PEMFC system and low-grade bioethanol processor unit development for back-up and off-grid power applications

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## Summary

In this document, the hydrogen quality optimization studies performed at VTT have been described. These studies include both a literature study and experimental measurements. The experiments have been carried out at both single cell and system level to determine the optimal hydrogen quality to be produced for the fuel cell system. In addition, the test methods and test benches used are described in detail.
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1. The goal of hydrogen quality optimization

The goal of this task was to optimize the quality of hydrogen for the use in fuel cell system (FCS) developed in the project. The optimisation was done taken into account the complete system cost and performance.

One of the key ideas of the project is to use a reformate fuel compatible fuel cell stack in fuel cell system, as it will enable lower hydrogen quality, especially in terms of CO. This will allow simplification of both reformer and PSA units, thus decreasing the complete system cost.

The optimisation of quality for hydrogen requires that combination of fuel processor and FCS are seen as a complete system. Certain FCS level solutions and methods that increase FCS cost might allow use of lower quality hydrogen leading to cost reduction in fuel processing stage, and vice versa.

In the first part of the work in this task, hydrogen quality specifications were set as the approximation of the final specifications. These specifications were mostly based on the literature work and existing knowledge and existing data from earlier modeling and testing at VTT.

The data from first experimental testing of fuel cell stack in system test bench will be analysed to find optimal hydrogen quality level in terms of FCS performance and cost. This optimization will be carried out as soon as first reliable data from stack testing and subsystem modeling is available. This information will be combined with specifications for hydrogen quality produced by PSA.

1.1 The optimum hydrogen quality – literature results

One of the main issues is that there is limited amount of data with PtRu as catalyst, when pure hydrogen is used. The most of this type of data is also measured with very high CO concentrations, with several tens or even hundreds of ppm. The corresponding voltage drops have been much larger (hundreds of mV) than can be accepted in real FCS. It should also be noted that long term exposure to very high CO concentrations will lead to irreversible degradation due to formation of RuOx (Du, Pollard and Elter, 2006).

One important parameter is the transient time for the voltage drop. Usually, the data in the literature is in the form of steady state voltage drop. Only few studies with relevant voltage drops (tens of mV) and transient data have been published with PtRu as anode (Tingelöf, et al., 2008; Pérez, et al., 2013). Studies with high Pt loading on the anode as catalyst are also available (Alvarez, 2006; Bhatia and Wang, 2004).

Another difficulty for the interpretation of the literature results is the fact that different anode stoichiometric ratios are used. For example, if CO concentration of 10 ppm is combined with stoichiometry of 1.5 this corresponds 15 ppm in stoichiometry of 1, if molar flow rates of CO are compared. The work of Pérez et al. (2014) illustrates how the changing CO molar flow rate or concentration ppm affects the dynamics of poisoning and anode exit gas CO concentration.

In this analysis it is assumed that the maximum voltage drop in the end of life (EOL) is 50 mV. Then this correspond 15-20 mV voltage drop in the beginning of life according to data from Tabata, Yamazaki, Shintaku and Oomori (2009).

When both steady-state voltage drops and the transient times have been measured, most of the measurements have been done in open anode configuration, illustrated in Figure 1.
Open anode configuration is relevant, when reformate FCS are studied. However, when a FCS system operating with back-up mode or FCS system operating recirculation mode is studied, a corresponding configuration should also be used in laboratory experiments.

When CO is fed and anode potential has increased sufficiently, there will be a constant conversion rate for the anode so that stable CO level will be reached in the anode recirculation loop (Matsuda, et al., 2009).

When hydrogen based system is used without CO$_2$, the Ru dissolution rate can be increased (Cheng, et al., 2010). Ru dissolution and cross-over can lead to severe degradation of the performance (Cheng, Jia, and He, 2010). Therefore, in the FCS system management in PEMBeyond project the start-up and shut-down procedures should be such that Ru dissolution can be minimised.

1.1.1 Hydrogen quality in ISO standards

In the ISO standard 14687-2:2012 (Hydrogen fuel -- Product specification -- Part 2: Proton exchange membrane (PEM) fuel cell applications for road vehicles) the levels for the CO and CO$_2$ are 0.2 ppm and 2 ppm, respectively. The methane limit is in practice 100 ppm, as it is not considered as part of total hydrocarbons.

In the standard ISO 14687-3:2014 (Hydrogen fuel -- Product specification -- Part 3: Proton exchange membrane (PEM) fuel cell applications for stationary appliances) the contaminant levels for the Category 3 (hydrogen fuelled stationary PEMFC system) most of the limits are the same as in ISO 14687-3:2014. Especially CO and CO$_2$ limits are the same, which is not well justified, as higher Pt loading as well as Pt alloy catalyst can be used in stationary PEMFC applications.

1.1.2 The question of CO tolerance

The most relevant results concerning PEMBeyond project are those of Pérez, et al., (2013) and Tingelöf, et al., (2008). Based on the measurements of Pérez, et al., (2013) the effect of CO can be seen immediately in the current of the first segment. However, only when the current of the fourth segment starts to decrease, CO can be detected at the anode exit gas. In these measurements, however, the fuel utilisation was relatively high and recirculation was not applied.

Pérez, et al., (2014) have shown that the flow rate will effect on the poisoning dynamics and CO concentration at the exit gas. Therefore, it can be assumed that if recirculation is applied, it will affect contamination dynamics.

The main issue with the single cell results from the literature is that they have been usually been done using open anode configuration, applying constant voltage.
When the cell voltage is kept constant the current decreases as poisoning is proceeding. In the constant voltage (potentiostatic) measurements the anode overpotential stays low and the voltage oscillations are avoided (Tingelöf).

The voltage oscillations clean the surface by oxidising the CO from the surface (Zhang, Fehribach and Datta, 2004). When this takes place in the measurements with single cell the average cell voltage is only marginally decreased even with very high CO concentrations (Tingelöf, et al., 2008). It is however, unclear how harmful this is for the stability of PtRu catalyst as oscillations can bring the anode potential over the Ru oxidation potential leading to Ru dissolution.

Based on the results in the literature, a first estimate for the acceptable (voltage drop 50 mV) CO concentration is 5-25 ppm CO, when the current density is between 0.5-1 Acm$^{-2}$. When these CO concentration levels are applied the estimated transient time is between one and 6 hours.

1.1.3 The effect of inert gas (N$_2$, CH$_4$)

When a FCS is operated, there will be inert gas enrichment in the anode loop. The level of enrichment can be even tens of percent (Ahluwalia and Wang, 2007; Nikiforow, et al., 2013).

When there is a significant amount of inert gases in the recirculation loop, the effect of CO can be multiplied, as shown by Bhatia and Wang (2004). However, in the study of Bhatia and Wang the anode catalyst was Pt, not PtRu.

The effect of inert gas or the combined effect of inert gas and contaminant can also be dependent on the design and operation of the stack and system.

1.1.4 The effect of carbon dioxide (CO$_2$)

The effect of CO$_2$ on the cell performance has been studied with both Pt and PtRu by Tingelöf et al., (2008). According to their results, CO$_2$ has only a very minor effect on the cell voltage even at very high concentrations (25%). However, CO$_2$ can have different effects depending on the anode catalyst type (De Bruijn, Papageorgopoulos, Sittersand and Janssen, 2002).

The carbon dioxide limits in the ISO standards are 2 ppm both in in 14687-2:2012 and in 14687-3:2014 Category 3 (hydrogen fuelled system).

When there is 2 ppm in the fuel, then at the maximum fuel utilisation level (about 99.8%) this would lead to the level of 1000 ppm in the anode recirculation gas. However, when CO$_2$ level on the anode side exceeds the CO$_2$ level on the cathode, there will be net transfer of CO$_2$ to the cathode due to the high permeability of CO$_2$ in wet conditions (Ma, Odgaard and Skou, 2005). This causes problems in the CO/CO$_2$ molar balance measurements and can limit the level of CO$_2$ enrichment.

On the other hand, CO$_2$ from the cathode permeates to the anode as long as the CO$_2$ level on the anode side is lower than on the cathode. Therefore, there will always be some CO$_2$ on the anode even if the hydrogen fuel is completely CO$_2$-free.

When there is CO$_2$ on the anode side it means that there can always be formation of CO via a reverse water gas shift (RWGS) reaction. This possibility and the importance of CO formation via RWGS have been discussed in a number of studies. These studies are reviewed by Du, Pollard, Elter and Ramani, (2009).

However, the effect of CO\textsubscript{2} has not been studied experimentally in the levels relevant to ISO 14687-2:2012 and 14687-3:2014. The combination of CO and CO\textsubscript{2} has not been studied with the levels relevant to the PEMBeyond project.

In order to be relevant to the FCS in PEMBeyond project, this type of research would require very high fuel utilisation in order to quantify the accumulated effect of CO\textsubscript{2} and CO.

The high permeability of CO\textsubscript{2} via membrane means that contamination studies should not be performed with CO\textsubscript{2}-free air, as there can be formation of CO via RWGS. On the other hand, if molar balance of carbon containing contaminant (e.g. formic acid, formaldehyde) is needed to be measured, the permeation to the cathode and oxidation to CO\textsubscript{2} may be impossible to measure if CO\textsubscript{2} containing air is used.

1.1.5 Conclusions

Based on the literature results, the main issue is the unknown effect of the anode gas recirculation and enrichment CO in the anode recirculation loop on the cell voltage. In these conditions high fuel utilisation (>90%) is applied. The transient time during this poisoning is another unknown parameter.

The effect of carbon dioxide is most probably a minor one, but should be studied with the MEA applied in the stack of the PEMBeyond project as anode catalyst composition is known to have a significant effect.

1.2 The expected hydrogen quality from PSA – literature

The quality of the hydrogen is expected to have a very low CO\textsubscript{2}, CH\textsubscript{4} and N\textsubscript{2} concentrations compared to CO (Papadias, Ahmed, Kumar and Joseck, 2009), when it is purified by conventional PSA with carbon and zeolite as adsorbents.

Therefore, as a first estimate the CO is expected to be the only limiting component. The effect of CO\textsubscript{2} may become of importance if other types of adsorbents are applied and CO\textsubscript{2} levels could be tens or even hundreds of ppms. Even in these cases, the fuel utilisation should be very high (>99%) before CO\textsubscript{2} level reaches potentially harmful concentrations.

It should be noted that some CO tolerant catalyst, such as PtMo are, in fact, sensitive for CO\textsubscript{2} (Janssen, De Heer, and Papageorgopoulos, 2004). Since the MEA suppliers are not giving the compositions of their catalysts, it may be necessary to verify the CO\textsubscript{2} tolerance of the applied MEAs, with and without CO.

1.3 The expected hydrogen quality from PSA – preliminary target

The preliminary target for hydrogen quality produced by the PSA unit developed for the project is:

- Hydrogen concentration of 95-98%
- CO concentration of 20-50 ppm.

This preliminary target was set in the project planning phase based on literature and past experience, and has been used for selecting the PSA unit main design and components. These preliminary targets have been considered to be indicative, and the actual final target quality will be determined on the basis of this document.
2. Single cell measurements with low quality hydrogen

As discussed in the previous chapter, in single cell measurements the focus has been to get an estimate for the right CO level for the further measurements with the stacks in the system test bench.

2.1 Methods

2.1.1 Experimental set-up

The experiments were performed in a fuel cell test station (G60 series, Greenlight Innovation, Canada) with automated control and measurement of gas flow rates, temperatures, dew points, pressures and electronic load. The station and cell hardware have been used in our earlier works (Pérez, et al., 2014; Koski, Pérez and Ihonen, 2015).

Compared to the previous work there has been some modifications and improvement. The low temperature humidity sensors (HMP110) have been replaced by humidity sensors (Vaisala HMT 317) tolerating 180° C temperature.

The cell hardware consisted of a 25 cm$^2$ single cell (Fuel Cell Technologies Inc.) fitted with custom graphite (ISEM-3) bipolar plates with single channel serpentine flow fields (1 mm width x 1.5 mm depth, rib width 1 mm).

The cell was installed with a commercial MEA (0.25 mg cm$^{-2}$ of PtRu on anode, and 0.4 mg cm$^{-2}$ of Pt on cathode) and Freudenberg gas diffusion layers. Freudenberg (35 FC - PO 100) 350 μm thick polyolefin gaskets were used and the clamping force was regulated with disc springs. Reactant gases were fed in counter-flow.

The load of the fuel cell test station was in repair and was replaced by two externally controlled loads connected in parallel (Thurlby Thandar Instruments LD300). The use of externally controlled load hindered the use of more complicated measurement procedures such as overnight measurements, as some of the automatic safety features must be deactivated.

In the measurements, the highest targeted fuel utilisation was 99%. As it is seen in the results, this was not reached. Reaching a very high and repeatable fuel utilisations in bleed mode requires stable mass flow controllers (MFC), as well as stable and calibrated electronic loads (Koski, Pérez and Ihonen, 2015).

In the applied measurement system the accuracy of MFC applied was ±0.8% of reading and ± 0.2% of full scale (about 400 ml/min). In addition, the repeatability was ±0.2% of full scale. In addition, there is ±0.02 (%/° C) shift in both zero and span. When the used flows were 30-50% of the full scale the total error could be 1.4-1.8%, even if the MFC were recently calibrated.

For the applied electronic loads the setting accuracy was ± (0.2% + 30 mA) and temperature coefficient was (0.02% + 5 mA) per °C. Since the current was monitored via analog current monitor output (4 V for 80A), additional error of ± 0.5% is possible due to limited accuracy of the current monitor output.

When all these error sources are added the expected maximum total error is in the range of 3%. Therefore, it is obvious that very high fuel utilisations are difficult to reach. Since exceeding fuel utilisation of 100% will lead to fuel starvation, 98% can be considered practically maximum fuel utilisation, which can be reached with bleed controlled system. When the flow is controlled by the purge, higher fuel utilisation could be reached, but it would be less controllable as gas volume in purge can be different (Koski, Pérez and Ihonen, 2015; Nikiforow, et al., 2013).
Table 1: Results from hydrogen source gas analysis

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Gas type</th>
<th>CO (ppm)</th>
<th>CH$_4$ (ppm)</th>
<th>CO$_2$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.5.2015</td>
<td>Line H$_2$ 2.5</td>
<td>&lt;0.05</td>
<td>0.7±0.1</td>
<td>23±1</td>
</tr>
<tr>
<td>12.6.2015</td>
<td>Line H$_2$ 2.5</td>
<td>&lt;0.05</td>
<td>0.6±0.1</td>
<td>22±1</td>
</tr>
<tr>
<td>15.6.2015</td>
<td>Bottled H$_2$ 5.0</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>3.9±0.2</td>
</tr>
</tbody>
</table>

2.1.1.1 Recirculation system

The single cell recirculation system used in these measurements is a further development version of the recirculation systems developed originally in Finnish national project DuraDemo and in FCH JU project HyCoRA.

The system currently used is shown in Figure 2 and in photograph in Figure 3.

Figure 2: Schematic of the anode side experimental setup. H$_2$ feed is shown in red, recirculation loop in yellow and gas analysis loop in green. Nitrogen (N$_2$) lines used for diluting H$_2$ feed and drying sampled gas are shown in blue.
The hydrogen feed shown on the top right corner is here mixed with recirculated gas after the recirculation pump. In the previous set-up (Koski, Pérez and Ihonen, 2015) the mixing was done before gas enters the recirculation pump (KNF Neuberger AB PM24927-86.12(AP.DCB-4)).

The previous arrangement has shown to be relatively complicated. The reason for the complicated system was that to the best of our knowledge, no laboratory scale H\textsubscript{2} recirculation pumps are available. The applied pump has, however, been operated several hundred hours between 70-80° C even is the pump manufacturer has given 60° C as maximum continuous operation temperature.

Two separately controlled heating cables were installed around the piping, forming the two heating zones shown in Figure 2. One of the heating zones controlled the temperature of the recirculation loop so that no condensing and evaporation of the water could take place. The other heating cable controls the anode exit point temperature, which is kept as the coldest point of the recirculation loop. At this point some of the humidity of the anode gas can condense. Therefore, this can be used for controlling the anode gas humidity, together with recirculation rate.

Several thermocouples were installed around the system to monitor the most critical locations. The heating zone temperatures were chosen so that the pump remains at a sufficiently low temperature while water condensation in the recirculation loop is avoided.

The most critical issue for this system is a well-functioning liquid water knock-out system. Without this, no stable operation can be reached. The second critical issue is the keeping the pump free from condensed water. If there is condensing of water in the recirculation pump, it will not work.

When recirculation of humid anode gas is used, the recirculation rate can be measured placed at anode inlet and outlet. The use of H\textsubscript{2} concentration sensors is also possible, but it.
requires significant enrichment of nitrogen in the recirculation loop. The measurement of recirculation rate with the help of humidity sensors is more straight-forward.

In contrast to using conventional mass flow meters, condensation of water prior to measurement is not necessary; thus, humidity and contaminants will proceed to recirculation unaffected.

In this set-up, anode gas dew points, temperatures, pressures and H$_2$ concentrations were measured with sensors (Vaisala HMP HMT317, Sensortechnics CTEM70350GY4, AppliedSensor HPS-100) at two separate locations, as shown in Figure 2. Vaisala HMP110 sensor was used to measure the dew point of the gas after the condensing device.

2.1.1.2 Gas analysis system

The gas chromatograph (GC) used in this set-up was an Agilent 6890N equipped with a methanizer and a flame ionization detector (FID). The method used in this work was able to detect CO, CH$_4$ and CO$_2$. The oven temperature is set to 80 °C. Depending on the situation, the system can use either one or two columns (Porapak N or Carboxen1000). Each analysis takes 7 minutes, depending on how the method is tuned. The analysis time can be minimized if not all of the compounds need to be quantified. The GC sample loop size id 0.5 ml, which in a closed analysis loop means that every time a sample is taken, 0.5 ml of sample gas is exchanged to He used as a carrier gas in the GC.

The recorded chromatogram files are further analyzed with a Matlab® peak integration routine. After baseline correction, the peak areas can be calculated by trapezoid integration algorithm. Alternatively the chromatogram signal can be directly fitted with the sum of exponentially modified Gaussian peak function and the baseline function.

The gas blend used for daily calibrations contains 10.2 ± 0.2 mol-ppm of CO and 9.63 ± 0.19 mol-ppm of CO$_2$ balanced with He (AGA OY). Since there was no CH$_4$ in the calibration blend, the detector response for CO and CO$_2$ was used for converti CH$_4$ peak areas to concentration. Further details on the gas analysis system can be found in (Koski, Pérez and Ihonen, 2015).

2.1.2 Test procedures

2.1.2.1 Operation conditions

Some of the parameters were the same in all the experiments. The cell temperature was 70° C, cathode stoichiometry was 2 and cathode gas dew point was 68° C. In the Table 2, the rest of the parameters are

Table 2: The parameters for the measurements with varying current density and CO level

<table>
<thead>
<tr>
<th>FC Experiment ID</th>
<th>The main observation</th>
<th>i (Acm$^{-2}$)</th>
<th>dP Cathode (kPa)</th>
<th>Anode dew point (°C)</th>
<th>Anode fuel utilisation (%)</th>
<th>Anode pressure drop (kPa)</th>
<th>Anode pressure at the exit (kPa)</th>
<th>Anode fuel utilisation per pass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200215</td>
<td>The problem of H$_2$O droplets</td>
<td>1.0</td>
<td>40</td>
<td>45</td>
<td>80</td>
<td>5</td>
<td>1</td>
<td>35-45</td>
</tr>
<tr>
<td>250215</td>
<td>CO contamination with low grade H$_2$</td>
<td>1.0</td>
<td>40</td>
<td>60</td>
<td>80-99</td>
<td>8-10</td>
<td>0.5</td>
<td>25-30</td>
</tr>
<tr>
<td>270215</td>
<td>CO contamination with high grade H$_2$</td>
<td>1.0</td>
<td>42</td>
<td>60</td>
<td>80-99</td>
<td>8-10</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>090315</td>
<td>CO contamination</td>
<td>1.0</td>
<td>25</td>
<td>61</td>
<td>95-99</td>
<td>7-8</td>
<td>0.5</td>
<td>28</td>
</tr>
</tbody>
</table>
with fresh MEA

<table>
<thead>
<tr>
<th>Experiment ID</th>
<th>CO2 level</th>
<th>CO2 concentration has no major effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>100315</td>
<td>1.0</td>
<td>25</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Contamination level with 5-20 ppm CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>120315</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Contamination level with 5-20 ppm CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>160315</td>
</tr>
</tbody>
</table>

**Table 3: The parameters for the measurements with current density of 0.6 Acm-2.**

<table>
<thead>
<tr>
<th>MEA and FC Experi</th>
<th>The main observation(s)</th>
<th>H2</th>
<th>dP Cathode /kPa</th>
<th>Anode dew point /°C</th>
<th>Anode fuel utilisation (%)</th>
<th>Anode pressure drop / kPa</th>
<th>Anode pressure at the exit / kPa</th>
<th>Anode fuel utilisation per pass / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRu 300415</td>
<td>10 mV due to inert gas 10 mV due to CO. Methane production could be observed.</td>
<td>2.5</td>
<td>14</td>
<td>65</td>
<td>98</td>
<td>8</td>
<td>0.5</td>
<td>21-23</td>
</tr>
<tr>
<td>PtRu 040515</td>
<td>10 mV due to inert gas 10 mV due to CO. Methane production could be observed.</td>
<td>2.5</td>
<td>14</td>
<td>65</td>
<td>98</td>
<td>8</td>
<td>0.5</td>
<td>21-23 (check)</td>
</tr>
<tr>
<td>PtRu 050515</td>
<td>10 mV due to under gas 10 mV due to CO. CO2 production from CO more clear. Methane production clear.</td>
<td>5.0</td>
<td>14</td>
<td>65</td>
<td>98</td>
<td>8</td>
<td>0.5</td>
<td>21-23 (check)</td>
</tr>
<tr>
<td>MEA A 200515</td>
<td>A very large drop with 5 ppm CO. A very significant methane production. 10 ppm CO at the exit.</td>
<td>5.0</td>
<td>12</td>
<td>65</td>
<td>98</td>
<td>8</td>
<td>0.5</td>
<td>21-23</td>
</tr>
<tr>
<td>MEA A 210515</td>
<td>A very large drop with 5 ppm CO. A very significant methane production. 15 ppm CO at the exit.</td>
<td>2.5</td>
<td>12</td>
<td>64-65</td>
<td>98</td>
<td>8</td>
<td>0.5</td>
<td>21-23</td>
</tr>
<tr>
<td>205015</td>
<td>CO2 alone does not cause degradation. Methane production increases, when CO2 level is increased. However, it decreases slowly indicating CO adsorption on the surface.</td>
<td>2.5</td>
<td>12</td>
<td>64-65</td>
<td>98</td>
<td>8</td>
<td>0.5</td>
<td>21-23</td>
</tr>
<tr>
<td>080615</td>
<td>A smaller drop with 5 ppm CO when MEA B used. A clear methane production, but not so clear as methane in the fuel. 1.5 ppm CO at the</td>
<td>2.5</td>
<td>18</td>
<td>65-66</td>
<td>98</td>
<td>11</td>
<td>0.5</td>
<td>21-23</td>
</tr>
</tbody>
</table>
A smaller drop with 5 ppm CO when MEA B used. A very clear methane production, as no methane in the fuel. 2 ppm CO at the exit. | 5.0 | 22 | 65-66 | 98 | 11 | 0.0-0.5 | 21-23 |

2.1.2.2 CO poisoning measurements
In the measurements, the cell was first run with pure hydrogen until a steady-state was reached after which the CO in \( \text{N}_2 \) flow was injected. In some of the measurements, the recovery of the cell performance could also be observed in the end of the measurement. However, the measurement time was limited to maximum 12 hours, and therefore the full recovery could not be studied.

2.1.2.3 CO level characterisation
The GC response to the mixed fuel feed was tested by using mass flow controllers to mix an impurity source (90.9 ppm CO/\( \text{N}_2 \)) to \( \text{H}_2 \) or \( \text{N}_2 \) feed. Figure 4 shows the response curve that illustrates the mixing reliability. The GC results seemed to match the mixing composition.

The CO level used in the following test relied upon correct calibration of the mass flow controllers used for the mixing. However due to intrinsic uncertainty of the mass flow controllers, relative error of the CO level is expected to be in the range of 5-10% of the target value.

2.2 Results and discussion

2.2.1 The control of the anode recirculation loop
The recirculation system presented in Figure 1 is optimised for the purpose in PEMBeyond measurement. As discussed by Koski, Pérez and Ihonen (2015), in the work with single cells using anode gas recirculation each set-up should be optimised for the purpose of the measurements.
In this system, the recirculation loop gas volume is not optimised to smallest possible and neither the gas volume to the GC. This is due to the fact that in most of the measurements the transients will be so slow that the time delays will not endanger the validity of the results.

When the current recirculation system was build, there were some difficulties with the water separation. In the measurement 200215, shown in Figure 5, it was observed that water separation was insufficient and water droplets were entering the recirculation loop, in which they were re-evaporated causing fluctuation of the anode gas humidity.

Figure 5: The illustration of unstable anode humidity due to water droplet problem.

The problem was taking place already at relatively low recirculation flow rates and with low anode exit point temperature. The combined effect of these difficulties resulted in low anode gas humidity.

The improvement action was to re-build the water separation system after the cell and to install a separate heating control for the exit gas point. As the results in the Figure 6 show the recirculation rate could be doubled, while the anode gas humidity could be stabilised.

Figure 6: The illustration of stable anode humidity.

2.2.2 Transient CO poisoning with PtRu anode catalyst

In Figure 7 are presented the results from a typical CO poisoning experiment. This data is from the experiment with ID 250215. There are number of important observations that can be done from the data.
First of all, the time for reaching a steady-state poisoning with 8.5 ppm CO and 1 Acm\(^2\) was about two hours. It should be, however, note that during this period the fuel utilisation was only 80%. This time scale is in good accordance with literature values, especially with those of Tingelöf, et al. (2008).

It can be seen from the data that the voltage started dropping almost immediately after the CO contaminated fuel was switched on. Some CO can be detected almost immediately after it was injected in the cell. However, it took almost an hour before significant amounts of CO could be detected in the exit gas. At that point the major part of the voltage drop has already taken place. These results are well in accordance with our previous findings (Pérez, et al., 2013, Pérez, et al., 2014).

As can be seen in the GC data in Figure 7, CO is enriched significantly in the anode recirculation loop. With 80% fuel utilisation the enrichment is about 2.5 times (20 ppm) the initial concentration. With fuel utilisation of 99% (target utilisation) the exit gas concentration is over 50 ppm meaning enrichment is up to 6 times.

Since the ppm level of CO is kept constant in the incoming hydrogen, the actual molar flow rate of the CO in to the cell is actually decreased when utilisation is increased. When fuel utilisation was increased up to the target value of 99%, the poisoning continues. It is doubtful if the steady-state poisoning was reached in this experiment.

Carbon dioxide level in the exit gas was also increased as fuel utilisation was increased. It has observed earlier that the carbon molar balance is very difficult to use to estimate the level of CO oxidation (Pérez, et al., 2014). The change of gas flows and fuel utilisation further complicates the analysis.

![Graph showing cell voltage, impurity flow and gas chromatograph data for CO and CO2 for experiment 250215.](image)

**Figure 7:** Cell voltage, impurity flow and gas chromatograph data for CO and CO2 for experiment 250215.
2.2.3 The effect of CO\(_2\) on CO poisoning

The effect of CO\(_2\) has been studied briefly in several of the measurements.

In the beginning the same measurement was repeated with hydrogen containing about 2 ppm (5.0 grade) and 15 ppm (2.5 grade). The results of these measurements (270215 and 250215) are compared in Figure 8. The CO is injected at \(t = 195\) min.

![Figure 8: The cell voltage and CO concentration data for experiments 250212 and 270215.](image)

As can be seen from the data in Figure 8, the poisoning times are comparable. However, the total voltage drop with better hydrogen quality is about 10 mV smaller. In addition, it can be seen that the CO enrichment in the anode recirculation loop is slightly higher and it takes place slightly faster. This result indicates that CO\(_2\) can have effect on CO poisoning affecting both transient time and steady-state voltage drop. The initial and final CO\(_2\) concentration in the experiment 270215 were 20 ppm and 150 ppm, while for 270215 they were 80 and 400 ppm, shown in Figure 9.

The possible effect of CO\(_2\) was studied in the end of CO poisoning experiments by switching the extra gas from nitrogen to CO\(_2\) in the end of the measurement, when the cell was recovering from the CO poisoning. The goal was to see if level of 1-2 % CO\(_2\) can have effect on the cell voltage and if CO could be detected in the exit gas.

The results from one experiment (100315) are shown in Figure 9. In this measurement, the CO in N\(_2\) was switched to N\(_2\) at \(t = 360\) min. Carbon dioxide was fed into system between cell between 500 and 595 minutes, when the cell voltage was mostly recovered and CO was not any more detected at the anode exit gas. Due to the time lag in the lines upstream from the mass flow controller, the increase carbon dioxide in the anode exit gas could be measured between 560 and 670 minutes.

From the results if can be seen first that that the level of 1% has no effect on the cell voltage, when CO is absent. It can also be seen that no CO could be detected in the anode exit gas during or after the CO\(_2\) injection.

Based on the measurements here it can be concluded that %-level of CO\(_2\) in the anode recirculation gas does not affect the cell performance to large extend. However, it remains unclear what is the effect of CO\(_2\) on CO poisoning, concerning both the poisoning time and total voltage drop.
2.2.4 The effect of MEA aging

The CO tolerance of MEA decreases as it is aging (Tabata, Yamazaki, Shintaku and Oomori 2009). This effect was studied by repeating some of the measurements with an aged MEA and fresh MEA. The “aged MEA” had been used only in few hundred hours and exposed frequently to high anode potentials. Therefore, it could be expected that there will be some dissolution of ruthenium and catalyst particle agglomeration on the anode side.

The results of two experiments (270215 = aged MEA, 090315 = fresh MEA) are shown in Figure 10.

It can be seen clearly from the data that the voltage drop with the fresh MEA is significantly smaller, about 40 mV, compared to 70 mV voltage drop with the aged MEA, when highest (target 99%) fuel utilisation value is applied.

What is even more interesting is the lower CO concentration measured in the anode exit gas, when fresh MEA was used. In the end of the both experiments 99% (target value) fuel utilisation was used. In the measurement with fresh MEA the enrichment of CO was from 8.5 ppm to about 20 ppm, while with aged MEA the enrichment was up to 47 ppm. This is a clear indication that an “aged” MEA has lower conversion rate for oxidising CO to CO$_2$. 

Figure 9: Cell voltage, impurity flow and gas chromatograph data for CO and CO$_2$ for experiment 100315.

Figure 10: Cell voltage and exit gas CO concentration data for experiment 270215 and 090315.
There is some difficulty to interpret the results. In the measurement with "aged" MEA (270215) target fuel utilisations of 80%, 90%, 95%, 98% and 99% were used. In the measurement with fresh MEA only 95%, 98% and 99% were used.

The MEA aging is affecting significantly the CO tolerance. If these results are interpreted together with the results of Tabata, Yamazaki, Shintaku and Oomori (2009), then 15-20 mV could be considered as acceptable CO poisoning criteria in the beginning of life (BoL). In the end of life (EoL) 50 mV would be CO poisoning criteria.

### 2.2.5 Determining the acceptable CO level with varying CO concentrations

After the initial measurements with 1.0 Acm$^{-2}$, the level of acceptable CO concentration was determined close to the expected operation point of the FCS in PEMBeyond project.

As shown by Bender, Angelo, Bethune and Rocheleau (2013) the CO tolerance is strongly dependent on the current density. Therefore, the acceptable CO level should be determined with the expected current density of the FCS.

Based on the expected operation point of FCS, 0.6 Acm$^{-2}$ was selected as current density and experiments were run with CO concentrations of 20, 10 and 5 ppm. The poisoning was first done with 20 ppm CO and the recovery of cell voltage was observed, when CO level was decreased to first 10 ppm and then 5 ppm.

The results of one experiment (160315) are shown in the Figure 11. The experiment was started with the targeted fuel utilisation of 98%. At $t = 400$ min the fuel utilisation was decreased to 95% and the effect of lower CO levels was studied using this fuel utilisation.

![Figure 11: Cell voltage, impurity flow and gas chromatograph data for CO and CO$_2$ for experiment 160315.](image)

It can be seen that the voltage drop with the 20 ppm CO in the fuel was about 35 mV and decreases to 20 mV, when CO level was reduced to 10 ppm. A further recovery of 5 mV was gained, when the CO level is decreased to 5 ppm.
When GC data is studied it can be seen that there was a clear enrichment of CO concentration in the recirculation loop, for the 20 ppm CO. The CO concentration reaches 35 ppm at the anode recirculation loop. When the inlet CO concentration was decreased to 10 ppm, the CO concentration at the anode recirculation loop decreased to less than 10 ppm. This means that there is no enrichment of CO in the recirculation loop due to the conversion of CO to CO$_2$. When the CO inlet concentration is further decreased to 5 ppm, the CO concentration at the anode recirculation loop is only 2.5 ppm.

Based on these results and results from the literature, the acceptable maximum CO concentration for the FCS system is about 5 ppm with the chosen current density of 0.6 Acm$^{-2}$. Even if the voltage drop due to CO poisoning is very small (15-20 mV) it can be expected to increase to 50 mV, when the MEA is aging.

Therefore, for the final experiments with single cell, the CO concentration was fixed to 5 ppm and current density to 0.6 Acm$^{-2}$.

2.2.6 Transient poisoning with 5 ppm CO level and 0.6 Acm$^{-2}$ – commercial PtRu

The measurements with 5 ppm CO level and 0.6 Acm$^{-2}$ were done with three different MEAs intended for the reformate fuel cell systems to estimate the difference due to MEA. One of the MEAs ("commercial PtRu") was the same as used in the previous measurements, while the other MEAs were supplied by Powercell Sweden and called here PC MEA type A and PC MEA type B.

Before the poisoning inert gas (N$_2$) was fed in the cell to distinguish between inert gas and poisoning effect. In all the measurements, the effect of inert gas was about 10 mV. Hydrogen concentration was decreased to about 30-50% in the recirculation loop during the CO poisoning.

The measurements with each of the MEAs were performed with low and high grade hydrogen reported in Table 1.

The results from measurements commercial PtRu MEA are shown in Figure 12 - Figure 14. It can be seen from the results that there is very little difference, when hydrogen quality (CO$_2$ level in hydrogen) is changed. The voltage drop due to inert gas is 10 mV and another 10 mV is lost due to CO poisoning. From the cell voltage and CO/CO$_2$ data it can be estimated that the steady state is practically reached.

Reaching the steady-state in gas composition is important as the CO tolerance can be based on CO adsorption as long as there are enough free Pt sites for hydrogen oxidation. Transient CO tolerance is, therefore, based on CO adsorption on the platinum surface. The data from Hashimasa, Matsuda and Akai (2010) shows that adsorption capacity for the Pt catalyst is about 1.2 mmol/gPt.

If a similar capacity is assumed for PtRu, then it would take 5.4 hours (324 minutes) to absorb a monolayer with 0.25 mgcm$^{-2}$ PtRu loading, when hydrogen fuel contains 5 ppm CO and current density is 0.6 and stoichiometry is close to one. This adsorption time estimate is very close to the one observed in the measurements of this study with commercial PtRu catalyst.
When methane data is studied it can be seen that significant amount (10 ppm) of methane can also be detected, when high grade hydrogen is used (Figure 14). Since there is no detectable amount of methane in the fuel, most of this methane must be formed in-situ. Based on the CO$_2$ enrichment data with high grade hydrogen, the real fuel utilisation can be estimated to be about 96-97% and therefore the methane level (0.05 ppm maximum) in high grade hydrogen cannot explain the accumulated hydrogen.

In-situ formation of methane in fuel cell conditions have previously been studied by Lopes and Ticianelli (2010). They noticed that the formation of methane can be observed for Ru, but not for PtRu. This indicates that in the commercial PtRu MEA there is also some free Ru, which can produce methane.

Lopes and Ticianelli (2010) observed also transients in methane production, when CO injection is started or stopped. When CO injection is started there initially high methane production before too many catalyst sites are occupied by CO, which then decreases methane production.

For low grade hydrogen the interpretation is more difficult as a major part of the methane is coming with the hydrogen fuel. When using the enrichment estimate of 25-30 and methane level 0.6-0.7 ppm, it can be estimated that most of the methane (22-23 ppm) is actually coming from the hydrogen fuel.
2.2.7 Transient poisoning with 5 ppm CO level – PC MEA type A

The results from measurements – PC MEA type A are shown in Figure 15 - Figure 17. The absolute voltage scale in these and measurements with PC MEA type B is masked. However, the visible part is always 100 mV, as with the measurements with commercial PtRu MEA.

It can be seen from the results that there is very significant voltage drop (55 mV) in the same time scale compared to the commercial PtRu MEA. It should be noticed that 10 mV is due to dilution by nitrogen. The exit concentrations of CO at the exit are 12 ppm and 16 ppm, thereby indicating that CO is enriched in the anode loop at higher level than

When hydrogen quality (CO$_2$ level in hydrogen) is changed, the poisoning takes place faster and steady state level in CO concentration is reached. Also, the exit CO concentration is higher. This indicates that the catalyst surface is “pre-filled” either with adsorbed CO$_2$ on in-situ formed CO.

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**Figure 15**: Voltage degradation and CO at the exit with a) low grade and b) high grade hydrogen.
Figure 16 Voltage degradation and CO$_2$ at the exit with a) low grade and b) high grade hydrogen.

The formation of CO on the catalyst surface with higher CO$_2$ level is further supported by the methane concentration data. Methane concentration data in Figure 17 shows how there is continuous decrease in methane level, when CO is injected in the low grade hydrogen. When high grade hydrogen was used there is a clear increase in the methane production, before the CO is filling the surface and methane production is decreased.

Figure 17: Voltage degradation and CH$_4$ at the exit with a) low grade and b) high grade hydrogen.

Due to the sensitivity of PC MEA type A for CO$_2$ level in the hydrogen further studies were carried out for studying the effect of CO$_2$ without CO.
Figure 18: Voltage degradation, gas compositions and cell data.

The CO\textsubscript{2} sensitivity was tested by injecting about 2% CO\textsubscript{2} with the hydrogen, so that the gas in the recirculation loop consisted more CO\textsubscript{2} than H\textsubscript{2}. The data in the figure shows that there was a minor (10-20 mV) decrease in the cell voltage.

During the experiment, no CO could be measured at the exit gas. However, there was a transient (increase → decrease) in the methane production, which indicates formation of CO in the catalyst surface. The injection time was only about 2 hours and therefore, no final conclusions should be made.

2.2.8 Transient poisoning with 5 ppm CO level – PC MEA type B

The results from measurements – PC MEA type B are shown in Figure 19 - Figure 21. The voltage degradation rate and exit gas concentrations are much closer to the commercial PtRu MEA than PC MEA type A. CO\textsubscript{2} data is not usable as there were remains of CO\textsubscript{2} in the contaminant feeding lines.

Figure 19: Voltage degradation and CO at the exit with a) low grade and b) high grade hydrogen.
Figure 20: Voltage degradation and CO$_2$ at the exit with a) low grade and b) high grade hydrogen.

Even if voltage degradation and exit CO concentrations are almost similar to the commercial PtRu MEA, the methane production is significantly higher. This is seen when Figure 14 and Figure 21 are compared. This indicates a large amount of Ru on the catalyst.

Figure 21: Voltage degradation and CH$_4$ at the exit with a) low grade and b) high grade hydrogen.

2.3 Conclusions from single cell measurements

Work has been conducted with single cells at 70°C with CO level between 5 ppm using 0.6 Acm$^{-2}$ as current density. The single cell (25 cm$^2$) results with commercial PtRu MEA and Freudenberg H2415 GDL show that when CO concentration is about 5 ppm, then voltage drop is 15-20 mV in 6-8 hours, which is acceptable.

Work with commercial PtRu MEA and Freudenberg H2415 GDL do not indicate strong sensitivity to CO$_2$. However, the work with PC MEA Type A shows both much higher sensitivity for CO poisoning and minor, but clear sensitivity for CO$_2$.

All PtRu MEAs show activity for the methane production, methane production is an indication of Ru in the catalyst.

The performance of PC MEA type A is not acceptable, when compared to commercial PtRu MEA with 0.25 mg/cm$^2$ PtRu loading. PC MEA type B shows comparable CO tolerance and better performance compared to commercial PtRu MEA.
The results here are pre-screening measurements with relatively high uncertainties. The 12 hours of measurement time may not have been enough to get a complete picture of CO tolerance in steady-state conditions, as the adsorption time to reach a monolayer CO on the catalyst surface may be about 5 hours. Unfortunately, overnight measurements were not possible due to safety reasons.

3. System level measurements with low quality hydrogen

The acceptable CO levels determined with the single cell experiments also need to be verified on stack scale, to be absolutely sure about the chosen fuel quality. As the level has to be decided before the reformate system is built, the best option is to study the effects in a small scale system operating with the same stack design as the end application. With on-line gas analysis available, the results can be compared to the ones obtained with single cells.

This chapter describes the equipment and hardware used for stack testing and presents result from the CO tolerance measurements performed with a 10-cell S2 reformate stack.

3.1 The fuel cell stack test bench instrumentation

This section describes the 1-2 kW in-house fuel cell test bench and lists the components, as it is at present moment.

1-2 kW in-house fuel cell test bench’s instrumentation is presented in Figure 22 and the block diagram in Figure 23. In following, the subsystems and their components are described in detail.

![Test bench assembled in a fume hood](image-url)
Figure 23: Piping and instrumentation diagram of the 1-2kW system test bench.

3.1.1 Hydrogen subsystem

Table 4: Component listing of hydrogen subsystem. Essential components in bold.

<table>
<thead>
<tr>
<th>Component</th>
<th>Manufacturer</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>High pressure</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Manual H2 Valve</td>
<td>Swagelok</td>
<td>SS-44S10MM</td>
</tr>
<tr>
<td>H2 throttle valve</td>
<td>Swagelok</td>
<td>SS-6MG-MM</td>
</tr>
<tr>
<td>Metal hydride container</td>
<td>Hydrocell</td>
<td>MH-200</td>
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<tr>
<td>MFM (fast resp.)</td>
<td>Alicat Scientific</td>
<td>MS-250SLPM</td>
</tr>
<tr>
<td>MFM (slow resp.)</td>
<td>Bronkhorst</td>
<td>F-111AC-70K-AAD-33-V</td>
</tr>
<tr>
<td>H2 supply valve</td>
<td>ASCO</td>
<td>SC E238B003</td>
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<tr>
<td>Supply p sensor</td>
<td>SensorTechnics</td>
<td>CTE9010GY4</td>
</tr>
<tr>
<td><strong>Pressure regulator</strong></td>
<td>Swagelok</td>
<td>KLF1CJB417A20000</td>
</tr>
<tr>
<td><strong>Low pressure</strong></td>
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<td></td>
</tr>
<tr>
<td>MFC Impurity</td>
<td>Bronkhorst</td>
<td>F-201CV-100-AAD-33-V</td>
</tr>
<tr>
<td>H2 circulation pump</td>
<td>Rietschle-Thomas</td>
<td>118ZC20/24-117</td>
</tr>
<tr>
<td>Purge valve</td>
<td>Sirai</td>
<td>D132V20</td>
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<td>Sensor blocks</td>
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<td>H2 sensor</td>
<td>AppliedSensor</td>
<td>HPS-100</td>
</tr>
<tr>
<td>Diff. p sensor</td>
<td>Omega</td>
<td>PX2300-5DI</td>
</tr>
<tr>
<td>Inlet p sensor</td>
<td>SensorTechnics</td>
<td>CTE9001GY4</td>
</tr>
<tr>
<td>RH% &amp; T sensor</td>
<td>Vaisala</td>
<td>HMT330</td>
</tr>
<tr>
<td>T sensor</td>
<td>Labfacility</td>
<td>XE-3230-001</td>
</tr>
<tr>
<td>Heating elements</td>
<td>Horst</td>
<td>HST42</td>
</tr>
<tr>
<td>H2 safety</td>
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<td></td>
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<tr>
<td>H2 safety sensor 1</td>
<td>Crowcon</td>
<td>Xgard type 5</td>
</tr>
<tr>
<td>H2 safety sensor 2</td>
<td>NTM</td>
<td>SenseH2</td>
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</tbody>
</table>
The hydrogen is fed passively through a pressure regulator (Swagelok, KLF1CJB417A20000) in order to reduce the pressure and control the pressure fluctuations on the anode. The hydrogen feed rate is measured continuously using two mass flow meters (Bronkhorst, EL-FLOW F-111AC and Alicat Scientific, MS-250SLPM), due to the different characters of the two meters (slow but reliable vs. fast but drifting).

The unconsumed hydrogen leaving the stack is recirculated to the anode inlet using a diaphragm pump (Rietschle-Thomas, 118ZC). Due to the hydrogen recirculation no hydrogen humidification is needed. As a result of the closed hydrogen loop and the recirculation, inert gas and impurities enrich in the hydrogen stream. To remove impurities, the purge valve (Sirai, D132V20) is opened periodically for a short period of time or when the voltage of at least one cell drops below a certain limit.

The effects of impurities or inert build-up can be investigated by feeding additional gas (N₂, CO, CO₂ etc.) through a mass flow controller (Bronkhorst, F-201CV) into the anode loop. The concentration of hydrogen in the anode loop is measured before and after stack with a hydrogen sensor (Applied Sensor, HPS-100).

Other instrumentation includes pressure sensors that measure the H₂ supply pressure before the regulator (SensorTechnics, CTE9010GY4), pressure at anode inlet (SensorTechnics, CTE9001GY4) and differential pressure over stack anode compartment (Omega, PX2300-5DI). Humidity and temperature sensors (Vaisala, HMT330) are also installed at stack inlet and outlet. Heating elements (Horst, HST42) are wrapped around the sensor housings to prevent condensation. Thermocouples (Labfacility, XE-3230-001) are used to monitor that the heating is sufficient to keep the sensors above gas dew point.

For hydrogen safety purposes the system is also installed with two H₂ sensors. First one is fixed to the fume hood (Crowcon, Xgard type 5) while the other (NTM, SenseH2) can be transported with the system. In case of a hydrogen leak, the H₂ supply valve (ASCO, SC E238B003) closes automatically.

To further improve the hydrogen safety of the system, H₂ supply’s maximum flow is throttled with a pinch valve (Swagelok, SS-6MG-MM). In case of a major leak at the high pressure side, this decreases the amount of hydrogen released to the room. As the maximum flow is limited, metal hydride container (Hydrocell, MH200) is used as a buffer to provide sufficient flow while purge valve is opened.

### 3.1.2 Air subsystem

*Table 5: Component listing of air subsystem. Essential components in bold.*

<table>
<thead>
<tr>
<th>Component</th>
<th>Manufacturer</th>
<th>Model</th>
</tr>
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<tbody>
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<tr>
<td>Air filter</td>
<td>Freudenberg</td>
<td>FC F-0412-A</td>
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<tr>
<td>Blower</td>
<td>AirSquared</td>
<td>P16H30N3.25R</td>
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<tr>
<td>Humidifier</td>
<td>PermaPure</td>
<td>FC200-780-7MP</td>
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<td>Total flow meter</td>
<td>TSI Incorporated</td>
<td>42350101</td>
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<tr>
<td>Hum. bypass flow meter</td>
<td>Honeywell</td>
<td>AWM720P1</td>
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<tr>
<td>Hum. bypass propo valve</td>
<td>ASCO</td>
<td>SC E202A027V</td>
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<td>Air inlet/outlet RH%&amp;T</td>
<td>Vaisala</td>
<td>HMP110</td>
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<td>Back pressure controller</td>
<td>Equilibar</td>
<td>GS3 - SS316 GR</td>
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<tr>
<td>Sensor blocks</td>
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</tr>
<tr>
<td>Diff. p sensor</td>
<td>Omega</td>
<td>PX2300-5DI</td>
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<td>p sensor</td>
<td>Sensor Technics</td>
<td>CTE9001GY4</td>
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<tr>
<td>RH% &amp; T sensor</td>
<td>Vaisala</td>
<td>HMT330</td>
</tr>
<tr>
<td>T sensor</td>
<td>Labfacility</td>
<td>XE-3230-001</td>
</tr>
</tbody>
</table>
Heating elements Horst HST42

The air is fed to the fuel cell stack using a blower (AirSquared, P16H30N3.25R). Before the blower, the air is filtered (Freudenberg, FC F-0412-A) and its flow rate is measured (TSI Incorporated, 42350101). The dry air entering the system flows through a membrane humidifier (PermaPure, FC300-1660-10HP) where it is humidified by the moist air leaving the stack.

For adjusting the humidity of the air entering the stack, the humidifier can be partially bypassed. The amount of air bypassed is controlled with a proportional valve (ASCO, SC E202A027V) and measured with another flow meter (Honeywell, AWM720P1).

The pressure on cathode side can be controlled with a back pressure controller (Equilibar, GS3 - SS316 GR). This component has not yet been installed to the system.

As in the anode subsystem, cathode side has sensor blocks fitted to stack inlet and outlet (although H2 sensors are not needed on cathode). For system level water balance measurements, humidity and temperature (Vaisala, HMP110) are also monitored at air filter inlet and humidifier outlet.

### 3.1.3 Cooling subsystem

**Table 6: Component listing of cooling subsystem. Essential components in bold.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Manufacturer</th>
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<tr>
<td>Manual metering valve</td>
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<td>Flow propo valve</td>
<td>ASCO</td>
<td>SC G203B002</td>
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<td>Heat exchanger</td>
<td>SWEP</td>
<td>BX8THx20/1P-SC-S</td>
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<td>De-ionization filter</td>
<td>Spectrapure</td>
<td>DI-MBHT-Q2.5x6L-21</td>
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<td>Coolant pump</td>
<td>Johnson Pump</td>
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<td>Expansion tank</td>
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<td>Flow meter</td>
<td>Bürkert</td>
<td>8012</td>
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<tr>
<td>T sensor</td>
<td>Labfacility</td>
<td>XE-3230-001</td>
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</tbody>
</table>

Heat is removed from the fuel cell stack by recirculating de-ionized coolant water in a closed loop between the stack and a liquid-liquid heat exchanger (SWEP, BX8THx20/1P-SC-S). The stack temperature is automatically controlled by opening and closing the water supply to the cold side of the heat exchanger. The coolant water in the closed loop is pumped (Johnson Pump, CM30P7-1) at constant speed and its flow rate is measured (Bürkert, 8012).

A de-ionization filter (Spectrapure, DI-SAC-10) is used to remove impurities dissolved from the coolant loop, mainly from the fuel cell stack. The maximum flow rate through the de-ionization filter is lower than commonly used flow rate of coolant, so a major part of the coolant water is by-passed.

The amount of cool water fed to the heat exchanger can be controlled either manually (Swagelok, SS-1RS10MM) or automatically with a proportional valve (ASCO, SC G203B002). Stack inlet and outlet temperatures are measured with thermocouples (Labfacility, XE-3230-001).

### 3.1.4 Sensor blocks (Temperature, humidity, pressure, H2 concentration)

As mentioned in the subsystems, sensor blocks are fitted for all stack inlets and outlets. The block consists of a stainless steel pipe bend, and an assortment of fittings welded altogether. In the anode subsystem, the pipe has fittings for H2 sensor (AppliedSensor, HPS-100),
pressure sensors (SensorTechnics, CTE9001GY4 and Omega, PX2300-5DI) as well as RH & temperature probes (Vaisala, HMT330).

The cathode sensor block is made in the same way, but without the H₂ sensor fittings. In the cooling subsystem, only temperature of the coolant is measured.

### 3.1.5 Electrical components

The current drawn by the load (Chroma, 63203) is monitored by a current sensor (LEM, DHAP S/25) connected to the cRIO control system. A relay (Tyco Electronics, EV200AAANA) that is operated by the cRIO control system is installed between the stack and load. This ensures that the fuel cell stack can be safely disconnected in case of a load fault.

A PWM signal converter is used for converting the H₂ sensor (AppliedSensor, HPS-100) signal to voltage signal.

Other electrical components consist of various power supplies (PSUs) by Phoenix Contact. One 20A 24VDC PSU is dedicated for the cathode blower. Second, 10A 24VDC PSU is for all the other 24V components. In addition to 24V, some instruments also require 12V or 5V PSU.

Table 7: Component listing of electrical components. Essential components in bold.

<table>
<thead>
<tr>
<th>Component</th>
<th>Manufacturer</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electric load</td>
<td>Chroma</td>
<td>63203</td>
</tr>
<tr>
<td>Current sensor</td>
<td>LEM</td>
<td>DHAP S/25</td>
</tr>
<tr>
<td>Relay</td>
<td>Tyco Electronics</td>
<td>EV200AAANA</td>
</tr>
<tr>
<td>PWM signal converter</td>
<td>Axiomatic</td>
<td>AX13020X</td>
</tr>
<tr>
<td>24 VDC PSU 20 A</td>
<td>Phoenix Contact</td>
<td>QUINT-PS/1AC/24DC/20</td>
</tr>
<tr>
<td>24 VDC PSU 10 A</td>
<td>Phoenix Contact</td>
<td>QUINT-PS/1AC/24DC/10</td>
</tr>
<tr>
<td>12 VDC PSU</td>
<td>Phoenix Contact</td>
<td>MINI-PS-100-240AC/10-15DC/2</td>
</tr>
<tr>
<td>5 VDC PSU</td>
<td>Phoenix Contact</td>
<td>MINI-PS-100-240AC/ 5DC/3</td>
</tr>
</tbody>
</table>

### 3.1.6 Control and measurement system

National Instruments’ compactRIO with LabView program are used for control and measurement system. The hardware consists of NI cRIO-9014 real-time controller with FPGA chassis cRIO-9116 and following I/O modules:

- MOD1 : NI 9206, 16-channel, 16-bit **analog input** module
- MOD2 : NI 9203, 8-channel, ±20 mA, 16-bit **analog input** module
- MOD3 : NI 9205 32-channel, ±10 V, 16-bit **analog input** module
- MOD4 : NI 9205 32-channel, ±10 V, 16-bit **analog input** module (same as MOD3)
- MOD5 : NI 9264 16-channel, ±10 V, 16-bit **analog output** module
- MOD6 : NI 9481 4-channel **digital output** module
- MOD7 : NI 9474 8-channel **digital output** module
- MOD8 : NI 9213 16-channel **thermocouple input** module

The control system is powered with a NI PS-15 24 VDC PSU.

Table 8: Component listing of the control and measurement system. The essential components are marked in bold.
3.1.7 Piping, tubing and electrical wiring

In addition to all the actual system components, a lot of piping and tubing was necessary to connect the individual components. On the high pressure side, 6 mm stainless steel tubing was used with Swagelok connectors. On the low pressure side the tubing was done with 12 mm OD Teflon tubes and corresponding Swagelok fittings.

On cathode side, flexible 19 mm ID silicon tubing was used. POM or stainless steel hose fittings were used with hose clamps. The closed loop of the cooling subsystem was assembled with 16 mm ID silicon tubing, whereas the secondary side (tap water) was done with 10 mm OD polyurethane tubing.

The system cabling was organized in cable ducts to keep the electrical cabling separate from fluid piping. Shielded cables were used in instruments when necessary.

3.2 Experiments with S2 reformate stacks

3.2.1 Overall tests performed

The test station was built during spring/summer 2014, and the functionality of the test bench and gas analysis system has been thoroughly tested in fall 2014 with and old SGL stack shown in Figure 22. However, the test could only be carried at very low currents (<60A).

First S2 stack was received and installed in fall 2014, but had to be returned due to problems with anode manifold leakages. In 2015 Powercell sent an older S2 reformate prototype to proceed with benchmarking the final functionality of the test bench. The stack was installed and a brief CO-tolerance experiment with 26 ppm of CO in fuel was performed. The gas analysis system was functioning properly and the test bench was functioning at the desired operation point.

<table>
<thead>
<tr>
<th>Component</th>
<th>Manufacturer</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Real-time controller</td>
<td>National Instruments</td>
<td>cRIO-9014</td>
</tr>
<tr>
<td>8-slot chassis</td>
<td>National Instruments</td>
<td>cRIO-9116</td>
</tr>
<tr>
<td>24 VDC PSU</td>
<td>National Instruments</td>
<td>NI PS-15</td>
</tr>
<tr>
<td>Modules</td>
<td>National Instruments</td>
<td>NI 9206</td>
</tr>
<tr>
<td>16CH CVM analog input</td>
<td>National Instruments</td>
<td>NI 9203</td>
</tr>
<tr>
<td>8CH ±20 mA analog input</td>
<td>National Instruments</td>
<td>NI 9203</td>
</tr>
<tr>
<td>32CH ±10 V analog input</td>
<td>National Instruments</td>
<td>NI 9205</td>
</tr>
<tr>
<td>32CH ±10 V analog input</td>
<td>National Instruments</td>
<td>NI 9205</td>
</tr>
<tr>
<td>16CH ±10 V analog output</td>
<td>National Instruments</td>
<td>NI 9264</td>
</tr>
<tr>
<td>4CH 24 V digital output</td>
<td>National Instruments</td>
<td>NI 9481</td>
</tr>
<tr>
<td>8CH 24 V digital output</td>
<td>National Instruments</td>
<td>NI 9474</td>
</tr>
<tr>
<td>16CH TC analog input</td>
<td>National Instruments</td>
<td>NI 9213</td>
</tr>
</tbody>
</table>
During the next phase, a 10-cell pre-production reformate version of an S2 stack was installed and tested with CO impurity. Figure 24 shows the system during a CO tolerance test. The details are described in the following section.

Overall, the test bench functioned as expected and the S2 stacks tested were able to be operated at the designed current density. The main drawback that was noticed during the tests at over 100A currents was water condensation in the sensor blocks. This caused water droplets to enter the humidity sensors.

The sensor block geometry was re-designed to better shield the sensors from droplets, and the water knock-out at the anode exit side has been re-assembled with larger volume liquid separator.

### 3.2.2 S2 stack CO tolerance test with 4.9 ppm CO level in fuel

#### 3.2.2.1 Test procedure

Both of the tests were performed on same conditions listed in Table 9: Parameters for the S2 stack CO tolerance tests. The current drawn from the stack was chosen to be 0.6 A/cm² (117A), which corresponds to the nominal operation point of an S2 stack. Hydrogen feed pressure was adjusted to 200 mbar(g) and the cathode pressure was unregulated.

Temperature was regulated to 70 °C. The cathode side was humidified by a membrane humidifier at full capacity, thus the dry air bypass flow valve was completely closed. Anode side was humidified with the recirculation pump, with control set-point at 10% of full power. The sensor block temperatures were kept at 80 °C by the line heaters.
The stack was first ramped up to the 0.6 A/cm² operation point. During the first phase N₂ feed to the stack was started at 8.17 slmpm and the purge was adjusted to open for 200 ms every 300 seconds. After further stabilization period of 30 minutes, the N₂ flow was switched to an impurity source of 5000 ppm of CO in N₂. The CO concentration target was 5 ppm of CO in the fuel feed and with the realized H₂ consumption of 8.27 slpm this totals to approximately 4.9 ppm of CO in the fuel feed. The corresponding N₂ concentration in the fuel feed was 0.099% = 990 ppm.

The CO poisoning phase was continued in both tests for approximately 210 minutes, after which the CO/N₂ feed was switched back to N₂. After 10 minutes stack power was ramped down and the system was shut down. GC was used to take samples from the recirculation loop at 7 minute interval.

The first test (110615) was performed by using the 2.5 hydrogen quality (99.5% pure). The second repetition was performed with bottled 5.0 hydrogen (99.999% pure). The details are shown in Table 9.

Both H₂ sources used were analysed for CO, CH₄ and CO₂ and the results are shown in Table 10.

### Table 9: Parameters for the S2 stack CO tolerance tests

<table>
<thead>
<tr>
<th>Test ID</th>
<th>H₂ quality</th>
<th>CO in fuel</th>
<th>N₂ in fuel</th>
<th>Current density</th>
<th>Total fuel utilization</th>
<th>Per-pass fuel util.</th>
<th>Stack temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: 110615</td>
<td>Line 2.5</td>
<td>4.9 ppm</td>
<td>990 ppm</td>
<td>0.6 A/cm²</td>
<td>98.6%</td>
<td>73%</td>
<td>70 °C</td>
</tr>
<tr>
<td>B: 160615</td>
<td>Bottled 5.0</td>
<td>4.9 ppm</td>
<td>990 ppm</td>
<td>0.6 A/cm²</td>
<td>98.5%</td>
<td>69%</td>
<td>70 °C</td>
</tr>
</tbody>
</table>

### Table 10: Results from hydrogen source gas analysis

<table>
<thead>
<tr>
<th>Sampling Date</th>
<th>Gas type</th>
<th>CO (ppm)</th>
<th>CH₄ (ppm)</th>
<th>CO₂ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27.5.2015</td>
<td>Line H₂ 2.5</td>
<td>&lt;0.05</td>
<td>0.7±0.1</td>
<td>23±1</td>
</tr>
<tr>
<td>12.6.2015</td>
<td>Line H₂ 2.5</td>
<td>&lt;0.05</td>
<td>0.6±0.1</td>
<td>22±1</td>
</tr>
<tr>
<td>15.6.2015</td>
<td>Bottled H₂ 5.0</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>3.9±0.2</td>
</tr>
</tbody>
</table>

3.2.2.2 Results

Figure 25 shows a comparison of the data recorded during the two experiments. In the first test, the average cell voltage dropped 30 mV during the test. On the second test with 5.0 grade H₂, the voltage drop was only 10 mV with same CO concentration at inlet feed.

When comparing the CO-levels in the recirculation, CO starts to pass through the stack in much higher quantities in the first test than in the second one. This will increase the molar flow of CO at the inlet and contribute to faster poisoning.

Although the control parameters were kept the same, there were some differences in the hydrogen inlet and outlet concentrations, as shown in Figure 25. The H₂ concentration was lower in the first test with H₂ 2.5 mainly due to higher inert (N₂) concentration in the fuel.

In addition to the lower cell voltage drop during the CO injection, also the starting level of the cell voltages was 30 mV higher in the second test. The cell voltage could be affected by
difference in anode inlet H\textsubscript{2} concentration; gas feed humidities or combined effect of CO and CO\textsubscript{2} during the poisoning. These factors alone do not explain a 30 mV initial difference in the average cell voltages, and the difference is most probably mainly due to insufficient MEA activation before shipping the stack. CO stripping after the first poisoning could also contribute to the activation. This also explains why the CO tolerance was much higher in the second test.

The anode fuel utilizations calculated based on the hydrogen flow meter data are displayed in Table 9. The total fuel utilization was within 0.1% margin on both tests, but as the H\textsubscript{2} sensor reading showed, the per-pass fuel utilization was marginally higher on the first test.

![Cell voltage trends: Avg/Max/Min (mV)](image)

![Recirculation loop CO level (ppm)](image)

![Anode H2 concentration (%)](image)

*Figure 25: Comparison of cell voltages, CO levels at recirculation and H\textsubscript{2} concentrations at anode inlet and outlet. The first test (A110615) was performed with 2.5 H\textsubscript{2} and the second one (B160615) with 5.0 H\textsubscript{2}. The 4.9 ppm CO injection start (t=0 min) and stop (t=210 min) are marked with black vertical lines. Note that the absolute cell voltage has been masked as the data is from pre-production version stack.*
Figure 26 shows the CH\textsubscript{4} and CO\textsubscript{2} levels from the recirculation loop during the poisoning. In test A with H\textsubscript{2} 2.5 (0.6 ppm CH\textsubscript{4}, 22 ppm CO\textsubscript{2}), the CO\textsubscript{2} level has a slight increase during the CO injection period, suggesting the oxidation of CO to CO\textsubscript{2} increases. The same trend is also evident in the latter test performed with H\textsubscript{2} 5.0 (<0.05 ppm CH\textsubscript{4}, 3.9 ppm CO\textsubscript{2}), although the CO\textsubscript{2} level is lower. As shown with the single cell experiments, we can see that in both stack experiments CH\textsubscript{4} concentration increases just after the poisoning starts. As the CO poisoning continues further CH\textsubscript{4} levels start to decrease. This suggests that the PtRu catalyst is not perfectly alloyed and some Pt and Ru catalyst particles are on individual sites (Lopes, Ticianelli, 2010). The latter test also proves that CH\textsubscript{4} is produced in the anode as the levels are magnitudes higher that would be expected by simple enrichment from the CH\textsubscript{4} present in the H\textsubscript{2} 5.0.

3.3 Conclusions from system level measurements

The CO tolerance of the S2 was measured at 4.9 ppm CO level with two H\textsubscript{2} grades used as the fuel. The stack performance seems to match with the single cell tests at 0.6 A/cm\textsuperscript{2} current density and the methanation reaction was also observed at stack level. According to the test with 5.0 grade H\textsubscript{2}, the stack tolerates 5 ppms of CO for three hours with average cell voltage drop in 10 mV range.

Overall, the test bench functioned as expected and the S2 stacks tested were able to be operated at the designed current density. The main drawback that was noticed during the tests at over 100A currents was water condensation in the sensor blocks. This caused water droplets to enter the humidity sensors, thus very little useful humidity data was collected.

The sensor block geometry was re-designed to better shield the sensors from droplets, and the water knock-out at the anode exit side has been re-assembled with larger volume liquid separator.
4. Overall conclusions

Main issue in hydrogen quality with regard to PEMBeyond system is the effect of enrichment of CO in the anode recirculation loop with membrane using PtRu catalyst. According to the results from both single cell and system level measurements, hydrogen production quality of 5 ppm CO should be targeted from the PSA. With this level of CO concentration the voltage drop in FCS can be limited to 15-20 mV/cell in the beginning of life. This corresponds to an expected voltage loss of 50 mV/cell when the MEA is aged. On the other hand, even %-level of CO\textsubscript{2} in the anode recirculation gas does not affect the cell performance to large extent. However, it remains unclear what is the effect of CO\textsubscript{2} on CO poisoning, concerning both the poisoning time and total voltage drop.

It is still unclear what the actual CO concentration is that is reached with the PSA prototype to be developed for the project. Implementing different mitigation methods should be evaluated in the FCS development if the hydrogen quality produced is foreseen to be significantly lower than what is proposed here in this document.

References:


Alvarez, M.V.S. 2006, Investigations of current density inhomogeneities in polymer electrolyte fuel cells, ETH/PSI


