FCH JU Grant Agreement number: 325262

Project acronym: CISTEM

Project title: Construction of Improved HT-PEM MEAs and Stacks for Long Term Stable Modular CHP Units

Work package: 1 Management

Deliverable: 1.3 Annual Management Report

Period covered: 01.06.2013 – 31.05.2014

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1. Introduction

Deliverable 1.3 asks for annual reporting of management issues related to the CISTEM project.

The objective of the CISTEM project is to develop a new fuel cell (FC) based CHP technology, which is suitable for fitting into large scale peak shaving systems in relation to wind mills, natural gas and SMART grid applications. The technology should be integrated with localized power/heat production in order to utilize the heat from the FC via district heating and should deliver an electrical output of up to 100kW. Additionally the CHP system should be fuel flexible by use of natural gas or use of hydrogen and oxygen which can be provided by electrolysis. This gives the additional opportunity to store electrical energy in case of net overproduction by production of hydrogen and oxygen for use in the CHP system and gives an additional performance boost for the fuel cell.

The main idea of the project is a combined development of fuel cell technology and CHP system design. This gives the opportunity to develop an ideal new fuel cell technology for the special requirements of a CHP system in relation to efficiency, costs and lifetime. On the other hand the CHP system development can take into account the special advantages and disadvantages of the new fuel cell technology to realize an optimal system design.

The purpose of the CISTEM project is to show a proof of concept of high temperature PEM (HT-PEM) MEA technology for large combined heat and power (CHP) systems. A CHP system of 100 kW_{el} will be set up and demonstrated. This CHP system size is suitable for district heat and power supply. The system will be build up modularly, with FC units of 4 kW_{el} output each. This strategy of numbering up will achieve an optimal adaption of the CHP system size to a very wide area of applications, e.g. different building sizes or demands for peak shaving application.

The major task within CISTEM is to bring together and combine all views and perspectives from a single fuel cell stack component to assembled membrane-electrode-assemblies, further on to stacks and in the final stage with the inclusion of balance-of-plant-materials the final CHP unit design. This requires understanding of both involved technological sides, the scientists improving materials which extend SoA to beyond SoA-materials as well as engineers involve in designing a new reformer and CHP concept. Therefore, the CISTEM project brings together industry and research to achieve the main project objectives.

All work within CISTEM has been guided by the goals coming from the Multi Annual Implementation Plan and Annual Implementation Plan which are in general:
Operational stationary CHP unit fitting into midscale commercial application range with 5 to 50 kW power
- Improved electrical efficiency of > 40%
- Overall efficiency above 90%
- Long term durability with a lifetime of > 20,000 hours
- Increased knowledge on degradation and failure mechanisms.

The first annual management reporting includes
- Summary of project progress
- Project meetings
- WP meetings and telephone conferences
- Dissemination of project results
- List of Deliverables
2. Summary of project progress

According to deliverables and milestones, the activities within CISTEM have been focused on several tasks like

a) Definition and chemical and electrochemical investigation of state-of-the-art fuel cell components like MEAs and bipolar plates;

b) On determining test protocols for MEA testing between all partners to be applied within the whole consortium;

c) Increase of electrical efficiency through several singular steps including backpressure increase, utilization of oxygen to enrich the cathode air with O₂ from electrolyzers, new designs in heat recovery in the BoP design etc.

d) Determination of design criteria for setting up a modular CHP unit based on HT-PEM technology with several modules (consisting of two 4 kw stacks and one reformer);

e) Determination of CHP operation scenarios distributed throughout Europe with demands and requirements in Northern, Central and Southern Europe;

f) Taking into account further demand requirements from the vision of new built apartment blocks or industrial complexes and on the other hand district heating with local ½ family households.

For this purpose all project partners are involved in the several work packages described in detail in the Description of Work (DoW).

Within these work packages several deliverables have been identified that are supposed to upload for further investigation to the Joint Undertaking (JU).

The achievements and the progress within CISTEM can be summarized within some bullet points

- An improved electrical efficiency of 20% on MEAs has been achieved by utilization of oxygen enriched cathode air and increased backpressure.
- The proposed durability of at least 1.000 hours with modified MEAs (beyond SoA) has been shown.
- Large area MEAS of 200 cm² have been manufactured.
- First short stack testing with large area MEAs is in progress.
- Durability testing of materials under new operating conditions shows promising results to extend the desired lifetimes.
- Gross electrical efficiency of the CHP unit has been calculated to be 42%.
- Test of new reformer design with large modulating capabilities (required for the module) is currently in progress.
- Simulation of the CHP system operation by taking into account European regional operational strategies and demands has started.
Workpackage 1: Management
Management covered all management tasks for the overall coordination of the projects and work package coordination. Within the first year this was mainly

i) On-time distribution of pre-financing to the participants;
ii) Coordination and communication with the project officer of the JU;
iii) Preparation of Review Days reports and posters for the JU;
iv) Monitoring of the project progress within the tasks;
v) Organization of project meetings;
vi) Organization of WP meetings and telephone conferences;
vii) Providing style guides and templates for reporting, presentations etc.
viii) Cover all required reporting issues like deliverables and reports;
ix) Disseminate the CISTEM project to the outside through implementation and managing of a project website;
x) Design, printing and distribution of a CISTEM Project flyer at the Hannover Trade Fair and many other events/possibilities.
3. **Project meetings**

The CISTEM project meetings are summarized in table 1. Meeting protocols are available in the CISTEM intranet.

**Table 1: List of CISTEM project meetings**

<table>
<thead>
<tr>
<th>Period</th>
<th>Date</th>
<th>Location</th>
<th>Host</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beginning of 1st semester</td>
<td>17.07.2013</td>
<td>Oldenburg/Germany</td>
<td>NEXT ENERGY</td>
<td>Kickoff</td>
</tr>
<tr>
<td>End of 1nd semester</td>
<td>26./27.11.2013</td>
<td>Herzogenrath/Germany</td>
<td>OWI</td>
<td></td>
</tr>
<tr>
<td>End of 2nd semester</td>
<td>24./25.06.2014</td>
<td>Osterode im Harz/Germany</td>
<td>Eisenhuth</td>
<td></td>
</tr>
</tbody>
</table>

4. **Work package meetings and telephone conferences**

Within CISTEM a large number of meetings between WP participants as well as telephone conferences had to be organized, especially in the project starting period.

Whereas the first semester was mainly dominated by clarification of projects goals, different desired approaches and individual tasks between the project partners and determination of several standard test protocols with regard to long term testing, the second project semester telephone conferences were much more driven by detailed engineering and CHP design questions that need to be answered by various participants. Only a minor part was caused by scientific questions and challenges that need to be discussed and to be decided on.

Because the project partners have a lot of experience in project related management and work, the working atmosphere between all partners was highly professional and all addressed technical challenges could be solved up to now.

We resign from explicitly stating all telephone conferences and work package meetings in this report but would like to refer the reader to the internal CISTEM web site where all minutes of telephone conferences and work package meetings are available.
5. Dissemination of project results

Dissemination of CISTEM project results within the scientific and industrial community and bringing the ideas of CISTEM to the general public is an important requirement for managing projects under the umbrella of JTI-JU.

Table 2 summarizes several different dissemination events from press releases, scientific lectures on conferences or publications in scientific and technical journals.

Table 2: List of dissemination events within CISTEM

<table>
<thead>
<tr>
<th>Press / World Wide Web</th>
<th>Event</th>
<th>Date</th>
<th>Lead participant</th>
<th>Title</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project website online</td>
<td>30.08.2013</td>
<td>NEXT ENERGY</td>
<td>Also on NEXT website</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Technical description of the CISTEM project</td>
<td>31.08.2013</td>
<td>OWI</td>
<td>OWI homepage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brief description of UCLM participation within CISTEM</td>
<td>August 2013</td>
<td>UCLM</td>
<td>UCLM homepage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Note in German H2 Journal 1/2014</td>
<td>January 2014</td>
<td>OWI</td>
<td>“OWI baut BZ Kraftwerk”</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Lectures 2013</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Saxony Fuel Cell Summer School 2013</td>
</tr>
<tr>
<td>E2KW 2013 – Energy and Environment Knowledge Week</td>
</tr>
<tr>
<td>224th ECS Meeting, San Francisco, USA</td>
</tr>
<tr>
<td>-----------------------------------------</td>
</tr>
<tr>
<td><strong>224th ECS Meeting, San Francisco, USA</strong></td>
</tr>
<tr>
<td><strong>Piero Lunghi Conference</strong></td>
</tr>
<tr>
<td><strong>EHEC 2014, Seville, Spain</strong></td>
</tr>
</tbody>
</table>

### Papers (Journals, Proceedings)

| **224th ECS Meeting, San Francisco, USA** | October 2013 | NEXT | Micro-Computed Tomography Imaging of HT-PEM Fuel Cells under Contact Pressure Control | ECS Transactions, 58 (1) 443 - 452 (2013) |
## Posters

<table>
<thead>
<tr>
<th>Year</th>
<th>Event Details</th>
<th>Presenter</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>2013</td>
<td>Piero Lunghi Conference EFC2013, Rome, Italy</td>
<td>December 2013</td>
<td>NEXT</td>
</tr>
<tr>
<td>2014</td>
<td>Inno.CNT-Jahreskonferenz 2014</td>
<td>17.-19.02.2014</td>
<td>Eisenhuth</td>
</tr>
</tbody>
</table>

## Trade Fairs

<table>
<thead>
<tr>
<th>Year</th>
<th>Event Details</th>
<th>Presenter</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>2014</td>
<td>Expocomfort Milano 2014</td>
<td>18.-21.03.2014</td>
<td>ICI</td>
</tr>
<tr>
<td></td>
<td>Hannover Trade Fair 2014</td>
<td>07.-11.04.2014</td>
<td>NEXT</td>
</tr>
</tbody>
</table>
6. List of submitted deliverables

Table 3 summarizes the CISTEM project deliverables that have been submitted to the JU during the first project year.

Table 3: List of submitted deliverables

<table>
<thead>
<tr>
<th>Deliverable</th>
<th>Title</th>
<th>Submitted on</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3</td>
<td>Management report</td>
<td>29.07.2014</td>
<td></td>
</tr>
<tr>
<td>1.4</td>
<td>Technical report</td>
<td>29.07.2014</td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td>Optimized PBI membrane with a durability of 1000 hours</td>
<td>29.07.2014</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>MEA test protocols</td>
<td>12.12.2013</td>
<td></td>
</tr>
<tr>
<td>4.1</td>
<td>BoP component specification</td>
<td>19.06.2014</td>
<td></td>
</tr>
<tr>
<td>5.1</td>
<td>Basic System Setup</td>
<td>07.02.2014</td>
<td></td>
</tr>
<tr>
<td>6.1</td>
<td>Single HT-PEM MEA model</td>
<td>19.06.2014</td>
<td></td>
</tr>
<tr>
<td>7.1</td>
<td>CISTEM web site</td>
<td>02.09.2013</td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>Project poster</td>
<td>28.07.2014</td>
<td></td>
</tr>
<tr>
<td>7.4</td>
<td>Exploitation Report</td>
<td></td>
<td>Uploaded with annual update – final submission in 2016. In agreement with project officer.</td>
</tr>
</tbody>
</table>
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Introduction

Deliverable 1.4 asks for an annual report of the technical project progress (Month 12).

So the results obtained by the project partners during the reporting period will be presented by summarizing results and achievements in some details covering the work packages from 2 to 6.
Summary

The project progress from the technical point of view is on progress. According to the time frame and the schedule no major deliverables or required important results are behind the schedule.

Highlights within the first year can be summarized by

- Oxygen enrichment of cathode air to 30% v/v O₂ concentration is already suitable to obtain a good performance improvement and at the same time avoid additional degradation issues due to the higher oxidant environment.
- Reformer design and improved heat recovery promise an electrical efficiency above 40%. There will be tradeoff between further improvement in electrical efficiency and costs.
- Small scale reformer has been developed and successfully tested.
- Long term and accelerated stress test have been defined and performed for single cells.
- In-situ and ex-situ investigation have revealed an optimized contact pressure of 0.75 MPa for single cells.
- Component testing and development disclose a good approach for beyond State of the Art materials and their definition.
- First short stack is assembled and testing is successfully in progress.

The goals within the work packages for the first year have been mainly achieved with only slight deviations from the overall main objectives. According to construction requirements of the CHP and full stack design the consortium had to reduce the stack power to 4 kW. Due to the fact that the modular CHP concept can still be fully achieved this is not a critical issue. A 100 kW CHP unit with modules consisting of two 4 kW stacks and one reformer can still be designed by extending the number of required modules from 10 to 12.
WP 2: Materials beyond State of the Art

The goal of this work package is to optimize the performance and durability of the MEAs towards the target of the project by:
- Optimization of fuel/oxidant strategy;
- Optimization of electrodes and membranes;
- Optimized MEA design for the chosen fuel/oxidant strategy.

The result of the activities will be at MEA designed for the proposed CHP application.

The activities are aligned with the project scope using:
- Pressurized hydrogen
- Pressurized hydrogen and air/oxygen from electrolysis
- Reformate from natural gas.

Task 2.1: Fuel and Air/O₂ optimization

Oxygen enriched air

Figure 1 shows the performance of two Dapozol® MEAs from DPS operating with hydrogen as fuel and different oxygen concentrations in the air as oxidant. As it can be seen, the higher the oxygen concentration, the better the performance of the fuel cell is due to the increased oxygen partial pressure on the cathode side. Thus, the oxygen molecules find less diffusion resistance to the catalyst active sites when the oxygen concentration is increased.

![Figure 1: Polarization curves for the fuel cell operating with H₂/Air* as function of oxygen enriched air. MEA: (a) DPS-17, (b) DPS-18. 5-fold serpentine flow field, Pₑ = 0.75 MPa, T=160 °C, p=1 atm. *λH₂=1.2; λAir=2, λAir-30% O₂=2.85, λAir-75% O₂=7.1](image)

As expected, both MEAs show the same voltage behavior when the oxygen concentration has been increased on the cathode side. On the one hand, when
the oxygen concentration has been increased from 21% (air) to 30% at 0.3 A/cm² the voltage in both MEAs has developed an improvement of between 6-8%. On the other hand, further increase in the oxygen concentration until 75% has turned to a voltage improvement of 4% in both of the MEAs. Thus, most of the voltage enhancement has been observed with the first step of oxygen concentration increase.

Figure 2 shows polarization curves, impedance spectra (EIS), cyclic voltammetries, hydrogen crossover and internal resistance of a DPS G55 MEA operated at different cathode/anode backpressures.

The fuel cell performance increases after pressurization of the system by 13% from 1 to 2 bar (Figure 2 (a)). Fuel cell performance enhancement was expected in the whole range of backpressure studied due to pressurization of the system increases partial pressure of the reactant gases, leading to enhanced electrode kinetics and improved mass transfer in the fuel cell. Nevertheless, a decrease in the fuel cell performance can be observed from 2 to 2.75 bar. As it can be seen in Figure 2 (b), the ohmic resistance is increased for the highest backpressure.
Moreover, Figure 2 (c) shows a huge decrease of the hydrogen adsorption peak which means reduction of active sites for the reactant gases. Internal resistance can be considered unaffected by backpressure but not in case of the hydrogen crossover (Figure 2 (d)). The increase of backpressure in anode side generates hydrogen concentration gradient across the membrane. Thus, the hydrogen crossover has been increased from 1.75 to 2.5 mA/cm² when the backpressure of the fuel cell increases from 1 to 2.75 bar. Nevertheless, hydrogen crossover from 1 to 2 bar was slightly reduced and it could be considered unaffected. Backpressure will be further investigated in the future in the whole range proposed in the “Test Protocols” document (from open cathode/anode to 4.25 bar).

In addition, preliminary studies with increased back pressures have been performed. The materials and test conditions are described in Table 1. The results of the preliminary tests are shown in Figure 3.

**Table 1: Operation 160 °C,(Air/H₂), \( \lambda_{air}/\lambda_{H₂}=2.5/1.5 \).**

<table>
<thead>
<tr>
<th>Fuel cell No.</th>
<th>Operation condition</th>
<th>Electrodes</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>MEA-12-B157</strong></td>
<td>Unpressurized; (Air / H₂) : 0 bar g / 0 bar g</td>
<td>E-12-019</td>
<td>M-11-792</td>
</tr>
<tr>
<td><strong>til MEA-12-161</strong></td>
<td></td>
<td>(A/C): 0.77/0.77 mg Pt/cm²</td>
<td>D.L* 8.7</td>
</tr>
<tr>
<td><strong>MEA-12-B157</strong></td>
<td>Pressurized; (Air / H₂) : 1 bar g / 0 bar g</td>
<td>E-12-019</td>
<td>M-11-792</td>
</tr>
<tr>
<td><strong>til MEA-12-161</strong></td>
<td></td>
<td>(A/C): 0.77/0.77 mg Pt/cm²</td>
<td>D.L 8.7</td>
</tr>
</tbody>
</table>

*D*L=Acid Doping Level

Furthermore, preliminary studies have been performed to determine the influence of the oxygen enrichment on the cathode side; hence the result has been compared with the effect of the increased back pressure on the cathode side. Operating conditions are described in Table 2.

The MEAs followed the operation conditions mentioned in Table 4 once the break-in procedure was completed at a constant current of 200 mA/cm². The results are presented in Figure 4.

Clarification of the mechanisms that take place in the fuel cell is crucial to determine the best conditions of oxygen enrichment and back pressures. The optimized operating conditions will be applied to the best MEA in order to achieve beyond state of art performance.
Table 2: Oxygen enrichment and total pressure operating conditions for 25 cm² MEAs

<table>
<thead>
<tr>
<th>Fuel cell No.</th>
<th>% Vol O₂</th>
<th>Oxygen pressure (P_{PO2})</th>
<th>Total pressure (P_T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA-12-B501</td>
<td>21 %</td>
<td>0.21 – 0.7 bar</td>
<td>1-3.5</td>
</tr>
<tr>
<td>MEA-12-B497</td>
<td>21 – 100</td>
<td>0.21 - 1 bar</td>
<td>1</td>
</tr>
</tbody>
</table>

Figure 3: Effect of the increased backpressures applied on the cathode side. (Empty squares), (Air / H₂) : 1 bar g / 0 bar g, λ_{air}/λ_{H₂}=2.5/1.5, 160 °C. (Solid squares), (Air / H₂) : 0 bar g / 0 bar, λ_{air}/λ_{H₂}=2.5/1.5, 160 °C.
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Figure 4: Comparison between oxygen enrichment and the increased back pressure in the cathode side. (Solid triangle), increased back pressure in the cathode side, MEA-12-BS01, $\lambda_{air}/\lambda_{H2}=4.28/2$, 160 °C, 200 mA/cm$^2$, 21 % oxygen in the air. (Solid circles), MEA-12-B497, different oxygen enrichment in cathode side, $\lambda_{O2}/\lambda_{H2}=4.28/2$, 160 °C, 200 mA/cm$^2$.

Task 2.2: Electrode and membrane optimization
This task has the following subtasks.

2.2.1 Reduction of Platinum
It is clear that an improvement in the activity of the catalyst or in the durability lead to a reduction of the Pt content. Thus, in this report we will discuss mainly the experiments related with the improvement of the catalyst.

2.2.2 Improvement of catalysts
In this task, different materials are being testing as catalyst supports at the UCLM. During this term, special attention has been paid to SiC based materials. Thus, the thermal stability, electrical conductivity and electrochemical stability have been tested to electrodes prepared with different materials. SiC and SiC-TiC were used to prepare different MPLs. First of all, the influence of the charge was studied, because it was observed by X-Ray diffraction one peak associated to carbon GDL, and by SEM micrographs it was observed that the thickness of MPL prepared with these materials were lower compared with MPL prepared with carbonaceous materials. This difference is attributed to the differences between molecular weight. So, the cover and protection of GDL provided by MPL with charge of 2 mg/cm$^2$ was poor. Thus, different charges were evaluated 2, 4 and 6 mg of sample/cm$^2$. SEM, XRD and Hg Porosity analyses were performed. The porosity results show that the porosity decreases with the increase of charge, and tortuosity values increase with higher charge values as it was expected because of the thicker layer when the charge increases. The permeability values were good in all cases. It was observed that the influence of SiC-TiC MPL on these values is higher than the influence of SiC MPL.
Thermal resistance in acidic media, conductivity and electrochemical stability (cyclic voltammetries) were studied for each charge level of each material tested. The degradation of materials was studied by XRD. Table 3 shows the obtained results for the charges of 2 mg/cm² for SiC-TiC and SiC. As is observed, the results show that these materials present excellent electrochemical resistance, due to the low increases of crystal size values.

**Table 3: Crystal size variations on SiC and SiC-TiC MPL**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Apparent Crystal size (Å)</th>
<th>d002</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC-TiC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 mg/cm²</td>
<td>initial</td>
<td>283.58</td>
</tr>
<tr>
<td></td>
<td>Thermal deg.</td>
<td>266.64</td>
</tr>
<tr>
<td></td>
<td>Electrochemical deg.</td>
<td>283.58</td>
</tr>
<tr>
<td>SiC</td>
<td>initial</td>
<td>278.54</td>
</tr>
<tr>
<td>2 mg/cm²</td>
<td>Thermal deg.</td>
<td>289.95</td>
</tr>
<tr>
<td></td>
<td>Electrochemical deg.</td>
<td>289.97</td>
</tr>
</tbody>
</table>

Electrical conductivity measurements were also performed, SiC and SiC-TiC show values around 150s/cm² for the lower charge, and a bit lower for higher charge values (120-130 s/cm²), which is similar to the conductivity obtained for commercial electrodes with Vulcan MPL (140 s/cm²). Thus, it can be concluded that with these novel materials increases of the ohmic resistance is not expected. To evaluate the electrochemical resistance of these MPL, CVs were performed in 2M phosphoric acid and 350 cycles were performed. Figure 5, as example shows a comparison of cyclic voltammogramms of SiC prepared with a charge of 6 mg/cm², and a graphic with a comparison of the increments of cycle amplitude measured at 0.25 V for SiC samples. As it is observed, with charges of 4 and 6 mg, the increase is similar, and much lower than the amplitude increase observed with charge of 2 mg/cm². The amplitude was measured at 0.25 V because in this region the upper and lower lines of cycle are parallels, and it is easier to compare the obtained values.
Catalysts based on Pt on different supports have been prepared using the formic acid method. They were characterized by XRD, TPR and cyclic voltammetries, CVs, in hot phosphoric acid, PA, (50 °C and 2 M) were carried out in order to check the electrochemical stability of the different catalysts. As example, Figure 6 shows the XRD pattern of Pt on SiC at two concentrations 20 and 40 % of Pt.

Electrodes with the different catalysts were prepared. From XRD analysis and using the Scherrer formula the crystallite size was calculated. In all cases, the crystallite size was around 6.5 nm but the case of the commercial catalyst (40 % Pt/Vulcan) which it was 4.2 nm and for the 40 % Pt/SiC which it was 8.8 nm. To evaluate the stability, CVs were carried out in a 2 M PA at 50 °C and during 400 cycles (as example, Figure 7a shows the voltamogramms of one electrode using 40 % Pt/SiC). The EAS at the beginning and at the 400th cycle were measured from the voltagramms. The % loss of EAS was assumed as % of degradation and Figure 7b shows the obtained values for the different prepared catalysts, the
commercial one appear for comparison purposes. It can be observed that the electrode prepared with the commercial catalyst suffers of a great degradation under our operation conditions. On the contrary, the electrodes with Pt onto SiC-TiC showed the lowest degradation. Nevertheless, the best and the worst results are going to be repeated to confirm these results. XRD analysis of the electrodes after the CV test confirms an increase of the crystallite size. TEM and XPS will be carried out in order to understand better the behavior of the different catalysts.

![Figure 7: Results from Cyclic Voltametry. Left) Cyclic voltamogramms for the 40% Pt/SiC; Right) Evolution of degradation with the number of cycles for different catalysts.](image)

In the framework of WP 2, the catalyst provided by WP leader UCLM was compared to commercial catalyst Johnson Matthey (JM) HiSpec 4000 by the Partner ICTP. The thin film method on rotating disc electrode (RDE) was used for catalyst evaluation. The methodology is based on published works. The main difference to the referred papers is in measurement also in hot phosphoric acid. The apparatus from Pine Instrument (USA) was used with modified electrode holder. Defined amount of catalyst was fixed on glassy carbon disc electrode and cyclic voltammograms were recorded in acid solution saturated by hydrogen or oxygen gas. Parallel to it the active Pt area was determined by hydrogen atom adsorption peaks in sulfuric acid.

The catalyst prepared by UCLM was 24% Pt deposited on carbon nanofibers (CNFs). The determined Pt active surface area was approx 4 times lower in contrast to JM catalyst. It can be explained by slightly higher particle size. The catalyst activity was determined mainly from Koutecky-Levich plot values for ORR. Better catalyst should have low slope of Koutecky-Levich plot; low intercept i.e. high $j_k$ - kinetic current density derived from Koutecky-Levich. Most visible is high current for ORR measured at $E=0.6 \text{ V vs } \text{Ag/AgCl}$. In 0.5 M $\text{H}_2\text{SO}_4$ 25°C the commercial JM catalyst shows better catalyst activity. Unexpected results were obtained with respect to the activity in 2M phosphoric acid at different temperatures (see Figure 8). However, commercial catalyst JM shows better catalytic activity at 25°C, the UCLM catalyst gives better results at elevated temperature 60°C. This behaviour was evaluated on three different RDE samples. The explanation for this behaviour is not clear now and is subject for further study.
2.2.3 Membrane optimization

In this task, DPS and UCLM are in close cooperation, exchanging materials for testing. Several MEAs were manufactured at DPS facilities and tested at UCLM. Those different MEAs were assembled with the following materials:

- **MEA (a):** Sulfonated PBI membrane + 2w% TiO₂ & standard DPS electrodes
- **MEA (b):** PBI membrane + 2 w% TiO₂ & standard DPS electrodes
- **MEA (c):** PBI powder and TiO₂ compound from UCLM and casted at DPS & standard electrodes (nothing has happened)
- **MEA (d):** Standard DPS membrane & standard DPS electrodes
- **MEA (e):** Thermally cured DPS membranes & standard electrodes
- **MEA (f):** Improved uniformity on PBI membrane + 2wt% TiO₂ & standard DPS electrode

It has to be pointed out that the MEA (c) has not been manufactured yet. Test results carried out by UCLM showed that thermally cured DPS membranes & standard electrodes MEA (e) and improved uniformity on PBI + 2wt% TiO₂ & standard electrodes MEA (f), are the best selection of materials to manufacture an MEA with. Those MEAs are currently being tested.

- **DPS** is testing the improved uniformity PBI membrane + 2 w% TiO₂ & standard DPS’s electrodes.
- **UCLM** is testing the thermally cured DPS membranes & standard electrodes.

The different MEAs were manufactured with the materials listed in Table 4.

The undoped PBI membranes developed by DPS, (M-13-386 and M-13-578) have a thickness variation of 40 µm ± 2. Doped PBI membranes have a variation of 80 µm ± 5, the doping agent is 85 % H₃PO₄ (PA). The samples PBI + TiO₂, sulphonated PBI + TiO₂, and two samples of improved PBI + TiO₂ developed by UCLM were measured before and after being doped 85 % PA. The average thickness value of the MEA-RD-14-012 was 53 µm before doping and 112 µm after that. For the MEA-RD-14-01, were 44 µm and 77 µm, before and after doping, respectively. For the case of MEA-RD-14-089 were 50 µm and 83 µm,
before and after doping, respectively and finally, for the MEA-RD-14-078 the values were 51 μm and 89 μm before and after the doping, respectively. Fenton tests and leaching test have been performed to different PBI membranes from DPS and UCLM. Figure 9 shows the results of the Fenton test. It can be observed that the membranes beyond state of the art from DPS and UCLM reached the best results, whereas the worst were obtained by the standard PBI from DPS and the sulphonated composite PBI from UCLM, the last one showed the best resistance in the first cycle. It must be pointed out that these results are unexpected according the previous report where the sulphonated PBI membrane showed a very good result. The differences can be explained according the different molecular weight of the polymer and the different sulphonation degree. Thus, the UCLM is currently working on this matter.

On the other hand, all the materials beyond state of the art, thermally cured from DPS, composite TiO₂ and sulphonated composite TiO₂ PBI membrane from UCLM showed better PA retention capabilities around 90 % while the PA retention of the standard PBI membranes was slight lower than 80 %.

Table 4: Crystal size variations on SiC and SiC-TiC MPL

<table>
<thead>
<tr>
<th>Fuel cell No.</th>
<th>Electrodes</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA-14-001(i)</td>
<td>E-13-014 (A/C): 1.6 mg Pt/cm²</td>
<td>M-13-386 D.L.* 10.7</td>
</tr>
<tr>
<td>MEA-14-002</td>
<td>E-13-014 (A/C): 1.6 mg Pt/cm²</td>
<td>M-13-386 D.L. 10.7</td>
</tr>
<tr>
<td>MEA-14-003</td>
<td>E-13-014 (A/C): 1.6 mg Pt/cm²</td>
<td>M-13-386 D.L. 10.7</td>
</tr>
<tr>
<td>MEA-RD-14-012(i)</td>
<td>E-12-019 (A/C): 1.5/1.5 mg Pt/cm²</td>
<td>PBI+ TiO₂ D.L 11.2</td>
</tr>
<tr>
<td>MEA-RD-14-013(i)</td>
<td>E-12-019 (A/C): 1.5/1.5 mg Pt/cm²</td>
<td>Sulphonated PBI + TiO₂ D.L 11.3</td>
</tr>
<tr>
<td>MEA-RD-14-077</td>
<td>E-14-002 (A/C): 1.4/1.4 mg Pt/cm²</td>
<td>M-13-578; Thermally cured D.L 10.3</td>
</tr>
<tr>
<td>MEA-RD-14-078</td>
<td>E-14-002 (A/C): 1.4/1.4 mg Pt/cm²</td>
<td>Improved PBI+TiO₂ D.L 8</td>
</tr>
<tr>
<td>MEA-RD-14-089</td>
<td>E-14-002 (A/C): 1.4/1.4 mg Pt/cm²</td>
<td>Improved PBI+TiO₂ D.L. 8.4</td>
</tr>
</tbody>
</table>

*DL=Acid Doping level. Operation conditions: λO₂/λH₂=1.5/2.5, 160 °C, PBI as binder. (i) MEAs tested at UCLM
Long term test of MEA with thermally cured membrane

Figure 12 shows the results from 1000 hours long-term test. MEA-RD-14-135 was based on the thermally cured membrane. After 48 hours of break in procedure the current density was increased up to 0.3 A/cm². The constant load conditions were interrupted in order to perform electrochemical characterisation.

Table 5: Materials for MEA manufacturing.

<table>
<thead>
<tr>
<th>Fuel cell No.</th>
<th>Electrodes</th>
<th>Membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>RD-14-135</td>
<td>E-12-041(A/C):1 mg Pt/cm²</td>
<td>M-13-384; D.L.* 10,5</td>
</tr>
</tbody>
</table>

*D.L. Doping Level
As observed in Figure 10 the performance drop was quite significant after the first chemical characterization that was performed after 168 h of long term testing. The MEA performance increased slightly over time for the rest of the durability test.

Polarization curves with air and oxygen as oxidant was obtained at 168, 336, 504, 672 and 840 hours, until 1000 hours long term test goal was achieved.

In Figure 11a, the obtained polarization curve at 168 h reached a maximum current density of 1.5 A/cm², (using O₂ as oxidant), the voltage at the mentioned current density was 0.407 V. The performance loss after the high current exposure was found to be 4 % at 0.3 A/cm². A performance improvement was
observed for the latest test (840 hours of long-term test), with respect to the previous data obtained at 504 and 672 h.

In Figure 11b, the obtained polarization curve at 168 h reached a maximum current density of approximately 0.81 A/cm² at 0.4 V (using air as oxidant). The performance loss was 15% at 0.3 A/cm². In this case, the performance was consistently decreasing over time until the 1,000 hours durability was reached.

The dramatic drop performance at 168 h (See Figure 10) was believed to be due to the high current density during the first polarization curves, using hydrogen and oxygen as oxidant at 168 h (1.5 A/cm²). Similar results were observed by UCLM when thermally cured membranes were tested into an MEA.

In order to avoid further degradation in the MEA, the maximum current density was set to approx. 0.53 A/cm² for the rest of the test.

### 2.2.4 Cell optimization

As it has been said previously, UCLM sent different PBI membranes and DPS performed the MEAs and were back to UCLM for testing (see Table 4). Thus, UCLM carried out some tests following the operation conditions of the protocol. The MEAs were tested during more than 100 h. The Figure 12 a shows the cell voltage behavior at 0.2 A/cm² during this 100 h-test at 160 ⁰C running with air ($\lambda_{H2}=1.5; \lambda_{Air}=2, \lambda_{O2}=9.5$). As example, Figure 12 b shows the polarization curves of the MEA with the composite TiO₂ PBI membrane running O₂. It can be observed that this MEA performed very well and a decay of power at high current density was observed the last day. But, from Figure 12 a, it is observed that the MEA with the TiO₂ composite PBI membrane performs bad and not very stable. It was noticed that through the conduction of air there were some leaks which would explained the worst results with air. In the case of oxygen and due to the high used stoichiometry these leaks were not very noticeable.
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![Figure 12 a (left): Cell voltage vs. time at 0.2 Acm⁻² and 160 °C of different MEAs. b (right): Polarization curves obtained with the MEA-RD-14-012 fed with O₂ at different days.](image)

Table 6 shows the initial and final values of ESA calculated from the CVs preformed to the different MEAs tested at UCLM. It can be observed a small degradation of the electrodes during this period.

<table>
<thead>
<tr>
<th>ESA (m²g⁻¹)</th>
<th>MEA-RD-14-012</th>
<th>MEA-RD-14-013</th>
<th>MEA-RD-14-001</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>20.08</td>
<td>17.71</td>
<td>16.14</td>
</tr>
<tr>
<td>Final</td>
<td>17.29</td>
<td>14.09</td>
<td>15.44</td>
</tr>
</tbody>
</table>

2.2.5 Bipolar plate optimization

In collaboration with Eisenhuth, NEXT ENERGY performed a number of investigations and analyses of BPP samples:

Corrosion Tests

LSV were carried out at different phosphoric acid concentrations. In Figure 13 a exchange current corrosion and anodic Tafel slope are presented as function of H₃PO₄ concentration. The exchange current corrosion has decreased from 7 to 2 μA/cm² when H₃PO₄ concentration has been also increased from 0.5 to 14.75 M at 20 °C. Moreover, the anodic Tafel slope has increased until 10 M H₃PO₄ and for further H₃PO₄ concentrations it has weakly decreased. Thus, it could be said that an asymptotic limit has been reach around 10 M H₃PO₄. The anodic Tafel slope rise as function of the H₃PO₄ concentration suggests slower anodic reaction kinetics so graphite corrosion rate dropped off.
Figure 13 a: Corrosion current density, anodic Tafel slope, b: current density at $E = 0.6$ V and $E = 0.1$ V as function of $\text{H}_3\text{PO}_4$ concentration. Data calculated from linear sweep voltammograms.

Figure 13 b shows current densities at potentials simulating fuel cell anode ($E = 0.1$ V) and cathode ($E = 0.6$ V) conditions as function of $\text{H}_3\text{PO}_4$ concentration. In both fuel cell anode and cathode simulating conditions, current density has been reduced as a consequence of the worse corrosion kinetics when $\text{H}_3\text{PO}_4$ concentration has been increased. Furthermore, the potential simulating the anode conditions is close to the oxidation peak potential so this suggests that the fuel cell anode test conditions are slightly favorable for the development of a passive layer. Conditions simulating the fuel cell cathode favor forming a passive layer in all graphite samples. Thus, current density is higher at fuel cell anode conditions than at fuel cell cathode conditions. Further experiences will be carried out in the half-cell at higher temperatures and at free potential conditions with the same reference graphite BPP material as function of $\text{H}_3\text{PO}_4$ concentration.

### Long-term stockpiling tests

In addition to the electrochemical corrosion tests, long-term stockpiling tests of BPP materials and sealing have been started.

Eisenhuth provided a number of new samples and materials which are summarized in Table 7.

**Table 7: Materials provided by Eisenhuth.**

<table>
<thead>
<tr>
<th>Bipolar plate-material (BPP-material)</th>
<th>Timcal</th>
<th>Compounds in %</th>
<th>Phenolic resin</th>
<th>PPS</th>
<th>CNTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPP4 A</td>
<td>80</td>
<td>20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPP4 B</td>
<td>81</td>
<td>19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPP4 C</td>
<td>82</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPP4 D</td>
<td>83</td>
<td>17</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The procedure of testing is the same like the treatment for the phosphoric acid uptake of the BPP in the first semester of the project. A number of samples with a size of roughly one square centimeter of each BPP material have been prepared and weighed. The sealing samples are slightly larger due to their shape. The samples are stored in a Teflon container and are treated by autoclaving at a temperature of 180 °C. Half of the samples are stored in 85% Phosphoric acid, the second half is stored in the cooling media **Galden 270**, which will be used within the final system setup.

After 3000 h and after 10,000 h, the acid-uptake will be analyzed via phosphoric acid titration. Furthermore, SEM- and EDX-Analysis of BPP and sealing X-cuts will be investigated. **The results of the 3000 h-testing will be presented in the midterm report.**

The low cost configuration, PVDF based plates, has been manufactured by Eisenhuth and supplied to a selected customer for in situ testing. In the fuel cell test the plated enabled an adequate initial performance and stability. After 1000 h test it has been returned recently and will be analysed post mortem (acid uptake). However, as described in the WP3 ‘Characterization’, some these materials fail in the thermomechanical test at 180°C. Further experiments will be performed for a decision about this low cost material.

Eisenhuth has prepared BPP-4 based (mature SoA material) plates with different contents of carbon nanotubes (CNT) in order to improve electrical conductivity. As shown in the Figure 14, conductivity has been increased by applying up to 4% CNT.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PPS A</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>PPS B</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>PPS C</td>
<td>90</td>
<td>10</td>
</tr>
<tr>
<td>PPS D</td>
<td>90</td>
<td>10</td>
</tr>
</tbody>
</table>

**Sealing**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>EPDM 50 SA</td>
<td>non-conducting</td>
</tr>
<tr>
<td>EPDM 50 SA</td>
<td></td>
</tr>
<tr>
<td>FKM 60 SH</td>
<td></td>
</tr>
<tr>
<td>FKM 65 SH</td>
<td>non-conducting</td>
</tr>
</tbody>
</table>
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Figure 14: BPP4 based plate materials different CNT contents. The electric conductivity (in-plane) has been increased by CNT

Gaskets:
SoA gaskets are FKM materials available in different shore hardness. FKW 47n was chosen for first CISTEM application. New materials are under evaluation at Eisenhuth, in particular highly fluorinated FFKM types. They are characterized with respect to their stability against the coolant (Galden HT 230) specified by the stack/system developer and phosphoric acid under operating temperature. Eisenhuth sent to NEXT Energy four samples for further characterisation, they are listed in Table 7.

Task 2.3 MEA design

μ-Computed Tomography (μ-CT)
Micro-CT investigations visualize degradations effects and defects due to the mechanical stress under which the MEA and the components itself suffer. Several measurements have been executed (see also Task 3.4). In the second semester of CISTEM, the μ-CT-studies concentrate on MEAs from DPS. Next to ante and post mortem analysis of DPS-MEAs (Figure 15 a) and b)), which have been electrochemically investigated within the test station, an ex-situ contact pressure cycling test by dint of the new developed compression device has been started.

Post mortem analysis
Figure 15 shows 3-dim models of DPS-MEAs, the required data belongs to the μ-CT investigation, its reconstructions and the CT-Analyzer. Figure 15 a represents a MEA, which has been slightly compressed with a serpentine Flow Field within the test bench (Pc = 0.2 MPa, time slot ≈ 20h). In addition, Figure 15 b exhibits a
DPS-MEA, which has been electrochemically investigated in-situ while contact pressure increasing until 2.5 MPa. Only slight deformations are visible; while drifting from top to bottom no defects within the single layers could be detected.

![Image](image_url)

**Figure 15: 3D-µ-CT model of DPS-MEAs, a) Reference / ante mortem sample, compressed with 0.2 MPa for 1d within the Test station, b) post mortem sample, in-situ test with contact pressure increasing until 2.5 MPa**

### Contact pressure cycling

To analyze the influence of contact pressure to degradation processes within single cells, an ex-situ accelerated stress test has been performed. Therefore a small piece of a new DPS-MEA exposed to contact pressure cycling within the new and smaller µ-CT compression tool. The used contact pressure are 0.2, 0.5, 1.0 and 1.5 MPa, this cycle has been repeated three times with the same sample. This allows an observation of which detected defects are reversible (dilations e.g.) and which ones are irreversible (like fibers intrusion or cracking of the catalyst layer). In the first cycle no cracks in the catalyst layers were observed, the constitution of the MEA seems quite stable. Only slight moving of the layers against each other was detected at this point. The results from the second and third cycle will be presented at the project meeting in June 2014 and the next report.

### Deliverable 2.1. Optimized PBI based membrane with a durability of 1000 h

According to the Project, the D2.1 “Optimized PBI based membrane with a durability of 1000 h” must be provided the month 12. From the results previously shown and after the discussion which was held in Seville during an International Meeting among NEXT ENERGY, DPS and UCLM it was decided to perform a 1000 h test with the TiO₂ PBI composite from UCLM at the facilities of DPS and test the MEA with the thermal cured membrane from DPS at the UCLM facilities. The MEA-RD-14-078 was tested for the 1000 h durability test at the DPS facilities. Continuous increase on MEA performance was observed at the beginning of life (BoL). The increased voltage rate was 116 µV hr⁻¹. Failure of the hydrogen supply took place after 238 hours. Due to the unexpected failure on the hydrogen supply, MEA-RD-14-089 was manufactured which is a replicate of MEA-RD-14-078 (see Table 4), which is currently under testing in order to
fulfill the Deliverable 2.1. Furthermore polarization curves were measured once a week according to the test protocol. The durability test is shown in Figure 16.

![Figure 16: Durability test with materials beyond state of art. Improved uniformity PBI membrane + 2 w% TiO$_2$ & Standard DPS electrodes MEA ID: MEA-RD-13-089, 160 °C, $\lambda_{O_2}/\lambda_{H_2}=1.5/2.5$.](image)

At the same time, the UCLM started a 1000 h test with a MEA provided by DPS using a thermal cured PBI membrane. Figure 17 shows the cell voltage during the test. Once a week, IV, EIS, CVs and LSV were carried out, it has been labeled as Protocol routine. At 765 h approx. the experiment was stopped because the value of the cell was very low, more than 10 % of the value at BoL. The beginning is very similar to the one showed by the MEA-RD-14-089, it is to say, after the break-in period, different tests were carried out (Protocol routine (0)) and then the cell voltage increased to reach values around 0.65 V. But after the second tests (protocol routine (I)) the cell voltage was down dramatically to values a little bit higher than 0.61 V. After each Protocol routine the cell decay was around 10 mV. Not explanation has been found to this behavior, not damaged of the facilities was detected. It will be discussed in detail during the Project Meeting in June.

![Figure 17: Durability test with materials beyond state of art from DPS. 160 °C, $\lambda_{air}/\lambda_{H_2}=2.0/1.5$.](image)

As example, Figure 18 a shows the values of the OCV with air and O$_2$. In the case of the oxygen it could be say that the OCV values were constant but not for
the case of air. No explanation has been found. What is noticeable is the EAS loss that can be observed in the Figure 18b where the cyclic voltammetries are shown. This fact could explain the decays observed in Figure 16. More results and better discussion will be done next month, in the Project Meeting.

Figure 18: Some electrochemical parameters of the 1000 h test, A) Values of the OCV; B) Cyclic voltamogramms

WP 3: Degradation with SoA Materials

The goal of this work package is:

- To achieve general agreement on various test and operating procedures as well as long-term and accelerated stress testing;
- To identify the optimal gas composition for oxygen enriched cathode air with respect to durability and degradation;
- To make some single cells with SoA components and test the MEAs for durability and degradation analysis under various operating conditions;
- To make a few short stacks for lifetime testing;
- Identify relevant degradation mechanisms;
- To do post mortem analysis;
- Verify the targeted life time of the system.

Task 3.1: Definition and general agreement on necessary test and operating procedures

MEA test protocol

The Deliverable D3.1 (MEA test protocol) has been uploaded to the Joint Undertaking User platform in November 2013. Accelerated Stress tests and long
term tests have been and will be carried out for intensive investigation on degradation of MEAs and its compounds. Testing of oxygen enriched cathode air and ASTs are required for durability investigations. The test protocol guaranties that measurements and results from all partners can be compared.

The test protocol will be adapted at regularly intervals.

**Task 3.2: Durability operating conditions for single cell testing**

SoA MEAs have been tested to observe the influence of different oxygen partial pressures and different temperatures on the MEA performance. Those measurements were obtained at 0.4 A/cm$^2$, which is presented in Figure 19.

![Figure 19: Effect of the temperature on the MEA voltage, with pure oxygen (square black symbol) and air (green triangle). 0.4 A/cm$^2$, $(\lambda_{H2}/\lambda_{Air}) =1.5/2$](image)

As expected, an increase on temperature results is an increase of the MEA voltage regardless of whether air or oxygen is used as comburent. The oxygen gain is approximately 100 mV in a temperature range 150 – 175 °C. Strange phenomenon is observed at lower temperatures since the oxygen gain result to be negligible or having negative values at lower temperatures 130 – 150 °C. More investigations are needed to understand this issue.

A single cell with a standard MEA from DPS was tested in the facilities of the UCLM. The accorded protocol was followed and hence a break in period of 48 h at 120 °C and 0.1 A/cm$^2$ was carried out. After that, different characterization tests were performed (polarization curves, impedance analysis, VCs and linear sweep voltammetries) at different days.

It can be observed, that during the break-in period a constant cell voltage was achieved and after the first tests an activation of the cell was found. During the
last hours of the experiments a small decay was observed. As an example, Figure 20 shows polarization curves with air at different days of the experiment.

![Polarization Curves](image)

**Figure 20:** Polarization curves of the standard MEA from DPS operating with air at different times of the test

The values of the polarization curves were fitted to the equation 1 in order to get some parameters to help to the discussion of the results. Thus, the Tafel slope, \( b \), and the ohmic resistance, \( R \), were calculated.

Table 8 and Table 9 show the results of the fitting with air and oxygen respectively. It can be observed in both cases, air and \( O_2 \), an increase of the Tafel slope and of the \( R \) with respect to the values at 50 h which is indicative of a degradation of the MEA after that period. In case of the use of \( O_2 \). The \( b \) is slight higher, which is not expected, but the ohmic resistance is almost four times lower than that obtained with air.

\[
E = E_0 - b \cdot \log(j) - R \cdot j + b \cdot \ln\left(1 - \frac{j}{J_{lim}}\right)
\]  

(1)

<table>
<thead>
<tr>
<th>Parameter ( (mV) )</th>
<th>Model value at 0 h</th>
<th>Error (%)</th>
<th>Model Value at 50 h</th>
<th>Error (%)</th>
<th>Model Value at 100 h</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E_0 )</td>
<td>895.3</td>
<td>5.1</td>
<td>950.1</td>
<td>4.2</td>
<td>915.2</td>
<td>6.3</td>
</tr>
<tr>
<td>( b ) (Tafel Slope)</td>
<td>98.13</td>
<td>2.31</td>
<td>101.41</td>
<td>2.35</td>
<td>98.70</td>
<td>3.61</td>
</tr>
<tr>
<td>( R ) (ohm)</td>
<td>0.193</td>
<td>0.01</td>
<td>0.193</td>
<td>0.01</td>
<td>0.212</td>
<td>0.02</td>
</tr>
<tr>
<td>( J_{lim} ) (mA/cm²)</td>
<td>1765.3</td>
<td>83.5</td>
<td>1542.0</td>
<td>62.9</td>
<td>1280.5</td>
<td>62.5</td>
</tr>
</tbody>
</table>
Table 9: Parameters from the fitting of eq. 1 to the polarization curves with oxygen.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Model value at 0 h</th>
<th>Error (%)</th>
<th>Model Value at 50 h</th>
<th>Error (%)</th>
<th>Model Value at 100 h</th>
<th>Error (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_0$ (mV)</td>
<td>1007.4</td>
<td>4.1</td>
<td>1083.2</td>
<td>6.5</td>
<td>1061.2</td>
<td>6.9</td>
</tr>
<tr>
<td>b (Tafel Slope)</td>
<td>116.42</td>
<td>2.28</td>
<td>138.52</td>
<td>2.89</td>
<td>135.60</td>
<td>3.61</td>
</tr>
<tr>
<td>R (ohm)</td>
<td>0.051</td>
<td>0.01</td>
<td>0.052</td>
<td>0.01</td>
<td>0.082</td>
<td>0.02</td>
</tr>
<tr>
<td>$J_{lim}$ (mA/cm$^2$)</td>
<td>1476.3</td>
<td>46.2</td>
<td>1505.9</td>
<td>62.9</td>
<td>1487.8</td>
<td>56.7</td>
</tr>
</tbody>
</table>

**Task 3.3: Durability testing of individual materials**

**Electrodes**

The UCLM has carried out tests to assess the electrochemical stability of standard Pt based catalyst. A commercial one (40 %Pt/C) which is used in the preparation of the electrodes of UCLM was tested. Thus, a catalytic ink was sprayed onto a commercial GDL and CVs were performed in a 2 M phosphoric acid solution and at 50 °C. Figure 21 shows the voltamogramms obtained at different cycles. From them, the EAS (gPt/m$^2$) was calculated in order to evaluate the durability of this catalyst. The EAS decreased from 6.14 at 25$^{th}$ cycle to 4.03 at the 400$^{th}$ cycle. This means around 35 % of degradation of the EAS under these conditions. This material has been compared with other materials beyond state of the art and is discussed in the WP 2 of the CISTEM Project.

![Figure 21: CVs of the commercial Pt/Vulcan. 400 cycles. (Reference electrode: Ag/AgCl. Electrolyte: 2 M Phosphoric Acid, Temperature 50 °C).](image)

**Gas Diffusion Layers**

The μ-CT investigations have been used to analyze the consequences on the MEA and its components due to mechanical stress. The investigations have been fulfilled for the BASF-Benchmark MEA, which have a cloth type GDL, and the paper
based MEA from DPS. The same tests for the UCLM MEAs are currently in preparation.
The MEA thickness changes within the compression tool (see Figure 22; M. Karwey, Bachelor Thesis, University of Applied Sciences Südwestfalen / Germany, 2012) and a grid flow field replica as function of the contact pressure (0.2, 0.5, 0.75, 1, 1.5, 2 and 2.5 MPa) are recorded for the behavior under land area and within the channels (see Figure 23).
The cloth based BASF MEA shows bulging into the channels and compressibility under land. The DPS MEA, which has a paper GDL, seems to be stable and incompressible.

![Figure 22: µ-CT Compression Tool](image)

Figure 23: MEA thickness changes under land (left) and within the channels (right) as function of contact pressure.

The imaging shows that the DPS MEA exhibit nearly no dilatation into the channel and no defects could be detected, as it can be seen in Figure 24:

![Figure 24: DPS and BASF MEAs under different compression forces.](image)

Figure 24: DPS and BASF MEAs under different compression forces.

The behavior of the BASF MEA on compression forces is contrary; bulging into the channels can be detected even at low contact pressures. With increasing contact pressure, especially over 0.75 MPa, the detection of irreversible failures like cracks in the catalyst layer or even fiber intrusion rises.
Membranes

Standard PBI membranes from UCLM and DPS were characterized and durability issues were analyzed. The average thickness of the PBI membrane from DPS was 43 ± 1.2 μm, and 49 ± 1.2 μm for the one from UCLM. Figure 25 shows the proton conductivity of the standard PBI membranes from UCLM and DPS at different temperatures and under relative humidity of the environment around 60 ± 5 % (we are now measuring the proton conductivity under harsh conditions with very low humidity). High proton conductivities have been reached by both membranes, due to the very high humidity and high doping levels. The PBI membranes from DPS reach better conductivities till 150 ºC and the UCLM has a better behavior at the highest temperature.

![Figure 25: Proton conductivity of standard PBIs (red columns for DPS and blue columns for UCLM)](image)

One of the problems of the PBI based membranes is the acid leaching. Thus, leaching tests were carried out to the standard PBI membranes. The PBI membranes were put in hot water (80 ºC) and the PA concentration was measured at different times during one hour. The doping level and water uptake after put them in an 85 % wt phosphoric acid (PA) bath and the acid retained after leaching test are shown in Table 10. Similar doping levels and acid retained were achieved by both PBI membranes. These results are compared with those obtained with membranes beyond state of the art and discussed in the 2.2.3 Membrane optimization.

The chemical stability of the both PBI membranes was evaluated through Fenton test at 67 ºC during 10 h. Figure 26 shows the obtained results. It can be observed that both membranes followed the same tendency and showed good chemical resistances. Neither of them was damaged after 7 tests. The UCLM showed a slightly better chemical stability, maybe due to the different molecular weight of the polymer.
Table 10: Doping level, water uptake and the acid retained after the leaching test.

<table>
<thead>
<tr>
<th>SOURCE</th>
<th>DOPING LEVEL (mol H₃PO₄/r.u. PBI)</th>
<th>Thickness after doping</th>
<th>WATER UPTAKE (mol H₂O/r.u. PBI)</th>
<th>RATIO ACID/WATER (mol H₃PO₄/mol H₂O)</th>
<th>% H₃PO₄ RETAINED</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPS</td>
<td>10.5</td>
<td>90 ± 1.1</td>
<td>14.9</td>
<td>0.70</td>
<td>80.5</td>
</tr>
<tr>
<td>UCLM</td>
<td>12.5</td>
<td>96 ± 1.3</td>
<td>10.4</td>
<td>1.20</td>
<td>78.7</td>
</tr>
</tbody>
</table>

Figure 26: Weight loss from Fenton Tests

**Bipolar Plates**

Eisenhuth has done some activities with regard to Bipolar plates (BPP) characterization. The state of the Art material is BBP4, is a compound based on a phenolic resin with the following characteristics:

a) Binder: Duromer from phenolic resin, cross-linked, insoluble in any solvent
b) Plate manufacturing with compression moulding
c) High thermal and electrical conductivity
d) Also available with integrated sealing
e) Sufficient tolerances and mechanical integrity for applications up to 3000h operating time
f) Implemented in commercially available fuel cell products
g) Moderate phosphoric acid uptake
h) Stability under CHP conditions (20-40.000 h) to be determined / improved

Various tests have been done at:

- In situ testing at partners and selected customers
During the first six months SoA BPP-4 material were tested at a customer in a HT PEM stack over 1000 hrs. The other one an experimental was a plate based on PPS/ graphite composite, (PPS=polyphenylsulfide).

Both, bipolar plates samples were returned for post mortem analysis with a focus on phosphoric acid uptake in both materials. The goal is to identify materials with a low phosphoric acid uptake and, additionally, analyse and understand the mechanism of acid uptake in more detail. REM analysis with EDX mapping at NEXT ENERGY shall clarify whether the acid only contaminates the surface of the plates or is absorbed in the bulk material of the plate. The results shall propose solutions for further material development.

Corrosion tests of BPP samples have been performed at potentiostatic conditions over time as a function of the H₃PO₄ concentration using the half-cell shown in WP 2. Thus, Figure 27 shows BPP tests at potentials simulating fuel cell anode (E = 0.1 V) and cathode (E = 0.6 V) conditions. In Figure 27 a and Figure 27 b, the half-cell has been purged with nitrogen to look at the acid concentration effect at the anode and cathode potential conditions. Besides, tests (Figure 27 c and Figure 27 d) have been also performed by bubbling hydrogen or air over time at anode or cathode conditions, respectively. Thus, the effect of fuel cell reactant gases has been also studied. In Figure 27a (anode conditions), a current density around -0.4 μA/cm² is obtained for 0.5 M H₃PO₄ solution. From a 5 M H₃PO₄ solution to higher H₃PO₄ concentration, the current stabilizes around -0.06 μA/cm². In case of Figure 27 b, there is no influence of H₃PO₄ solution concentration on corrosion current density. Thus, this suggests that the development of a protective passive layer is favored for the BPP samples on top of their surface at cathode conditions. When studying the reactant gases effect, the same trends can be seen in Figure 27 c (anode conditions) and Figure 27 d (cathode conditions). Thus, the higher the H₃PO₄ concentration, the closer the current stabilizes to 0 μA/cm². At anode conditions, the introduction of the H₂ bubbling reduces the corrosion current density to lower values than the ones obtained without H₂ bubbling. At cathode conditions, the corrosion current density has been hugely increased in comparison with the tests carried out without air bubbling for low H₃PO₄ concentrations. This may be explained in such a way that the corrosion of the BPP samples is influenced by the water, because the oxygen that corrodes the BPP samples may be generated by water electrolysis at positive potentials. So, the lower the water concentration is, the less is the amount of generated oxygen.

Additionally, the thermal stability of different BPP samples under HT PEM conditions was tested in collaboration with NEXT ENERGY. In order to characterize the plate material with respect to its thermo mechanical stability, a
test method\(^1\) was used, where the plate samples are loaded with pressure typical for fuel cell stacks (1 kg/cm\(^2\)) under operating temperatures. **Figure 28** shows a test array where 3x3 samples with 1x1 cm size are loaded with a 10 kg steel block each.

Without going into the details of the 9 samples, the result of this test at 180 °C is that all BPP samples based on the BPP-4 configuration (bonded by phenolic resin) were mechanically stable and showed no significant thinning. The same applies for the samples based on PPS as a binder polymer. As a reference, typical LT PEM materials based on polypropylene have been tested and, as expected, they are destroyed at 180 °C. Additionally, two samples bonded with PVDF have been tested, one with mechanical failure and one with thinning at 180 °C. Thus, PVDF is close to the limit of thermal stability and appears to be not very well suited for HT PEM applications.

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\(^1\) Test method was developed within the JU Project.

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**Figure 27:** Potentiostatic test for bipolar plate samples at different H\(_3\)PO\(_4\) concentrations. (a) E = 0.1 V and (b) E = 0.6 V, N\(_2\) bubbling before test. (c) E = 0.1 V and (d) E = 0.6 V, H\(_2\) and air bubbling during test. Flow rate H\(_2\) = Air = 10 ml/min
Further ex-situ tests of BPP materials have been performed or are in progress at CISTEM partners:

Different BPP samples were shipped to Next energy to test:

- Testing ex situ $\text{H}_3\text{PO}_4$ exposure, 160 °C, which can be found in Figure 27
- Testing ex situ Galden HT 270 exposure, 160 °C

Other characterizations were performed at Eisenhuth:

- Most simple tests (weighing, and optical inspection)
- Electrical conductivity in plane (RT)
- Electrical conductivity through plane (RT)
- Thermal conductivity
- Phosphoric acid uptake (Titration)
- REM/EDX acid distribution

Some of the test results are described in 2.2.5 Bipolar plate optimization, where new BPP materials have been developed and characterized with respect to the relevant parameters.

**Gaskets**

SoA gaskets for HT PEM are based on FKM with different shore hardnesses available. Here, FKM 47 shore has been chosen. The gasket materials will be tested by exposure to the cooling liquid Galden HT 230 (Solvay) specified by the stack/system developer Inhouse Engineering. This was defined during the CISTEM meeting in Aachen. The tests will be performed parallel with the material tests from WP2. Within WP 2 new highly fluorinated gasket materials will be tested, such as FFKM.

Following materials were sent to Next Energy:

- EPDM 60 Shore A
- EPDM 60 Shore A, non-conductive, 60023524
- FKM 60 Shore A
- FKM 65 Shore A, non-conductive, 60027053
Bipolar plates were sent to Next Energy:

- BBP 4 Standard – mixture Graphite / Polymer: 80 /20)
- BBP 4 – Set A (mixture Graphite / Polymer: 81 /19)
- BBP 4 – Set B (mixture Graphite / Polymer: 82 /18)
- BBP 4 – Set C (mixture Graphite / Polymer: 83 /17)

Also some other materials for “WP 3” – PPS compound:

- PPS – Set A (mixture Graphite / Polymer: 90 /10)
- PPS – Set B (mixture Graphite / Polymer: 88 /10 +2% CNT)
- PPS – Set C (mixture Graphite / Polymer: 88 /10 + 3 % CNT)
- PPS – Set A (mixture Graphite / Polymer: 90 /10 +4% CNT)

Other activities are related with plate milling for Inhouse, gasket production for Inhouse. Other tests and background information were performed with regard to degradation mechanisms in HT-PEM fuel cells.

**Task 3.4: MEA and single cell degradation**

**Accelerated Stress Tests**

Figure 29 shows the results from a 1,000 h accelerated stress test (AST) of a Dapozol® MEA. The fuel cell has been operated with a dry synthetic reformate (78% H₂, 22% CO₂) as fuel and 30% O₂ enriched air as oxidant. The current density cycling has been interrupted for MEA characterization once per week (black points in Figure 29 a). Besides, the oxygen enrichment has been switched back to normal air before carrying out the MEA characterization in order to perform the whole characterization at the same operating conditions as a recommendation of DPS.
Figure 29: (a) Accelerated stress test for the fuel cell operating with 78% H₂+22% CO₂/30% O₂ (λₕ₂/λ₃₀% O₂=1.5/2.85). Current density cycling was interrupted for MEA characterization on day: 0, 6, 13, 20, 27, 34 and 35 (black circles). (b) Polarization curves, (c) EIS spectra at 0.3 A/cm² and (d) ohmic (Rₚₐₜₚ), charge transfer (Rₖₚₜ) and mass transfer (Rₘₚₜ) resistances from (c) as function of operation time for the fuel cell operating with 78% H₂+22% CO₂/Air (λₕ₂/λₐir =1.5/2). MEA: DPS-28, T=160 °C, p=1 atm, 5-fold serpentine flow field, Pₖₚₜ=0.75 MPa

Figure 29 b, Figure 29 c and Figure 29 d summarizes the main results from the weekly MEA characterization. As it can be seen Figure 29 a, the voltage loss at 0.3 A/cm² is higher than OCV loss. Polarization curves show 7 % voltage loss at 0.3 A/cm² during the whole test. The different resistance contributions from impedance spectra at 0.3 A/cm² (Figure 29 d) show an increase of charge and mass transfer resistance. Those increases in the resistances are due to catalyst and porous structure degradation over time. Thus, the highest degradation rate has been observed during the first week of the test.

**Long-Term MEA Tests**

Figure 30 a shows the results from a 1,000 h long-term test of a Dapozol® MEA at constant current density (0.3 A/cm²). The fuel cell has been operated with pure hydrogen as fuel and air as oxidant. The constant load conditions have been interrupted for MEA characterization once per week (black points in Figure 30 a) Figure 30 b shows fuel cell polarization curves and Figure 30 d presents the different resistance contributions from the impedance spectra at 0.3 A/cm² shown in Figure 30 d.
Figure 30: (a) Long-term test for the fuel cell operating with \( H_2/Air \) (\( \lambda_{H2}/\lambda_{Air} = 1.5/2 \)). Current density was interrupted for MEA characterization on day: 0, 7, 14, 18, 28 and 35 (black circles). (b) Polarization curves, (c) EIS spectra at 0.3 A/cm\(^2\) and (d) ohmic (\( R_{\text{Ohm}} \)), charge transfer (\( R_{\text{ct}} \)) and mass transfer (\( R_{\text{mt}} \)) resistances from (c) as function of operation time. MEA: DPS-20, T=160 °C, p=1 atm, 5-fold serpentine flow field, \( P_c=0.75 \) MPa

From Figure 30 a, the voltage at 0.3 A/cm\(^2\) has been improved during the first week of the test and then, voltage loss has observed. Moreover, similar fuel cell performance is observed between day 0 and day 7 of the test. From impedance study it can be observed that ohmic and charge transfer resistances have increased more than mass transfer resistance. Thus, fuel cell degradation over time can be attributed to membrane and to catalyst deteriorations.

**Short stack**

Tests with the first shortstack are currently in progress (see WP 4, Stack design).

**WP 4: Balance of Plant Design**

The main aims of this work packages are:
The development of the main components of the plant (BoP) with respect to:
- Maximum electrical efficiency of the system,
- Lifetime of the components,
- Minimum component costs,
- Compliance to technical rules and legal aspects and limitations.

Design and test of plant components under system equivalent conditions
- Optimization of components in single components tests,
- Specification of components for system operation.

Construction and delivery of BoP components for two modules of 5 kWel each for the evaluation unit.

Introduction

The aim of this work package is the development of the main components of the plant (BoP) with respect to maximum electrical efficiency of the system, lifetime of the components, minimum component costs, compliance to technical rules and legal aspects and limitations.

Following up, the design and test of plant components under system equivalent conditions, optimization of components in single components tests and specification of components for system operation shall be done.

As outcome of this work package, the construction and delivery of BoP components for two modules of 4 kWel each for the evaluation unit is targeted.

System specification

As coordinator of WP4 and WP5, OWI summarizes all relevant component and system specification data. The current status of collected information is shown in the following

Table 11. In fields with missing data the responsible partners respectively component developers are shown.

In this early phase of the project, open questions are still present. The most important points conclude from the not yet fully defined partial load state and the off gas burner specification, since the components are still under development.

Table 11: List of relevant component and system specification data

<table>
<thead>
<tr>
<th>Target values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 submodule of 100 kWel system</td>
</tr>
<tr>
<td>Basis for system modeling / evaluation unit</td>
</tr>
</tbody>
</table>
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<table>
<thead>
<tr>
<th><strong>Reformer Module (incl. WGS)</strong></th>
<th><strong>P&lt;sub&gt;Min&lt;/sub&gt;</strong></th>
<th><strong>P&lt;sub&gt;Max&lt;/sub&gt;</strong></th>
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<td><strong>fuel input quality</strong></td>
<td>NG EN 437 class E G20</td>
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</tr>
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<td><strong>fuel input (basis LHV) in kW</strong></td>
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<td>25</td>
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<tr>
<td><strong>Inlet streams</strong></td>
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<td>CH&lt;sub&gt;4&lt;/sub&gt; in mol/s</td>
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<td>Steam-to-Carbon ratio (S/C)</td>
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<td>3,5</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O (fl) in g/min</td>
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<td>Inlet temperature of CH&lt;sub&gt;4&lt;/sub&gt;/H&lt;sub&gt;2&lt;/sub&gt;O mixture in °C</td>
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<tr>
<td>Temperature in °C</td>
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<td>Reformate gas volume flow in mol/s</td>
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<td>53,92</td>
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<td>operating pressure in bar (rel)</td>
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<td>maximum inlet temperature air in °C</td>
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<td>maximum thermal power input</td>
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<td>air excess ratio</td>
<td>ICI</td>
<td>1,25 - 1,35</td>
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<td><strong>Bi-Fuel Burner Startup limitations</strong></td>
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<td>fuel input heating value (LHV)</td>
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<td>maximum thermal power input</td>
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<td>air excess ratio</td>
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<td>electrical output (DC) gross in kW</td>
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<td>2</td>
</tr>
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<td>number of cells per stack</td>
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<td>90</td>
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<td>current density in mA/cm²</td>
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<td>fuel utilization in %</td>
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<td>min H&lt;sub&gt;2&lt;/sub&gt; stoichiometry</td>
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<td>&lt; 1,5</td>
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<tr>
<td>min. H&lt;sub&gt;2&lt;/sub&gt;/CO ratio at stack outlet</td>
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<td>air flow in Nl/min</td>
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<td>450</td>
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<tr>
<td>min O&lt;sub&gt;2&lt;/sub&gt; stoichiometry</td>
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### Deliverable 1.3: Annual Management Report

#### Deliverable 1.4: Annual Technical Report

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<td><strong>outlet temperature anode in °C</strong></td>
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<td>160-180</td>
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<td><strong>inlet temperature cathode in °C</strong></td>
<td>Inhouse</td>
<td>Inhouse</td>
</tr>
<tr>
<td><strong>outlet temperature cathode in °C</strong></td>
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<td>160-180</td>
</tr>
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<td><strong>maximal pressure difference Anode-cathode in bar</strong></td>
<td>Inhouse</td>
<td>&lt; 0,1</td>
</tr>
<tr>
<td><strong>maximal pressure difference Anode-ambient in bar</strong></td>
<td>Inhouse</td>
<td>&lt; 0,1</td>
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<tr>
<td><strong>maximal pressure difference Cathode-ambient in bar</strong></td>
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<td>Inhouse</td>
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<tr>
<td><strong>Idling temperature in °C</strong></td>
<td>Inhouse</td>
<td>Inhouse</td>
</tr>
<tr>
<td><strong>temperature gradient in K/min</strong></td>
<td>Inhouse</td>
<td>Inhouse</td>
</tr>
<tr>
<td><strong>type of cooling media</strong></td>
<td>Galden HT 230</td>
<td></td>
</tr>
<tr>
<td><strong>mass flow cooling media in kg/s</strong></td>
<td>Inhouse</td>
<td>Inhouse</td>
</tr>
<tr>
<td><strong>inlet temperature cooling media in °C</strong></td>
<td>Inhouse</td>
<td>120-160</td>
</tr>
</tbody>
</table>

#### Heating circuit

<table>
<thead>
<tr>
<th><strong>P&lt;sub&gt;Min&lt;/sub&gt;</strong></th>
<th><strong>P&lt;sub&gt;Max&lt;/sub&gt;</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>outgoing temperature heating in °C</strong> (single house with floor heating)</td>
<td>40</td>
</tr>
<tr>
<td><strong>return temperature heating in °C</strong> (single house with floor heating)</td>
<td>30</td>
</tr>
<tr>
<td><strong>hot water temperature in °C</strong> (single house with floor heating)</td>
<td>55</td>
</tr>
<tr>
<td><strong>outgoing temperature heating in °C</strong> (district heating)</td>
<td>75</td>
</tr>
<tr>
<td><strong>return temperature heating in °C</strong> (district heating)</td>
<td>30</td>
</tr>
<tr>
<td><strong>hot water temperature in °C</strong> (district heating)</td>
<td>55</td>
</tr>
</tbody>
</table>

### Stack design

#### Stack-parts and materials:

The gaskets, MEAs and flowfields for the first CISTEM-Short-Stack have been delivered to inhouse-engineering and are already assembled and under investigations.

#### Short-stack:

The general stack-concept and the clamping-concept are fixed. There have also been made final decisions on all materials.

A first short stack is already assembled (5 MEAs with 186.6 cm²) and under investigation. A photo of this short stack can be found in Figure 31.
Testing-rig for short-stacks:
The testbench\(^2\) for short-stacks is already in use and first tests with short-tacks are currently in progress. Short-stack testing will be done with synthetic reformate (mixed H2 and CO2, dry).

Stack specifications
First specification of the stacks’ working point has been done on the basis of characteristics-curve received from DPS. Operating-parameters could not yet be designed or validated. To fix values for these parameters tests have to be done with short-stacks. (First results not before June 2014)

Design of reformer-module

Bi-fuel burner development

\(^2\) Testing-rig has been developed within the German project MÖWE 3, GA number: 0327724F
The burner in developing for the fuel processor is a bi-fuel burner. The innovative design permits its utilization like startup burner while natural gas is used to rise the fuel processor temperature and it also permits its utilization like afterburner while syngas, coming from stacks anode exhaust, is available. The burner starts as standard premix burner, working with natural gas and air and with all the standard control and safety characteristics. This configuration (starting burner mode) could be used as long as necessary without limitation, but for efficiency reason, a switch to syngas is preferred when it is available. When syngas is available for the burner, syngas and extra air are feed to the burner through two different channels (after burner mode) and contemporary the starting mode burner is switch off. During starting mode the burner will remain available to increase the reformer reactor temperature if it will be necessary. Small scale prototype is been done and is currently under test. Tests are planned to run until begin 2014. Through data analysis, a scale up to correct size will be done from begin 2014.

Test on small scale bi-fuel burner ended successfully in March 2014. The scale up study is been done and a prototype will be ready for tests starting from mid of May 2014.

Apart from the size and the consequent dimensioning, the full scale prototype takes into account the possibility to use preheated air when it works in after burner mode.

Reformer development

A small scale reformer, suitable for 0,7 Nm³/h of natural gas, is been developed. Many hours of tests are already done both with burner running in starting burner mode and in after burner mode. The after burner mode configuration is obtained feeding the burner using a simulated gas composition compatible with anode exhaust.

The methane conversion in this small scale reformer prototype is higher than 96% with an average reactor temperature of 720°C and an optimum catalyst temperature, as indicated by the supplier, of 730°C. It is possible to modify the conversion by changing the reactor temperature, but temperatures higher than 750°C will reduce the lifetime of the catalyst. Up to now, no sign of degradation has been observed, neither in catalyst, nor in fuel processor components.

Small scale WGS reactor is under development and tests were planned to start before end of 2013. Starting from previous experience, no particular problem is expected from the WGS reactor side.

The scale up study of the fuel processor, both for reformer and WGS, is planned for begin of 2014.

Tests on small scale reformer were ended successfully in March 2014 (Figure 32). Design of full scale reformer was finished end of April 2014 and prototyping is now in progress planned to be finished by end of May 2014.

Like the development of the full scale bi-fuel burner, the full scale reformer takes into account the utilization of preheat air while the system is in after-burner mode operation.
Concerning WGS, tests on different small scale WGS show that it is not possible to use one single shift reactor, so the adoption of two shift stage configuration is necessary.

Tests on small scale two stage WGS are still in progress. The tests highlight the difficulty to obtain CO concentration in the syngas as low as 1% if the steam/carbon ration is not at least 3.5.

Discussion inside consortium is needed for understand the best compromise between water and CO content in the syngas.

The scale up of WGS to full size (design and prototyping) is planned to start end of June 2014.

![Figure 32: Photo of small scale fuel processor](image)

**Design of heating circuit**

The main focus is the support with heat for a cluster of single houses via near district heating. In addition the case of a single large house will be assessed. Primary the system has to guarantee the amount of the requested heat. The basic heat load is delivered by the fuel cell system, which provides a part of the electricity of the connected buildings. If the fuel cell system is not able to provide the heat for the buildings, a standard gas-burner will substitute the missing amount of heat.

The two variations of heater circuit interconnections are revealed in the following. One option is a local heat net for a cluster of single houses. The other
option is the heat supply for a large building. The heat demand is divided into the heating of the water for domestic use and the heating circuit water. The residual heat of the fuel cell process is extracted with two heat exchanger of each fuel cell part. The first HEX extracts the heat of the cooling circuit of the fuel cell stack. The warmed up medium attains to the next HEX, which transfers the residual heat from the reforming process. The single fuel cell systems are connected by an assembling tube. The heated water delivers the heat into a domestic hot water tank, which buffers the heat from the fuel cell system. The buffer balances the heat demand of the connected house system. Typical temperatures for a local heat net are assumed. A typical flow/return temperature couple for this requirement can be 90°C/70°C. For a single large house the temperature couple can be lower, i.e. 60°C/40°C. For the next examinations the flow/return temperatures are defined at 90°C/70°C. Heat demand statistics for the different climate zones in Europe are currently under research.

![Draft of heating circuit](image)

**Test rig for efficiency test**

In order to design the hardware test rig including BOP components (backup boiler, heat storage etc.) a dynamic system simulation is performed. The tests performed on the test rig will include the determination of the standard efficiency factor and the thermal and electrical coverage of standard load profiles. As a result of the simulation one gets the main design parameters (e.g. volume of the heat storage, mass flows and temperatures) of the test rig.
Figure 34: Interconnection of a CHP unit and a backup boiler for the standard efficiency factor test.

The German technical standard DIN 4709 defines a calculation method for the determination of the standard efficiency factor for micro-CHP-appliances of nominal heat input not exceeding 70 kW (VDI, 2011). In Figure 34 a possible interconnection of a CHP unit and a backup boiler is shown. The thermal load is included into the test rig applying different mass flow of heating water at a forward temperature \( T_{\text{wl}} = 50^\circ C \) and a backward temperature of \( T_{\text{vl}} = 30^\circ C \). The performance test rig includes a heat storage tank. The volume of the heat storage is one important technical design parameter.

Figure 35: Load profile of the test program

Figure 35 shows the test cycle for the determination of the standard efficiency. The X-axes depicts the cycle time, the Y-axes depicts the load of the cycle in percent. The test cycle starts at point (1) and ends at point (2). The corresponding load table is depicted in Figure 35 (right). Before the test begins, a preparation time represented in time ranges (3) and (4) is recommended in order to achieve steady state conditions at the beginning of the test.

**Definitions**

The fuel input is defined as

\[
Q_{\text{fuel}} = m_{\text{fuel}}H_u. \tag{2}
\]

The thermal output is defined as
$$Q_H = \int (\dot{m}_w c_p (T_{vl} - T_{rl})) \, dt. \quad (3)$$

The electrical output is defined as the difference between generated electrical work and electrical work for auxiliary units (pumps, etc)

$$W_{el} = W_{gen} - W_{aux} \quad (4)$$

The standard efficiency factor for thermal and electrical CHP share becomes.

$$\eta_{th,H} = \frac{Q_H}{Q_{fuel}} \quad \eta_{el,H} = \frac{W_{ges}}{Q_{fuel}} \quad (5)$$

The overall efficiency factor for the CHP module is calculated to

$$\eta_{ges} = \eta_{th,H} + \frac{f_{P,el}}{f_{P,fuel}} \eta_{el,H} \quad (6)$$

The primary energy factors $f_{P,el}, f_{P,Br}$ in Equ. (6) can be obtained from the German technical standard DIN V 18599-100.

**Simulation results**

The nominal thermal power of the CHP module is assumed to be 12.4 kW with an electrical efficiency of 40% and a total efficiency of 90%. The backup boiler is assumed to have a nominal capacity of 17 kW with a thermal efficiency of 95%.

The heat storage tank has a capacity of 2000 l. The CHP module works within a temperature of $T_{CHP}=70^\circ C \pm 4\%$. The hysteresis describes the switch on and switch off conditions. In order to achieve a priority of CHP runtime, the hysteresis of the Boiler is $T_{Boiler}=65^\circ C \pm 1\%$, and starts and ends below the temperatures of the CHP module.

![Figure 36: Thermal power of the CHP unit and the backup boiler](image)
Figure 37: Thermal energy of the CHP unit and the backup boiler

Figure 38: Electrical power and fuel power of the CHP module

Figure 39: Temperature curves of the CHP module and the boiler

Figure 36 shows the thermal power of the CHP unit and the backup boiler. The integrated values of the generated heat are shown in Figure 37.

Table 12: Simulation result of the test rig with V=2000 l

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_{ges}$</td>
<td>269.40 kWh</td>
</tr>
<tr>
<td>$Q_{Br}$</td>
<td>763.72 kWh</td>
</tr>
<tr>
<td>$Q_H$</td>
<td>379.13 kWh</td>
</tr>
<tr>
<td>$\eta_{th,H}$</td>
<td>0.50</td>
</tr>
<tr>
<td>$\eta_{el,H}$</td>
<td>0.35</td>
</tr>
<tr>
<td>$\eta_{ges}$</td>
<td>1.33</td>
</tr>
</tbody>
</table>
The determination of the standard efficiency is summarized in Table 12. Considering the primary energy factors of DIN V 18599-100, the resulting overall efficiency is simulated to $\eta_{ges} = 1.33$. The results of the simulation will be tested on the hardware test rig.

The dynamic system simulation of the test rig has been performed in order to find the necessary dimensions of the heat storage tank. As a result a storage volume of about 2000l should be implemented for one module.

### Status further system components (OWI)

#### Stack Cooling

The dimensioning of the stack cooling system is currently in progress. As cooling media “Galden HT230” by company “Solvay” has been chosen. Due to the variation in viscosity, the supply of suitable pumps is the main task.

#### Air supply Stack

The air blower for the stack will be dimensioned with data for mass flow and pressure drop from the partner Inhouse, when the stack design is finalized. The use of compressed air for the evaluation unit is also possible.

### WP 5: CHP Design and Setup

The main goals of this work package are:

- Proof of concept for the modular CHP design,
- Setup of 2 full stack modules in one “modular” CHP unit,
- Investigation of controls options and operational strategies,
- Detailed analysis of system potential,
- Providing guidelines and rules for numbering up to larger units.

### Introduction

The main goal of the system development is to enhance the thermal integration and identify the best operating point of the system in order to optimize the electrical efficiency of the fuel cell module. The design goal of the system is to achieve at least 40 % electrical efficiency (see Figure 40). The application range of the CHP application demonstrated in Figure 40 is limited to 100 kW electrical output. Within this range the proposed technology has important benefits
compared to reference technologies, e.g. internal combustion engines, stirling engines and gas turbines.

**Figure 40: Electrical efficiency over power for combustion and Stirling engines**

In the following it is described how the design goal of more than 40 % efficiency is intended to be achieved and demonstrated in the project. First of all, 0D calculations (static, non-time-dependent) are performed to define feasible system concepts. With the optimized system concept, a starting strategy is tested in a first version of the 1D system model (transient, time-dependent). In parallel the definition of the system specification is forwarded.

**Design evaluation**

The system design is developed and optimized by means of a 0-D model implemented in Matlab/Simulink. The model includes particular component models that can be composed to form an entire fuel cell system. The particular component models are:

- Reformer
- Heat Exchanger
- Evaporator
- Shift reactor
- Fuel cell
- Burner
Within the component models the energy balance and mass balance are solved by means of iteration. In reactors where chemical reactions take place, the chemical equilibrium is calculated by minimization of Gibbs free enthalpy using the algorithm from Gordon et al. Thermodynamic properties of substances are represented by a 9 constant data base from NASA properties and coefficients (PAC) program. The data is utilized to express heat capacity at constant pressure, enthalpy and entropy as a power series. In the applied model the following substances are considered: CH₄, H₂O, H₂, CO, CO₂, O₂, and N₂. The model provides molar gas flows and temperatures after either component.

Since the model uses iteration, steady-state operation of a system is calculated. Adiabatic operation is assumed adiabatic for all reactors. Using the model, a rapid optimization of the system design can be carried out, since derivatives can easily be investigated with respect to the system efficiency.

### System development

The main goal of the system development is to enhance the thermal integration of the system in order to optimize the electrical efficiency. The basic design of the system as shown in the project description was considered in a preliminary calculation. The boundary conditions of the simulation were set as given in Table 13.

**Table 13: Boundary conditions 0-D calculations**

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>ϑ_Reformer</td>
<td>700 °C</td>
</tr>
<tr>
<td>ϑ_HT</td>
<td>350 °C</td>
</tr>
<tr>
<td>ϑ_MTS</td>
<td>240 °C</td>
</tr>
<tr>
<td>ϑ_HT-PEM</td>
<td>170 °C</td>
</tr>
<tr>
<td>λ_H₂</td>
<td>1.4</td>
</tr>
<tr>
<td>U_cell</td>
<td>700 mV</td>
</tr>
<tr>
<td>P_system</td>
<td>1.5 bar</td>
</tr>
</tbody>
</table>

It was observed, that one WGS stage is not sufficient to obtain the required CO concentration for the HT-PEM operation. Therefore, in a first development step, HTS and MTS reactors were complemented to the system (Figure 41).
Figure 41: Fuel Processor with HTS and MTS

The system efficiency is defined as given in the following equation:

$$\eta_{el,\text{System}} = \frac{P_{el,\text{gross}}}{\dot{m}_{CH4} \cdot LHV_{CH4}}$$  \hspace{1cm} (7)$$

The system efficiency of the system shown in (Figure 41) results in $\eta_{el,\text{System}}=33.6\%$. The low efficiency is mainly caused by poor heat integration in the fuel processor. Heat from the hot flue gases and cathode off-gas is not effectively recovered. Therefore the effect of heat recovery from the cathode off-gas was calculated. The heat was exchanged to the afterburner air. Thus, the system efficiency was enhanced to $\eta_{el,\text{System}}=34.8\%$.

Still, most of the heat from the burners is not integrated in the fuel processor and can be utilized to enhance the electrical efficiency. However, heat exchange with the NG burner air is not reasonable since the air flow is much smaller than for the afterburner. Therefore, another option was considered recovering heat from the burners to heat the air for the afterburner (Figure 42). By this measure, the electrical efficiency was enhanced to $\eta_{el,\text{System}}=39.0\%$. 
Considering the occurring temperatures in the system, it was observed that the steam temperature at the reformer inlet was low. Therefore, further potential for the system exists in a more effective steam generation and steam super heating. Investigating several options, the system design illustrated in Figure 43 showed good results. Therein, steam is mainly generated in the evaporator after the reformer and after the shift reactors. The heat exchanger between reformer and HTS is used to super heat the steam from the evaporators. Thus the steam temperature entering the reformer is increased by 200 K. The electrical system efficiency is enhanced to $\eta_{\text{el, System}} = 40.3\%$.

In upcoming investigations the system will be adjusted in communication with ICI in order to find the final system setup for the demonstration module. Further potential for efficiency improvement exists in the heat recovery from cathode off-gas.
Definitions

For the evaluation of the system performance a separated look on the efficiencies is implemented. The reformer efficiency is defined as the relations between consumed reformate ($H_2$ output) and fuel input. $H_{u,\text{refo}}$ and $H_{u,\text{fuel}}$ denote the lower heating value of the reformate and the fuel input respectively.

$$\eta_{\text{refo}} = \frac{m_{\text{refo,cons}} H_{u,\text{refo}}}{m_{\text{fuel}} H_{u,\text{fuel}}}$$  \(8\)

The fuel cell efficiency is defined as the electrical power generated (output), related to reformate consumed in the fuel cell (input).

$$\eta_{\text{el,stack}} = \frac{P_{\text{el}}}{m_{\text{refo,cons}} H_{u,\text{refo}}}$$  \(9\)

The electrical efficiency of the reformer-fuel cell system is the product of reformer efficiency and stack efficiency.

$$\eta_{\text{el,module}} = \eta_{\text{refo}} \eta_{\text{el,stack}} = \frac{P_{\text{el}}}{m_{\text{fuel}} H_{u,\text{fuel}}}$$  \(10\)

The separation of the system efficiency to reformer and stack efficiency allows a more detailed insight to possible performance improvements.
The fuel utilization $FU$ is defined as the relation between consumed reformate and generated reformate. With increasing fuel utilization $FU$, less reformate is fed-back to the reformer process. The fuel utilization $FU$ is an important operating condition of the fuel cell.

$$FU = \frac{m_{\text{refo,cons}}}{m_{\text{refo}}}$$

(11)

The steam to carbon ratio $S/C$ is defined as the relation between the mole-mass of the process steam and carbons of the fuel.

$$S/C = \frac{n_{\text{H}_2\text{O}}}{n_{\text{C}}}$$

(12)

The fuel utilization, steam to carbon ratio and the process temperatures are the most important process parameters. The optimization of these parameters is topic of the following chapter *Optimization of system parameters by 0D-Simulation*.

---

**Basic system design – evaluation unit**

The final basic system design is shown in Figure 44. As goal of the project, one module of the overall system shall be realized (in the following *evaluation unit*) to provide experimental data and show the proof of concept. A single fuel cell module will produce 8 kW electrical energy and in the shown case, the gross electrical efficiency of one module will be app. 40 %.

All modules of the final system supply a central domestic hot water tank with a backup burner to provide peak heat loads. The electrical power of every module is used by the customer or fed to the grid. In the case of the evaluation unit, a resistor will simulate the electric load profile and a water-cooled heat exchanger will simulate the district heating demand.

In natural gas operation the reformer module produces the hydrogen rich gas for the fuel cell module. After utilization of the most of the hydrogen in the fuel cell module the remaining heating value of the syngas after the fuel cell is used to heat the endothermic steam reforming process. Evaporators between the reactors are used to produce the steam and to control the inlet temperatures of the following reactors and the fuel cell. The remaining amount of steam needed to reach the desired value of $S/C$ is evaporated using the burner flue gas after the reformer. For natural gas steam reforming, a desulfurization unit is required to protect the reforming catalyst from poisoning. The syngas at the outlet of the reforming module shall consist of not more than 1 % Carbon-monoxide (CO) to avoid deactivation of the fuel cell catalyst.
In the evaluation unit the high temperature PEM fuel cell will be operated. The syngas is converted with a fuel utilization rate $FU$ of up to 70%. Cathode air supply is carried out with a side channel blower. The air will be preheated by recovering heat from the cathode off-gas. The fuel cell stack is cooled by a cooling loop, using the heat transfer oil *Galden HT230*. The heat produced by the fuel cell is transferred to the district heating loop or is removed by an air cooler.

In upcoming investigations the system design will be optimized in communication with ICI in order to find the final system setup for the demonstration module.

**Optimization of system parameters by 0D-Simulation**

With the given design of the evaluation unit, a parameter variation is used to identify optimized working conditions. The parameter variation is performed using the dynamic system simulation in MATLAB/Simulink. The parameters are simulated in four loops, which lead to a total simulation of $3^4 = 81$ iterations. The goal of the parameter variation is to increase the electrical efficiency of the evaluation unit. The parameter matrix for the evaluation is given in Table 14. The
simulation has been performed using parallel simulation, using three iteration loops. The evaluation takes about 6 hours.

Table 14: Variables for parameter variation

<table>
<thead>
<tr>
<th></th>
<th>1.</th>
<th>2.</th>
<th>3.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{refo}$</td>
<td>650</td>
<td>700</td>
<td>750</td>
</tr>
<tr>
<td>$FU$</td>
<td>0.65</td>
<td>0.75</td>
<td>0.85</td>
</tr>
<tr>
<td>$SCR$</td>
<td>3.0</td>
<td>3.5</td>
<td>4.0</td>
</tr>
<tr>
<td>$CellNo$</td>
<td>60</td>
<td>90</td>
<td>120</td>
</tr>
</tbody>
</table>

The reformer output temperature $T_{refo}$ has an important impact on the gas quality of the reform gas. The fuel utilization $FU$ describes the degree of fuel usage within the fuel cell. With increasing $FU$, less reformate is fed back to the reformer process. The $CellNo$ leads to a change of the operating point of the fuel cell stack. With higher $CellNo$, the operating point of the fuel cell walks to lower current density, which increases the fuel cell efficiency.

### Model assumptions

For the parameter variation the system design introduced before is used. The reference points of the simulation (see Table 14) are the set points of the controllers used in the model. The parameter variation has been performed assuming a constant fuel input of 25 kW related to the lower heating value. The results of the parameter variation are determined by the given set parameters in Table 14. The electrical output $P_{el}$ is the result of the operating point of the fuel cell polarization curve.

For the stack model a state of the art fuel cell represented by a BASF CelTec P1100 MEA characteristic is assumed. The characteristically polarization curve is modeled using the product description of the manufacturer. The polarization curve of the CelTec MEA has been tested under reformate condition. The gas composition is assumed to be comparable with the gas composition within the CISTEM project. The course of the polarization curve has a direct impact on the stack efficiency formulated in Equ. (8).

In a later project stage, the dynamic system simulation model will be used with the characteristics of the developed fuel cell stack (WP 2 and 3). With this beyond the state of the art fuel cell, further improvements of system performance are expected.
Simulation results

The simulation has been performed using the parameters summarized in Table 14. In the simulation overview, a burner temperature of $T_{burner} = 900^\circ C$ has been used.

**Figure 45: System efficiency with parameter variation of T_refo and CellNo**

**Figure 46: System efficiency with parameter variation of T_refo and CellNo**
The results of the parameter variation are summarized in Figure 45 - Figure 48. Figure 45 - Figure 47 show the system efficiency as a bar plot, dependent on reformer temperature and cell number, steam to carbon ratio and fuel utilization respectively. The line plots depicted in the figures describe reformer efficiency and fuel cell efficiency at $FU = 0.75$, $SCR = 3.5$ and $CellNo = 90$ respectively. The lines depict the dependency of the reformate temperature on efficiency.

Figure 45 - Figure 47 show that the system efficiency decreases with increasing reformate temperature. The system efficiency increases with increasing cell number. Furthermore the system efficiency decreases with increasing fuel utilization and steam to carbon ratio.

In Figure 48 the impact of the cell number is shown. The reformer efficiency remains constant at $\eta_{\text{refo}} = 0.66$. The operating point of the fuel cell changes towards lower current density with decreasing cell number. With decreasing current densities, higher fuel cell efficiencies can be achieved. The system
efficiency increases with increasing cell number. A drawback of higher cell numbers in one stack is that the cost will increase significantly.

The simulation results have shown a possible system efficiency of 39%, which is quiet close to the project target. However, some recommendations can be concluded at this point of the project. Since the electrical system efficiency is the product of fuel cell efficiency and reformer efficiency, two major optimization approaches can be concluded.

First, the system simulation has been performed using state of the art materials. The CelTec MEA has a fuel cell efficiency of 52% at $j=0.3 \text{ A/cm}^2$. The polarization curve of the beyond of the state of the state materials (WP 2 and 3) has not been considered so far. A fuel cell with higher performance has an important impact on the module’s electrical efficiency. Second, the reformer efficiency depends on the heat recovery. After the simulation, the exhaust gas still has a high temperature. Reducing the exhaust gas temperature by heat recovery leads to less fuel input and increasing reformer efficiency.

**Dynamic system simulation – Start-Up strategy**

In order to start the reformer-stack module it is necessary to heat-up the system components before starting the reforming process. The basic idea behind the start-up strategy is to heat up the reformer and the steam generator after the reformer. This generates air and vaporized water to heat-up the system components. The reforming process starts (beginning of the natural gas flow), when the components have reached a sufficient temperature, to avoid water condensation in the system. The start-up process of the module consists of the following steps:

1. Preheating reformer with start burner
2. Air flow for heating up the components
3. Steam generation and shift heat-up
4. Start reforming operation
5. Fuel cell start with generation of electrical power

The start-up process is simulated in MATLAB/Simulink using a transient system model. The model represents one module of the CHP system. The thermal capacities and geometrical dimensions of the components (reformer, heat-exchanger, shift-reactor etc.) are at the moment not exactly known. So, in the simulation a system start-up time within one to two hours is proposed, which seems to be a reasonable period for the desired application. Once, exact data for the system components are available the start-up time can be validated.
A possible temperature course of the gas flows is shown in Figure 49. The abscissa shows the time in minutes, the ordinate shows the temperature of the fluids in degrees centigrade.

In a first step, the burner starts with a constant thermal power of 20 kW and heats up the reformer and the vaporizer after the reformer. In the second step air is feed in the reformer in order to heat up the steam generator and shift reactor. The temperature of the vaporizers is adequate to begin with the steam generation process. The steam passes the vaporizer (between reformer and shift reactor) and the reformer and heats up the remaining shift reactor and vaporizer. In the fourth step, the temperature of the steam and the reformer is assumed to be adequate for the reforming process. The controller for the water amount controls a constant steam to carbon ratio for the reforming process. The components heat up until they reach operating temperature. After about 45 minutes (fifths step), the fuel cell starts operation. If the molar concentration of the reform gas contains less hydrogen, the temperature of the bi-fuel burner falls. In the end of the shown temperature course, the temperature of the reform gas should be about 700 degrees centigrade.

**Figure 49: System temperatures in degrees centigrade**

In Figure 50 the molar composition of hydrogen and carbon-monoxide is shown. The reforming process starts after about app. 25 minutes. The composition is related to the reform gas before and after the shift reactor. The hydrogen generation starts with the reforming process and reaches a composition of about 43% (76% dry gas). After the shift-reactor, the hydrogen composition rises up to 46% (78% dry gas). Correspondingly, the share of carbon-monoxide decreases from 11% to 4.7% dry gas.
Figure 50: Molar composition of the reform gas before and after shift reactor

Up till now one possible start-up strategy for one reformer-stack module including temperature and composition courses has been shown. For a more precise simulation of the heat-up process, more details about the thermal capacities and geometric dimensions must be known.

At this early stage of the modeling and simulation process, two major points have not been considered yet. First, the system has changed introducing two shift reactors in order to reduce the output of carbon monoxide. Second, the water-gas-shift reactors should be heated up before the reforming process starts. In the starting procedure the vaporized water should not condense in the shift reactors, which can cause damages of the catalytic coating.

WP 6: Degradation Modeling

The goal of this work package is:
- to design, implement and validate mathematical model of the FC stack
- to provide parametric study of the stack behavior on the local scale with respect to the geometrical aspects and operational conditions
- to implement catalyst degradation phenomenon into the FC model and to extract kinetic information from the experimental data
- to provide case studies for the different modes of operation and their impact on the catalyst degradation rate
Summary

During the previous project period the concept of mathematical modelling of high temperature PEM fuel cell (HT PEM FC) stack was presented for the two-dimensional (2D) case. Within this period we have continued with the development of this mathematical model and significantly improved its physical accuracy and agreement with reality. We still kept in 2D approximation. Moreover the model has been validated experimentally and important model input parameters have been identified.

The model concept is based on the assumption of system macro-homogeneity, which is more or less fulfilled in the stack consisting of large number of cells. The model accuracy, especially with respect to prediction of local distribution of physic-chemical quantities decreases with decreasing number of cells in the stack. Thus, in the case of single cell the accuracy of this approach is limited. Therefore the model stack in the validation procedure consisted, at minimum, of 10 cells, while experiments were performed on a single fuel cell including MEA provided by DPS. Performance of the model stack was obtained by multiplying the results obtained for a single cell. The calculated and experimental load curves were compared and kinetic parameters of oxygen reduction reaction (ORR) were determined. The results of the model validation are summarized in chapter Model validation.

In the next step the validated model was used for the prediction of behaviour of large HT PEM FC stack consisting of 100 cells. The results of the fuel cell stack simulation are summarized in chapter Fuel cell stack simulation.

Mathematical model description

Main modifications in the model description
The modifications of the model description with respect to the model version presented in the previous project period are following:

1) The model was extended about the material balance of nitrogen in the cathode stream. The model is thus flexible with respect to variation of oxygen partial pressure in the oxidant stream that is from pure oxygen to moisture air.

2) The transport in the flow channels was described by Darcy’s law with fluid permeability evaluated from well know Hagen–Poiseuille equation verified/validated by solving Navier-Stokes equation. It allows more precise prediction of the pressure drop and gas flow distribution in the stack.
3) The prediction of effective conductivity of individual cells has been modified to be able to consider experimentally determined ohmic resistance of single MEA (from EIS).

4) A complex structure of real fuel cell has been described more precisely.

5) Basic thermodynamic parameters, like reversible electrode potentials of main electrode reactions, are not easily accessible in the case of HT PEM FC. However, they are important for the evaluation of stack total voltage and also of the rate of electrode reaction. It is because these parameters define reference state (zero current conditions). It is characterized as stack voltage at zero current and reference state, when overvoltage of main electrode reaction is near zero. To fulfil zero overvoltage at zero current the ORR kinetic expression was modified. To solve this problem experimentally determined open circuit voltage (OCV) of a single fuel cell has been employed.

For the purpose of completeness and comprehensibility, in the following text the complete description of the upgraded model is summarized, including the work performed within first project period.

### Summary of model description

The proposed model is two-dimensional (2D), stationary and macro homogeneous, and it was implemented in Comsol Multiphysics® v4.4. The coordinates system is oriented in z-coordinate (normal to the membrane plane – main direction of electric current flow) and x-coordinate (parallel to the membrane from inlet to the outlet – main direction of reactant gasses flow). Scheme of the modelled system is presented in Figure 51. The flow-field geometry considered is represented by straight parallel channels oriented vertically (in the direction of x-coordinate).

![Figure 51: 2D scheme of the modelled system](image)

Figure 52 and Figure 53 show the model geometry implemented in COMSOL, where individual subdomains and boundaries, respectively, are labelled by
numbers. Subdomain of anode plate was omitted from model geometry. Subdomain of cathode plates (number 1 in Figure 52) was included to enable model calculations in galvanostatic regime. Subdomain 3 represents working region of the stack and subdomains 2 and 4 represent inlet and outlet channels, respectively.

**Figure 52: Model geometry with numbering of individual subdomains.**

**Figure 53: Model geometry with numbering of individual boundaries, for the meaning of individual boundaries see Table 16.**

---

**Reaction system considered**

The model considers only oxygen reduction reaction (ORR) on the cathode (reaction(A)) and hydrogen oxidation reaction (HOR) on the anode (reaction(B)).

\[
\begin{align*}
O_2 + 4 H^+ + 4 e^- &\leftrightarrow 2 H_2O \\
2 H^+ + 2 e^- &\leftrightarrow H_2
\end{align*}
\]

**Dependent variables**

The model consists of 7 dependent variables. The overview of dependent variables is shown in Table 15.
Table 15: Overview of dependent variables

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
<th>Sub-domains</th>
</tr>
</thead>
<tbody>
<tr>
<td>$p_a(z,x)$</td>
<td>pressure of gas in anode stream referred to the outlet pressure</td>
<td>Pa</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>$p_c(z,x)$</td>
<td>pressure of gas in cathode stream referred to the outlet pressure</td>
<td>Pa</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>$y_{O_2}(z,x)$</td>
<td>molar fraction of O$_2$ in cathode gas stream</td>
<td>1</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>$y_{N_2}(z,x)$</td>
<td>molar fraction of N$_2$ in cathode gas stream</td>
<td>1</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>$y_{H_2O}(z,x)$</td>
<td>molar fraction of water vapour in cathode gas stream</td>
<td>1</td>
<td>2, 3, 4</td>
</tr>
<tr>
<td>$\phi(z,x)$</td>
<td>cell averaged electric potential</td>
<td>V</td>
<td>1, 3</td>
</tr>
<tr>
<td>$\eta(z,x)$</td>
<td>cell averaged overvoltage on anode and cathode</td>
<td>V</td>
<td>3</td>
</tr>
</tbody>
</table>

Model equations

Mass balance for anode stream

Presence of pure hydrogen is currently assumed in the anode stream (no water vapours permeation across the membrane or evaporation from H$_3$PO$_4$). Hydrogen is described as an ideal gas. Equation (13) represents mass balance of the anode stream.

$$-\nabla \cdot \left( \rho_a \mathbf{v}_a \right) + S_m,a = 0$$

$\rho(z,x)$ – density of the gas mixture; $S_m$ – mass source/sink; $\mathbf{v}(z,x)$ – local velocity vector, $a$ – anode stream

Mass source/sink by electrochemical reaction (HOR) is defined as

$$S_{m,a} = -\frac{N |j_z| HD}{WHD} \cdot \frac{M_{H_2}}{n_{HOR} F}$$

$N$ – number of cells in the stack; $|j_z|$ – vector of local current density; $|j_z|$ – absolute value of $z$-component of $j$; $W$, $H$, $D$ – width, height and deep of the working part of the fuel cell stack; $M_{H_2}$ – molecular weight of H$_2$; $n_{HOR}$ – number of exchanged electrons in HOR per one H$_2$ molecule; $F$ – Faraday constant.

Convective transport was described by Darcy’s law, when channel permeability in axial direction is predicted by Hagen-Poiseuille equation.

$$\mathbf{v}_a = -\mathbf{P}^s_a \begin{pmatrix} \frac{\partial p_a}{\partial z} \\ \frac{\partial p_a}{\partial x} \end{pmatrix}$$

$\mathbf{P}$ – tensor of gas permeability; $p$ – gas pressure referred to the outlet pressure, $s$ – subdomain number

$$\mathbf{P}^s_a = \begin{pmatrix} p^s_{a,z} & 0 \\ 0 & p^s_{a,x} \end{pmatrix}$$
\[ p_{a,x}^{2.4} = \frac{2d_{ch}}{K_{ch}\eta_H^2}; \quad p_{a,x}^{2.4} = 10 \cdot p_{a,x}^{2.4}; \quad p_{a,x}^3 = 0; \quad p_{a,x}^3 = \frac{2d_{ch}^2}{K_{dch}\eta_H^2} \cdot f_{dch} \]  

(17)

\( K \) – coefficient of Hagen-Poiseuille equation, \( \eta_H \) – dynamic viscosity of gaseous hydrogen, \( d \) – characteristic dimension of the channel, \( ch \) – main feed and drain channels, \( dch \) – distribution channel in the flow fields, \( f_{dch} \) – volume fraction of distribution channels in the single cell

Dynamic viscosity of hydrogen was estimated from the kinetic theory of gases. The characteristic dimension is defined as:

\[ d = \frac{4S}{C} \]  

(18)

\( S \) – channel cross-section flow area; \( C \) – channel circumference of the cross-section flow area

Density was calculated according to ideal gas behaviour:

\[ \rho_a = \frac{p_a + P_{out}}{RT} M_{H_2} \]  

(19)

\( P_{out} \) – pressure at the gas outlet from the stack

---

**Mass balance for cathode stream**

The stationary mass balance of cathode stream represents equation (20). The gas mixture consisting of N\(_2\), O\(_2\) and H\(_2\)O was described as ideal gas mixture. Water vapour is produced inside working area of the stack by ORR or comes as moisture in the feed gas. The water permeation across the membrane is not considered at this stage of model development.

\[ -\nabla \cdot (\nu_c \rho_c) + S_{m,c} = 0 \]  

(20)

\( c \) – cathode stream

The mass source/sink term has following form

\[ S_{m,c} = -\frac{N|j_z|HD}{WHDF} \left( \frac{M_{O_2}}{n_{ORR}} - \frac{M_w}{1 - \sum n_{ORR}} \right) \]  

(21)

\( M_{O_2} \) and \( M_w \) – molecular weight of oxygen and water

Convective transport was described by Darcy’s law, where channel permeability in axial direction is predicted by Hagen-Poiseuille equation.

\[ \nu_c = -P_c^\xi \left( \begin{array}{c} \frac{\partial p_c}{\partial z} \\ \frac{\partial p_c}{\partial x} \end{array} \right) \]  

(22)

\[ P_c^\xi = \left( \begin{array}{cc} p_{cz}^\xi & 0 \\ 0 & p_{cx}^\xi \end{array} \right) \]  

(23)
Calculation of cathode gas stream density was based on ideal gas mixture assumption:

\[
\rho_c = \frac{p_c + P_{\text{out}}}{RT} \sum_{i} (M_i) y_i = \frac{p_c + P_{\text{out}}}{RT} \left( M_{O_2} y_{O_2} + M_{N_2} y_{N_2} + M_w y_w \right)
\]

\( y_i \) – molar fraction of \( i \)-th component in the gas mixture; \( N_c \) – total number of components in the gas mixture

**Charge balance**

Stationary charge balance is represented by equation (26). Charge transfer is considered only by migration of ions and electrons. Specific conductivities of individual parts of the stack were considered constant and isotropic.

\[
\nabla \cdot \mathbf{j} = 0
\]

\( \mathbf{j} \) – local current density vector

Local current density \( \mathbf{j} \) is expressed by equation (27).

\[
\mathbf{j} = -G_s \left( \frac{\partial \Phi}{\partial z} + \frac{N}{W} (U_{OCV} - \eta) \frac{\partial \Phi}{\partial x} \right)
\]

\( G \) – tensor of specific conductivity in individual subdomains; \( s \) - subdomain number; \( U_{OCV} \) – open circuit voltage; \( \eta \) – cell averaged overvoltage on anode and cathode

Value of local current density is proportional to the specific conductivity (comprised in tensor of specific conductivity \( G \)) of the environment and \( \text{grad} \ \Phi \) representing driving force for electric current flow across the cell. \( \Phi \) is cell averaged electric potential. The meaning of \( \text{grad} \ \Phi \) is more apparent, when equation (27) is rearranged to equation (28). In the axial direction (\( x \)-coordinate) \( \Phi \) is identical to classical Galvani potential and \( \frac{\partial \Phi}{\partial x} \) is electric field intensity in the individual cell layers (comprises only mean ohmic drop of the cell in \( x \)-direction). The specific conductivity of the cell in this direction \( (G_{3,x}) \) is evaluated on the base of an equivalent circuit of resistors in parallel.

\[
\frac{\partial \Phi}{\partial z} = -\frac{N}{W} (U_{OCV} - \eta) - \frac{j_z}{G_{3,z}}
\]

\[
\frac{\partial \Phi}{\partial x} = -\frac{j_z}{G_{3,x}}
\]

On the contrary, in the normal direction (\( z \)-coordinate) \( \frac{\partial \Phi}{\partial z} \) comprises also contribution of electrode polarization and, therefore, \( \Phi \) significantly differs from
Galvanic potential, see Figure 54 (for zero current conditions) and Figure 55 (non-zero current conditions). $\frac{\partial \phi}{\partial z}$ in zero current conditions equals to gradient of open circuit voltage $\left(\frac{N}{W} U_{OCV}\right)$. It further decreases in non-zero current conditions by overvoltage of electrode reactions $\eta$ and ohmic drop in the cell layers $\left(\frac{j_z}{G_{3z}}\right)$. The specific conductivity of the cell in $z$-direction ($G_{3z}$) is evaluated on the base of the equivalent circuit of resistors connected in series. Evidently, introducing quantity $\Phi$ enabled omitting the need to calculate local distribution of Galvanic potentials ($\Phi_e, \Phi_i$) in electron- and ion-conductive phases separately.

![Figure 54: Schematic distribution of electric potential in a single cell under current-less conditions; red line \(\Phi_e\) - local Galvani potential in electron-conductive phase, blue line \(\Phi_i\) - local Galvani potential in ion-conductive phase, green line \(\Phi\) - local cell averaged electric potential, \(U_{OCV}\) - open circuit voltage of a single cell, \(N_{cell}\) and \(W_{cell}\) - number of cells in the stack and the stack width respectively.](image)

Figure 54: Schematic distribution of electric potential in a single cell under current-less conditions; red line $\Phi_e$ - local Galvani potential in electron-conductive phase, blue line $\Phi_i$ - local Galvani potential in ion-conductive phase, green line $\Phi$ - local cell averaged electric potential, $U_{OCV}$ - open circuit voltage of a single cell, $N_{cell}$ and $W_{cell}$ - number of cells in the stack and the stack width respectively.

![Figure 55: Similar to Figure 54, however for non-zero current conditions; \(U_{cell}\) - cell voltage under non-zero conditions, \(|j_z|\) - absolute value of current density passing across the cell in the normal direction (indicated by with arrow), $G_z$ - mean electric conductivity of the cell in the normal direction.](image)

Figure 55: Similar to Figure 54, however for non-zero current conditions; $U_{cell}$ - cell voltage under non-zero conditions, $|j_z|$ - absolute value of current density passing across the cell in the normal direction (indicated by with arrow), $G_z$ - mean electric conductivity of the cell in the normal direction.

The tensor of specific conductivity and its individual components for individual model subdomains are expressed by equations (29) to (32).
\[ G^s = \begin{pmatrix} G_x^s(z, x) & 0 \\ 0 & G_x^s(z, x) \end{pmatrix} \]  

\[ G_x^s = G_x^1 = 10^4 \text{ S m}^{-1} \]  

\[ G_x^3 = \frac{W}{N \frac{w_{\text{mea}}}{\sigma_{\text{mea}}} + 2 \frac{w_{\text{tp}}}{\sigma_{\text{e, bp}}} + (N - 1) \frac{w_{\text{bp}}}{\sigma_{\text{e, bp}}}} \]  

\[ \sigma = \text{specific conductivity of individual materials}, \ w = \text{width of individual layers}, \ W = \text{stack (working region) width}, \ \text{subscripts: mea - membrane electrode assembly, e - electron conductive phase, tp - terminal plate, bp - bipolar plate.} \]  

Specific conductivity of MEA (\( \sigma_{\text{mea}} \)) was calculated from MEA’s electric resistance (\( R_{\text{MEA}} \)) by equation (33), where \( R_{\text{MEA}} \) was determined by EIS.

\[ \sigma_{\text{mea}} = \frac{w_{\text{MEA}}}{R_{\text{MEA}} S_{\text{MEA}}} \] (33)

\( w_{\text{MEA}} \) – width of single MEA; \( S_{\text{MEA}} \) - active area of single MEA, respectively; \( R_{\text{MEA}} \) is MEA’s electric resistance.

In general, overvoltage \( \eta \) consists of contribution of the anode and the cathode. In this case, we assume only HOR at the anode and ORR at the cathode. HOR is considered to be considerably faster in comparison to ORR, thus the overvoltage on the anode can be neglected. The ORR kinetics is described by Butler-Volmer equation, see equation (34).

\[ \eta_{\text{ORR}} \]

\[ j_{\text{ORR}} = j_{\text{ORR}}^0 \left\{ \left( \frac{y_w (P_c + P_{\text{out}})}{P_{\text{ref}, w}} \right)^2 \exp \left[ \frac{(1 - \beta_{\text{ORR}}) \eta_{\text{ORR}} F}{RT} \right] \right\} \left\{ \left( \frac{y_{O_2} (P_c + P_{\text{out}})}{P_{\text{ref}, O_2}} \right)^2 \exp \left[ \frac{- \beta_{\text{ORR}} \eta_{\text{ORR}} F}{RT} \right] \right\} \] (34)

\( j_{\text{ORR}} \) – local volumetric current of electrode reaction at TPB, \( j_{\text{ORR}}^0 \) – corresponding volumetric current at zero current conditions (equal to product of exchange current density for ORR and specific surface area of TPB), \( \eta_{\text{ORR}} \) – local overvoltage in catalyst layer for ORR, \( P_{\text{ref}} \) – reference partial pressure, \( \beta \) – charge transfer symmetry coefficient, subscripts: \( \text{ORR} \) – oxygen reduction reaction, \( c \) – cathode, \( w \) – water vapour, \( O_2 \) – oxygen.

Therefore \( \eta = -\eta_{\text{ORR}} \). Its value is obtained by solving algebraic equation (1).

\[ 0 = j_{\text{ORR}} - \frac{j_z}{w_{\text{cl}}} \] (1)

\( w_{\text{cl}} \) – catalyst layer width
**Material balances of O₂, N₂ and H₂O in cathode stream**

Three components are considered (O₂, N₂, H₂O) in the cathode stream. Stationary material balance of O₂ and N₂ for cathode stream is following.

\[-\nabla \cdot \mathbf{J}_i + S_i = 0 \quad (2)\]

\(\mathbf{J}_i\) – intensity of molar flux of \(i\)-th species, \(S_i\) – source/sink term for \(i\)-th species

Oxygen and water vapour is consumed and produced, respectively, by ORR. Permeation of gases across the membrane or water evaporation from H₃PO₄ is neglected. Ideal gas mixture properties were taken into account. Transport of individual species occurs via diffusion and convection according to

\[\mathbf{J}_i = \left(\frac{P_c + P_{out}}{RT}\right)\left(-\mathbf{D}_{i}^{\xi}\nabla y_i + \mathbf{v}_c y_i\right) \quad (3)\]

\(\mathbf{D}_i^{\xi}\) – tensor of ternary diffusion coefficient in nitrogen-oxygen-water mixture in cathode stream and subdomain \(s\), \(y_i\) – molar fraction of \(i\)-th component

Tensor of ternary diffusion coefficient is defined as

\[\mathbf{D}_i^{\xi} = \begin{pmatrix} D_{i,x}^{\xi} & 0 \\ 0 & D_{i,z}^{\xi} \end{pmatrix} \quad (4)\]

\(D_{i,x}^{\xi}\) and \(D_{i,z}^{\xi}\) – ternary diffusion coefficients in \(x\) and \(z\)-direction in nitrogen-oxygen-water mixture in cathode stream and subdomain \(s\)

The ternary diffusion coefficients are identical for all species in the gas mixture and were evaluated from kinetic theory of gases. The properties of oxygen and water are relatively similar. Moreover, both these components are minor in the case of air. Because of these two reasons the ternary diffusivities were approximated by binary diffusivity of oxygen-nitrogen mixture.

Source/sink terms \(S_{O_2}\) and \(S_{H_2O}\) describe consumption of O₂ and production of H₂O by ORR according to the following equations.

\[S_{O_2} = -\frac{|j_{O_2}| N}{n_{ORRFW}} \quad (5)\]

\[S_{H_2O} = +\frac{|j_{H_2O}| N}{0.5n_{ORRFW}} \quad (40)\]

The molar fraction of water vapour \(y_w\) is calculated from

\[y_w = 1 - y_{O_2} - y_{N_2} \quad (6)\]
Boundary conditions
The boundary conditions used in the model are summarized in the following Table 16.

Table 16: Overview of boundary condition used in the model

<table>
<thead>
<tr>
<th>Boundary no.</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>( y_{O_2} = y_{O_2,\text{in}} )</td>
<td>Gas inlet</td>
</tr>
<tr>
<td></td>
<td>( y_{N_2} = y_{N_2,\text{in}} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( y_w = y_{w,\text{in}} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( y_{H_2} = y_{H_2,\text{in}} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( v_{c,\text{e}} \rho_c = \lambda_{O_2} \frac{IN}{n_{O_2} F} \frac{1}{HD} \left( M_{O_2} + \frac{y_{N_2,\text{in}}}{y_{O_2,\text{in}}} M_{N_2} + \frac{y_{w,\text{in}}}{y_{O_2,\text{in}}} M_w \right) )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( v_{a,\text{e}} \rho_a = \lambda_{H_2} \frac{IN}{n_{H_2} F} \frac{1}{HD} M_{H_2} )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \frac{\partial y_{O_2}}{\partial z} = 0 )</td>
<td>Gas outlet</td>
</tr>
<tr>
<td></td>
<td>( \frac{\partial y_{N_2}}{\partial z} = 0 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{\partial y_w}{\partial z} = 0 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( p_c = 0 \text{ Pa} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( p_a = 0 \text{ Pa} )</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>( j_z = \frac{I}{DH} \text{ A m}^{-2} )</td>
<td>Cathode current collector</td>
</tr>
<tr>
<td>12</td>
<td>( \phi = 0 \text{ V} )</td>
<td>Anode current feeder</td>
</tr>
<tr>
<td>7, 9</td>
<td>( j_x = 0 \text{ A m}^{-2} )</td>
<td>Electric insulation</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>Charge flux continuity</td>
</tr>
<tr>
<td>7, 9</td>
<td></td>
<td>Continuity of flux of gas components</td>
</tr>
<tr>
<td>4, 5, 6, 10,</td>
<td></td>
<td>Barrier for gas components transport (wall)</td>
</tr>
</tbody>
</table>
12, 13

\( \lambda_{o_2} \) and \( \lambda_{H_2} \) – stoichiometric excess of \( O_2 \) and \( H_2 \) respectively

## Mathematical model results

### Model validation

This chapter describes a validation procedure of the proposed model. The model under validation considered stack with 10 cells, while experimental measurements were performed on a single fuel cell. Performance of the model stack was obtained by multiplying the results obtained for a single cell. The calculated and experimental load curves were compared and kinetic parameters of oxygen reduction reaction (ORR) were determined.

The MEA from Danish Power System (DPS Dapozol® G55, Bach no.: INH-13-002, ID: MEA-13-498, Manufactured: 05.11.2013) was chosen for this purpose. MEA’s thickness was approximately 0.6 mm in fresh state and its active area was 25 cm². The MEA’s electric resistance was determined by EIS to be of \( R_{\text{MEA}} = 7.7 \times 10^{-3} \Omega \) (at current load 0.2 A cm⁻²). A mean specific conductivity of this MEA was calculated from equation (33) and it is of 31.2 S m⁻¹. During the experiment dry air and pure hydrogen were feed to the cathode and anode, respectively (i.e. for the case of the model validation \( Y_{O_2} = 0.21, Y_{H_2} = 0.79, Y_w = 0 \) and \( Y_{H_2} = 1 \)).

The load curves were recorded from OCV to minimum voltage of 0.4 V, where maximum current approximately 0.84 A cm⁻² was expected. The volumetric flow rate of \( H_2 \) and air was constant during the experiment and corresponded to maximum expected current load 0.84 A cm⁻² under stoichiometric excess of hydrogen \( \lambda_{H_2} = 1.2 \) and oxygen \( \lambda_{O_2} = 2 \). The input parameters of the model were set similar to the experimental one.

The only unknown model input parameters to be fitted was kinetic parameter of ORR \( J_{\text{ORR}}^0 \) (see equation (34)). The other kinetic parameter \( \beta_{\text{ORR}} \) (see equation (34)) was adopted from the kinetics of ORR known for low temperature PEM FC (\( \beta_{\text{ORR}} = 0.25 \)). \( J_{\text{ORR}}^0 \) was fitted from comparison of calculated and measured load curves (dependence of cell voltage (\( U_{\text{cell}} \)) on applied current density (\( j \))). A comparison of \( U_{\text{cell}}-j \) curves calculated by mathematical model (for optimized \( J_{\text{ORR}}^0 = 1.5 \times 10^6 A m^{-2} \)) and that determined experimentally is shown in Figure 56. A reasonable agreement was reached especially when considered, that only one input parameter was fitted. Some discrepancies were observed in the region of load curve driven by cell ohmic resistance. The model predicts slightly higher ohmic resistance. It is expectable observation, because experimentally determined MEA’s resistance decreases with current load in the following manner: 10 m\( \Omega \) (0 A cm⁻²), 7.7 m\( \Omega \) (0.2 A cm⁻²) and 5.9 m\( \Omega \) (0.4 A cm⁻²). This phenomenon is however not yet considered in the model.
Fuel cell stack simulation

Input data

The MEA’s characteristic used in this simulation corresponds to MEA from Danish Power System (DPS Dapozol® G55, Batch no.: INH-13-002, ID: MEA-13-498, Manufactured: 05.11.2013) used for model validation in previous chapter. Dry air and pure hydrogen were fed to the cathode and anode, respectively (i.e. for the case of the model validation $y_{O_2} = 0.21$, $y_{N_2} = 0.79$, $y_w = 0$ and $y_{H_2} = 1$). The mass flow rate of $H_2$ and air increased with increasing current load to keep stoichiometric excess of hydrogen $\lambda_{H_2} = 1.2$ and oxygen $\lambda_{O_2} = 2$. The other input parameters for fuel cell stack simulation are following:

\[
\begin{align*}
N &= 100 & \text{number of cells in the stack} \\
w_{ccl} &= 10 \times 10^{-6} \text{ m} & \text{width of the cathode catalyst layer} \\
w_{acl} &= 10 \times 10^{-6} \text{ m} & \text{width of the anode catalyst layer} \\
w_{bp} &= 5 \times 10^{-3} \text{ m} & \text{width of the bipolar plate} \\
w_{tp} &= 3.5 \times 10^{-3} \text{ m} & \text{width of terminal plates} \\
H &= 2 \times 10^{-1} \text{ m} & \text{height of the stack working area} \\
w_{ep} &= 0.02 \text{ m} & \text{width of the end plates} \\
D &= 0.1 \text{ m} & \text{deep of the stack working area}
\end{align*}
\]
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_{ch}$</td>
<td>$1 \times 10^{-2}$ m</td>
<td>height of the feed and drain channel</td>
</tr>
<tr>
<td>$N_{dch}$</td>
<td>45</td>
<td>number of distribution channels</td>
</tr>
<tr>
<td>$w_{dch}$</td>
<td>$1 \times 10^{-3}$ m</td>
<td>width of the distribution channel</td>
</tr>
<tr>
<td>$h_{dch}$</td>
<td>$1 \times 10^{-3}$ m</td>
<td>height of the distribution channel</td>
</tr>
<tr>
<td>$U_0$</td>
<td>0.9 V</td>
<td>single cell open circuit voltage</td>
</tr>
<tr>
<td>$\lambda_{H2}$</td>
<td>1.2</td>
<td>stoichiometric excess of $H_2$</td>
</tr>
<tr>
<td>$\lambda_{O2}$</td>
<td>2</td>
<td>stoichiometric excess of $O_2$</td>
</tr>
<tr>
<td>$P_{out}$</td>
<td>101325 Pa</td>
<td>output pressure</td>
</tr>
<tr>
<td>$T$</td>
<td>433 K</td>
<td>operating temperature</td>
</tr>
<tr>
<td>$F$</td>
<td>96485 C mol$^{-1}$</td>
<td>Faraday constant</td>
</tr>
<tr>
<td>$R$</td>
<td>8.314 J mol$^{-1}$ K$^{-1}$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$n_{HOR}$</td>
<td>2</td>
<td>number of exchange electrons in HOR</td>
</tr>
<tr>
<td>$n_{ORR}$</td>
<td>4</td>
<td>number of exchange electrons in ORR</td>
</tr>
<tr>
<td>$M_{H2}$</td>
<td>$2 \times 10^{-3}$ kg mol$^{-1}$</td>
<td>molecular weight of $H_2$</td>
</tr>
<tr>
<td>$M_{O2}$</td>
<td>$32 \times 10^{-3}$ kg mol$^{-1}$</td>
<td>molecular weight of $O_2$</td>
</tr>
<tr>
<td>$M_w$</td>
<td>$18 \times 10^{-3}$ kg mol$^{-1}$</td>
<td>molecular weight of water vapors</td>
</tr>
<tr>
<td>$\eta_{H2}$</td>
<td>$1.14 \times 10^{-5}$ Pa s</td>
<td>dynamic viscosity of hydrogen</td>
</tr>
<tr>
<td>$\eta_{O2N2}$</td>
<td>$1.92 \times 10^{-5}$ Pa s</td>
<td>dynamic viscosity of air</td>
</tr>
<tr>
<td>$j_0^{ORR}$</td>
<td>$1.5 \times 10^{-6}$ A m$^{-3}$</td>
<td>exchange volumetric current of ORR</td>
</tr>
<tr>
<td>$\beta_{ORR}$</td>
<td>0.25</td>
<td>symmetry coefficient of ORR</td>
</tr>
<tr>
<td>$P_{O2,ref}$</td>
<td>$y_{O2,in} \times 101325$ Pa</td>
<td>reference pressure of $O_2$</td>
</tr>
<tr>
<td>$P_{w,ref}$</td>
<td>0.001 $\times 101325$ Pa</td>
<td>reference pressure of water vapors</td>
</tr>
<tr>
<td>$\sigma_{e,bp}$</td>
<td>300 S m$^{-1}$</td>
<td>specific conductivity of bipolar plates</td>
</tr>
<tr>
<td>$\sigma_{mea}$</td>
<td>31.2 S m$^{-1}$</td>
<td>specific conductivity of MEA</td>
</tr>
</tbody>
</table>
Selected model results

Figure 57: Dependence of average single cell voltage (blue curve) and power density of single cell (green curve) on applied current density; blue points indicate current loads, at which distribution of various local quantities is visualized in the subsequent Figure 59 to Figure 67.

Figure 58: Pressure in cathode gas stream (referred to the outlet pressure) in the FC stack at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.
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Figure 59: Pressure in anode gas stream (referred to the outlet pressure) in the FC stack at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.

Figure 60: Local current density in the FC stack at various current loads (in figure title), grey lines - contours, for inlet - outlet location see Figure 51.
Figure 61: Cell averaged electric potential in the FC stack at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.

Figure 62: Overvoltage ($\eta$) in the FC stack at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.
Figure 63: Derivative of overvoltage ($\partial V / \partial x$) in the FC stack at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.

Figure 64: Molar fraction of O$_2$ in cathode gas in the FC stack at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.
Figure 65: Molar fraction of H₂O vapors in cathode gas in the FC stack at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.

Figure 66: Local volumetric current corresponding to ORR on the TPB (j_{orr}) at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.
Figure 67: Local volumetric current corresponding to HOR on the TPB ($j_{HOR}$) at various current loads (in figure title), grey lines – contours, for inlet - outlet location see Figure 51.