\%$ / 1.000 h of voltage degradation. This test was performed only with steam electrolysis, further testing in co-electrolysis mode is advisable.

Based on these results, Milestone 3 of the HELMETH project "Short stack operation confirms degradation rate targets and co-electrolysis feasibility" is therefore reached.

Bibliography

1. Blumentritt, R. **HELMETH Deliverable 1.1: REPORT ON THE SPECIFICATION OF THE OVERALL SYSTEM AND MAIN COMPONENTS**. 2015.
2. 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.
3. D. Schimanke, C. Walter. **SOEC Development Status at sunfire**. *Proceedings 11th European SOFC Forum, Lucerne, Switzerland*. A0804, 2014.

Table of Figures

Figure 1: sunfire short stack 8

Figure 2: schematic test setup..... 8

Figure 3: Long term operation stack test 10

Figure 4: Gas composition change in idle mode for composition 5..... 11

Figure 5: I-V curves for different gas composition 12

Figure 6: Gas composition change within electrolysis (operation point 2) 12

Figure 7: Dependency of the stack voltage on the gas conversion..... 13

Figure 8: Degradation evaluation on the stationary operation test..... 14

List of Tables

Table 1: causes of degradation	6
Table 2: Inlet compositions for current variations.....	9
Table 3 Inlet composition for GC-variation	9