HyCoRA – Hydrogen Contaminant Risk Assessment
Grant agreement no: 621223
Interim progress report 3

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Summary

In this periodic activity report, the work progress of the fourth reporting period (M19-M24) of HyCoRA project is summarised. This report contains already some results for M25 and M26.

In WP1 the effect of formaldehyde (HCHO) has been studied further with a pre-mixture of HCHO in hydrogen. The results have strengthened the conclusion that HCHO limit in ISO 14687-2:2012 is too low. On the other hand, it seems that the main product of HCHO degradation is CO, which is a stronger poison than HCHO. The work to study the effect of CO at the system level with fuel cell dynamic load cycle has been started.

In WP2 the work has continued according to DoW with focus on pre-concentration strategies for fuel quality control. Deliverable 2.2 has been submitted.

In WP3 the second measurement campaign has been prepared by selecting the hydrogen refuelling stations to be studied.

In WP4 an internal risk assessment workshop was arranged in connection to M24 progress meeting to strengthen the integration between WPs. The preparation to implement the quantitative risk model in Matlab has been started.

In WP5 dissemination activities has continued with communication to standard drafting organisations and attending workshop "4th International Workshop on Hydrogen Infrastructure & Transportation".

The management WP6 has been executed as planned. Consortium is preparing to apply for 3 months extension for the project.

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Contents

1. Project objectives for the period and first half of the project

The objectives of the months 19-24 of the HyCoRA project have been to continue the research activities in all WPs after guidance from mid-term review and OEMs for the experimental work (especially in WP1) and development of the risk model.

2. Work Progress and Achievements during the 4rd Period

2.1 Determination of susceptibility of hydrogen contaminants for automotive applications (WP1)

Completed and planned measurements in the WP1

The work with hydrogen contaminants during the first 24 months of the project has been summarised mostly in deliverables D1.2, D1.3, D6.2, D6.3 and D 6.4. In the table 1 are listed the development work and experiments performed by each partner in WP1.

Table 1. A list of measurement performed in each institute in WP1.

Partner	Contaminant studied and ppm level	The issue studied / measurement type	Pt loading at the anode ($mgcm^{-2}$)	Single cell, stack or stack in system	Number of measurements (or estimate)	Results or development work reported in deliverable
VTT	CO (1 ppm)	Flow rate, stoichiometry, recirculation, current density, CO at the exit gas	0.05	single cell	~20	D 1.2 and D 6.2
VTT	HCOOH (5 ppm)	constant current tolerance, carbon balance	0.25 (PtRu)	single cell	2	D 6.3
VTT	HCOOH (7.8 ppm)	constant current tolerance, carbon balance	0.05	single cell	5	D 1.3
VTT	CO (few ppm)	System test bench and GC operation testing	0.4	SGL 20 cell demo stack in system	~30	D 1.2
VTT	CO (fem ppm)	System test bench and GC operation testing	unknown	S2 prototype stack in system	~45	D 6.2
VTT	CO (1,2,5 ppm)	constant current tolerance	0.05	S2 production unit in system	6	D1.3
VTT	CO (2 ppm)	start and stop	0.05	S2 production unit in system	7	D1.3
VTT	HCOOH (9.4 ppm)	constant current tolerance and with CO	0.05	S2 production unit in system	5	D 1.3
VTT	HCHO (2.0 ppm)	constant current	0.05	S2 production unit in system	1	D 1.3

		tolerance and with CO				
VTT	CO (1.86 ppm)	Internal air bleed / carbon balance	0.05	S2 production unit in system	1	D 6.4
VTT	CO (1.86 ppm)	Internal air bleed / carbon balance	0.05	single cell	1	D 6.4
VTT	CO (1.86 ppm)	Reference poisoning with 0.6 Acm^{-2}	0.05	S2 production unit in system	2	D 6.5 (this report)
VTT	HCHO (1.6 ppm) with 0.3 ppm CO	Poisoning with 0.6 Acm^{-2}	0.05	S2 production unit in system	2	D 6.5 (this report)
VTT	Reference for CO FC-DLC (1.86 ppm)	Decay without CO when FC-DLC applied	0.05	S2 production unit in system	3	D 6.5 (this report)
CEA	CO (1,2,5 ppm)	Constant current tolerance	0.2	SC	4	D1.3
CEA	CO (1,2,5 ppm)	FC-DLC (NEDC)	0.2	SC	3	D1.3
CEA	CO (2 ppm)	Constant current tolerance	0.3 (ion power)	SC	1	D1.3
CEA	H2S (20 ppb, X ppb)	Constant current	0.05 (ion power)	SC	1	D 6.4
CEA	CO	SU/SD	0.2	SC	2	D1.3
CEA	CO (2-5 ppm)	Constant current	0.2	Stack / system	~ 10	D1.3
JRC	CO (1-10 ppm)	System test bench and IMR-MS operation testing	unknown	SC	5	D 1.2
JRC	CO (1-2 ppm)	Flow rate, stoichiometry, recirculation, current density, CO at the exit gas	unknown	SC	5	D 6.3
JRC	CO (1-5 ppm)	Costant current open and Recirculation mode. FC-DLC test	unknown	SC	12	D 1.3
PC		Polarization curves at 65, 75 and 85 ˚C	0.05	S2 10 cell stack SN025	3	D 1.3
PC		Polarization curves at 65, 75 and 85 ˚C	0.05	S2 10 cell stack SN040	3	D 1.3
PC		Polarization curves at 65, 75 and 85 ˚C	0.05	S2 10 cell stack SN043	3	D 1.3

PC		Polarization curves at 65, 75 and 85 ˚C	0.05	S2 5 cell stack SN049	3	
PC		Polarization curves at 65, 75 and 85 ˚C	0.05	S2 10 cell stack SN067	3	D 6.5 (this report)

After the project mid-term review there has been some minor changes in the planned work schedule. These are discussed in Chapter 2.6.

2.1.1 Study of reversible impurities (Task 1.3)

VTT

During the period M19-M24 VTT has studied the effect of formaldehyde (HCHO) and also started the activities applying fuel cell dynamic lead cycle (FC-DLC) with aim to compare FC-DLC and constant current measurements using CO as poison..

HCHO measurements

VTT has purchased formaldehyde in hydrogen mixture from NPL (The National Physical Laboratory, UK), which has enabled fuel cell system level measurements with automotive fuel utilisation rates (99.5-99.6 %) and corresponding contaminant enrichment factors of 200-250. Measurements have been done with target level of 2 pm HCHO in hydrogen.

However, as shown in Chapter 2.2.1 HCHO in H_2 decomposes quickly and the HCHO level in the first measurements was 1.6 ppm with some 0.3 ppm CO as decomposition product (see Chapter 2.2.1). At the moment of writing this report, the repetition measurements are still ongoing as well as analysis of the results. Some first results of HCHO measurements are already shown in this report for illustrative purposes. The complete reporting will be done in Deliverable 6.6.

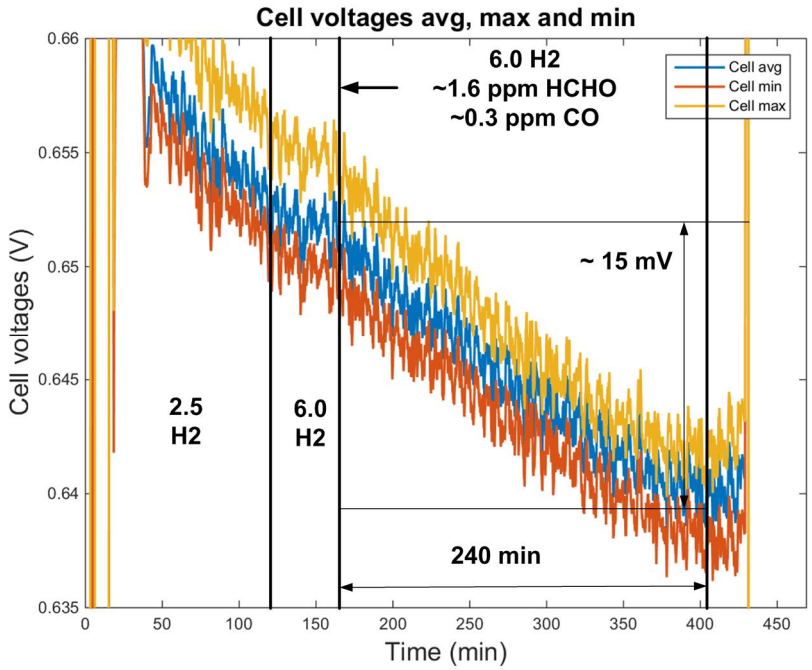


Figure 1. A four hour poisoning experiment with approximately 1.6 ppm HCHO and with approximately 0.3 ppm CO.

One result of the HCHO poisoning is shown in Figure 1. As can be seen, there is only a very small (~ 10 mV) average voltage drop in 4 hours due to HCHO (and CO), when reversible decay (5 mV in 4 hours, see Figure 53 in Deliverable 1.3) is taken into account. The conditions were similar as in previous measurements reported in Deliverable 1.3 (Table 15). Full results and experimental details of all the HCHO measurements will reported in Deliverable 6.6.

In two reference poisonings with CO (1.86 ppm) with similar conditions as in Figure 1, 50 mV average voltage drop was reached in 67 and 71 minutes. The first reference poisoning with CO was done before the HCHO poisoning measurements and the second one was done after HCHO poisoning measurements. This indicates that HCHO has no irreversible degradation effect, as already shown by Wang et al.[1] and Watanabe et al.[2]. However, it can be seen that the CO tolerance of the S2 stack (SN025) has slightly decreased, as initially the poisoning time was about 90 minutes with similar conditions (Table 6 in Deliverable 1.3).

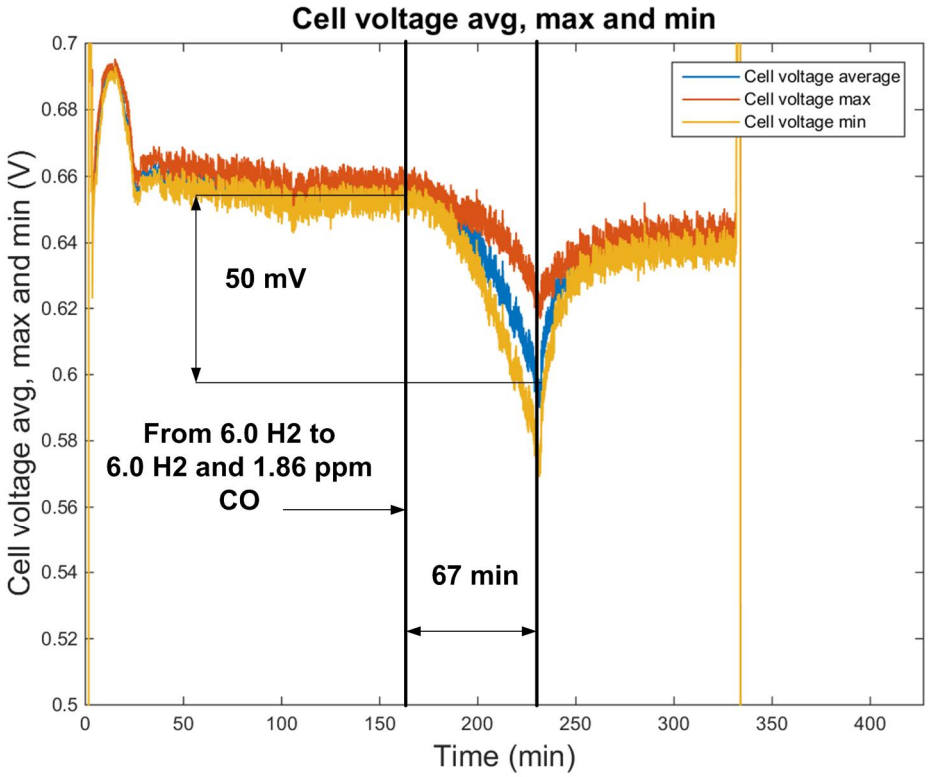


Figure 2. Poisoning with 1.86 ppm CO and 0.6 Acm^{-2}.

It has also been shown by Watanabe et al. that very high HCHO concentrations (10 and 20 ppm) can cause a clear poisoning effect even with high platinum loading anodes (0.3 $mg*cm^{-2}$). Therefore, if there is significant enrichment of HCHO in the recirculation loop, HCHO will cause a poisoning effect. Enrichment of HCHO can be limited by HCHO diffusion cathode, dissolution to anode purge water and because of HCHO conversion to other products (CO, CO_2, CH_4) on the Pt anode.

[1] Wang, X., Baker, P., Zhang, X., Garces, H.F., Bonville, L.J., Pasaogullari, U., Molter, T.M. An experimental overview of the effects of hydrogen impurities on polymer electrolyte membrane fuel cell performance (2014) International Journal of Hydrogen Energy, 39 (34), pp. 19701-19713

[2] https://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/fp_workshop_watanabe.pdf (slides 20, 22)

About 10% of injected HCHO was found in anode purge water in the measurement illustrated in Figure 1. A large Henry's constant for HCHO indicates that a significant part of HCHO in anode gas should dissolve in the exit gas water. Therefore, this result is expected.

The largest part 50% of HCHO fed in the anode loop seems to be methanated according to gas analysis measurements. The result in Figure 3 illustrates the increase of methane concentration in anode loop.

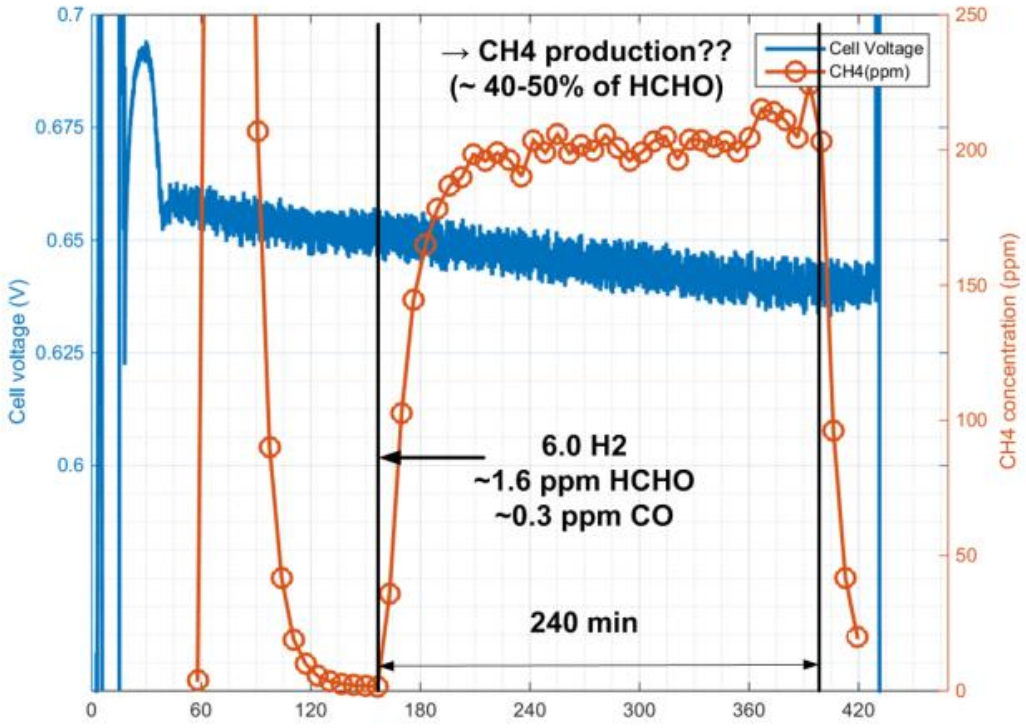


Figure 3. The level of methane in the anode recirculation loop.

Since GC measurements for HCHO mixed in hydrogen indicate that HCHO decomposes to CO (Chapter 2.2.1), this may have caused the main effect in poisoning also in previous measurements when HCHO mixed in N_2 or H_2 has been used. This applies both results in HyCoRA project (Figure Figures 50-51 in Deliverable 1.3), as well as results in the literature.

In summary, 1.6 ppm (160 x limit in ISO 14687-2:2012) seems to have HCHO a negligible effect even when a very high fuel utilisation is used.

However, HCHO decomposes forming significant amount of CO. Therefore, the limit in ISO 14687-2:2012 should not be relaxed over the limit of CO. If it can be shown that HCHO forms predominantly HCHO, when it decomposes, then the total limit for CO and HCHO should be 0.2 ppm, which is currently the limit for CO.

FC-DLC measurements

FC-DLC measurements at VTT have been started with trimming the thermal management of the miniature automotive system. The average current density and heat production can also be low in the measurements, if low maximum and average currents are used. Therefore, additional insulation in the system has been added and the system behaviour has been characterised. At the same time, the system has been studied to monitor the reversible performance decay without CO.

The result for one of the measurements is shown in Figure 4a. The applied FC-DLC profile is given in Figure 4b. When low average current (~ 0.2054 Acm^{-2}) was applied in this FC-DLC, heat production was not sufficiently high to warm up the system within a reasonable time. Time to reach 80 °C was over 2 hours. In addition, the system temperature was not stable during one FC-DLC sequence. The temperature variation during one FC-DLC was 6 °C.

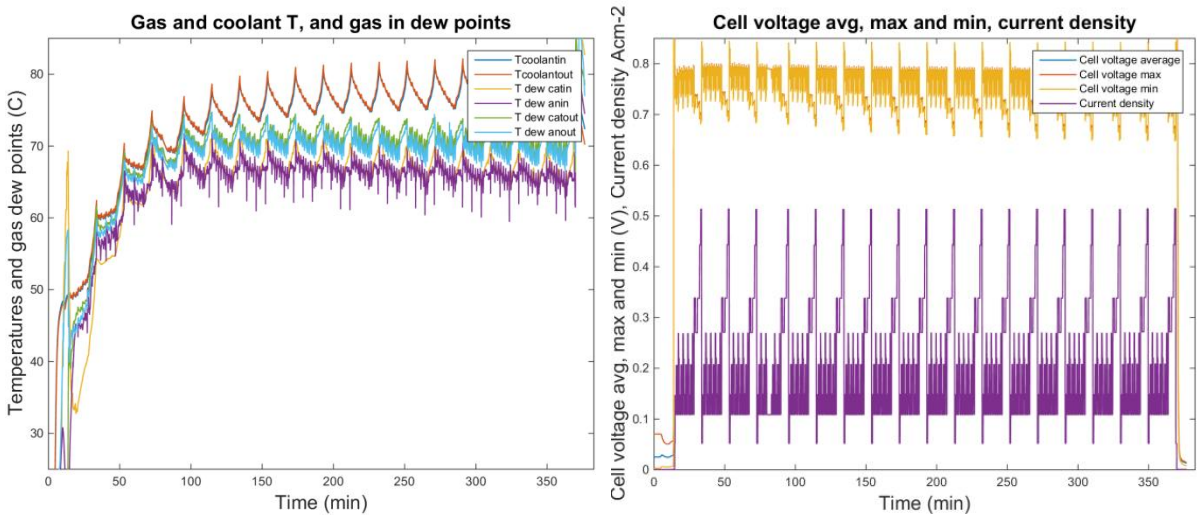


Figure 4. a) The dynamic behaviour of stack temperature and gas dew points and temperatures. b) FC-DLC used in the measurements.

Fluctuations of recirculation rate, gas dew points and many other parameters are unavoidable in this type of system. However, the similar fluctuations take place also in real automotive fuel cell systems. It can be considered most important to reach operation temperature (80 °C) sufficiently rapidly, as CO poisoning is strongly dependent on the temperature. The variation during one FC-DLC is considered acceptable if it can be kept under 4 °C. Based on these considerations and the result in Figure 4, 0.4 Acm^{-2} have been chosen as an average current and FC-DLC profile has been modified accordingly.

When FC-DLC measurements are continued, a reference reversible decay (without CO) should be measured for 4-6 hour measurement, similarly that has been done for steady-state poisoning measurements for HCHO.

CEA

CO measurements - Gas analyser for CO/CO_2 mass balance

CEA has been purchased an OFCEAs gas analyser with a probe for CO and CO_2. The same technology of gas analyser has been used in the first period to analyse the CO and H_2S containing H_2. (see deliverable 2.3). The equipment has been received and installed the 22nd of April 2016. It is under validation at ppb/ppm level (CO and CO_2) in H_2 from 25°C to 80°C and from dried gaz to 100%RH. The first preliminary results are presented in Table 2 below.

Table 2. Preliminary validation results for OFCEAs gas analyser with CO.

CO conc. theoret., ppm	CO conc. measured, ppm
0	0,254
5	3,5
10	7,4
15	11,35
20	15,2
25	18,65
25 (+T=60°C)	20,17

Impact of CO on single cell.

Impact of SU/SD protocols.

Impact of SU/SD on CO oxidation into CO_2 and release from the anode has been continued. The protocol already presented in midterm report has been used in order to check reproducibility of the results.

Table 2. SU/SD protocol description.

Operating time/condition	4 hours at 1 A/cm^2, 80°C, 50 % RH, 1,5 bara (anode and cathode), St_{H2} 1,2; St_{Air} 2
SD protocol	Stop current, stop H2 and Air flow, open cathode valve back pressure regulation (1.01 bara), keep anode valve back pressure closed, Shut down SC temperature regulation, Keep boiler temperature at 64 °C.
Off time	30 min, the SC temperature get down to 46°C
SU protocol	The SC is heated to 80°C, then anode flows corresponding to 1 A/cm^2 and stoichiometric flow of air are set. Back pressures are set to 1.5 bara. The current density is improved by steps of 6 min each to reach 1 A/cm^2, steps are (1; 2; 5; 10; 16; 20; 22 A/cm^2)

The results presented in Figure 5 showed that there is a recovery of performance for the SU/SD cycle. However 30 minutes seems to be too short to have a full recovery of performance. The two tests shows a good reproducibility between results. It has to be noticed that the history of the MEA is not the same, indeed the one corresponding to the red

curve has been previously aged a 0.37A/cm^2 under 5ppm CO/H_2 for 24 hrs, while the bleu curve has been obtained with a fresh MEA.

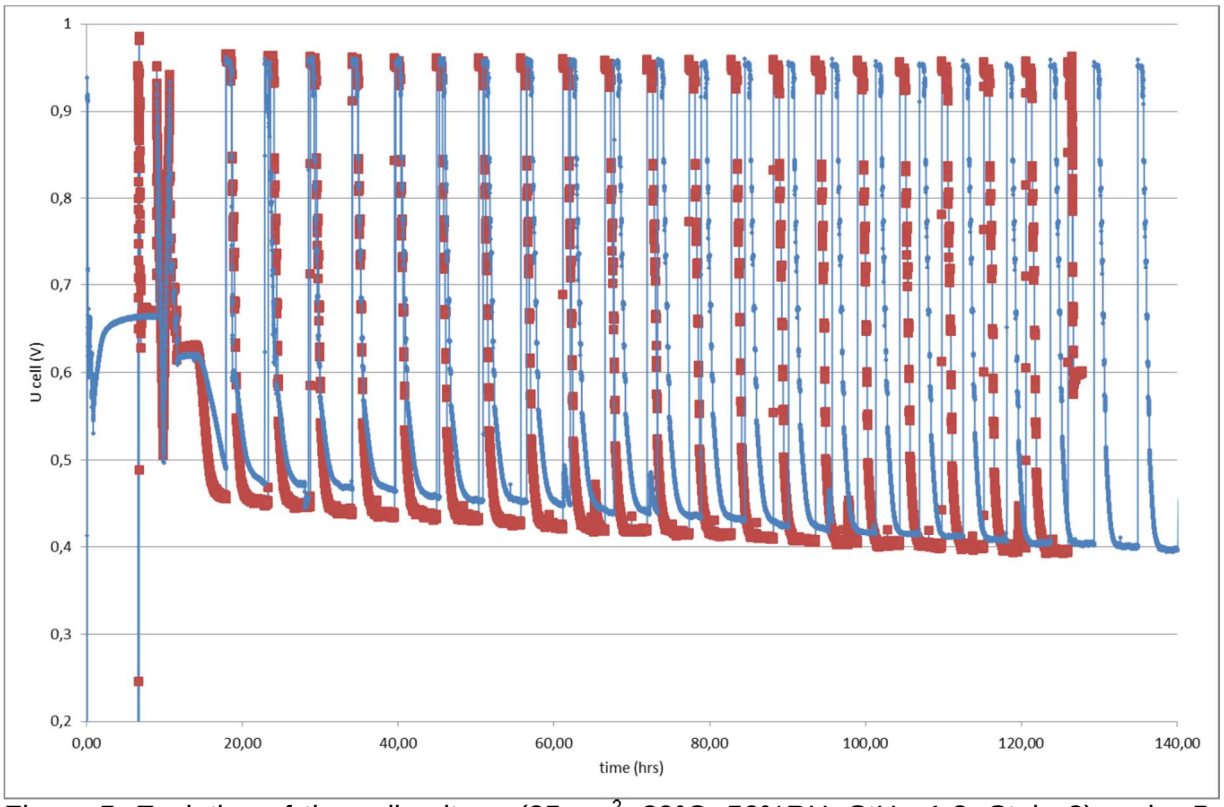


Figure 5: Evolution of the cell voltage (25 cm^2, 80°C, 50%RH, StH_2: 1.2, Stair: 2) under 5 ppm CO/H_2 and using SU/SD protocols for fresh MEA (bleu) and previously tested MEA under 5 ppm CO/H_2 @ 0.37 A/cm^2 (red)

The ECSA of the anode has been measured at BoL, after the test under 0.37 A/cm^2 and after the SU/SD test and is presented in Figure 6. The anode ECSA is decreased from 43 m^2/g_{pt} to 34 m^2/g_{Pt} which is constituent with the catalyst maturation during the first tens of hours of operation for fresh MEA.

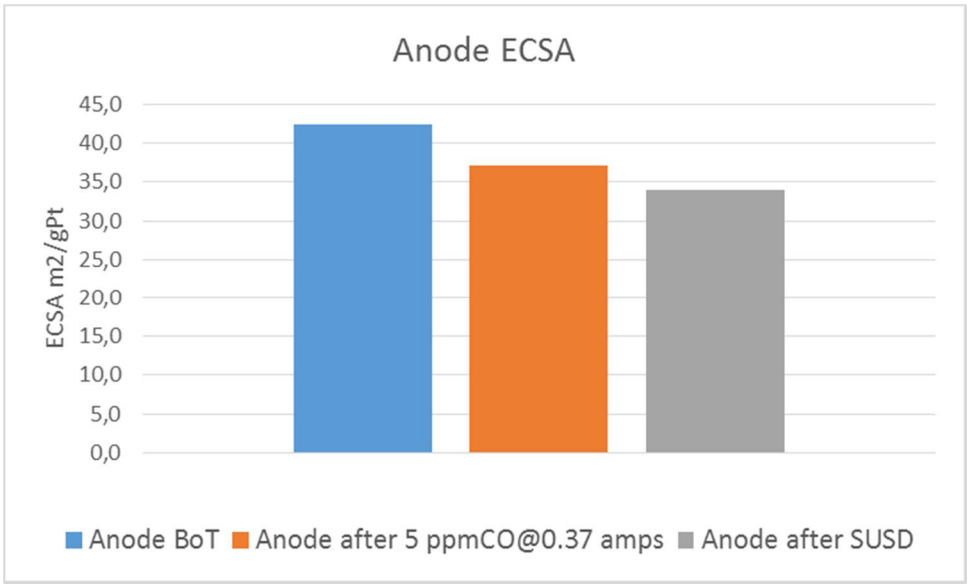


Figure 6: evolution of the anode ECSA after test under 5 ppm CO/H_2 at steady state (0.37 A/cm^2) and SU/SD.

Impact of FC-DLC on CO tolerance.

CEA has been measured impact of CO on MEA using steady state condition (constant current at 1 or 0.37 A/cm^2) or FC-DLC. The integration of the flow of H_2 used to feed the anode for FC-DLC test corresponding to the flow used at 0.37 A/cm^2 at stoichiometry 1.2 for steady state conditions.

For steady state current, it is possible to draw a graph with the horizontal axis representing the amount of CO entering the SC and the vertical axis representing the evolution of performance. The curve can be fitted with a polynomial curve.

For a similar amount of CO entering the single cell, the evolution of performance for FC-DLC test is lower than the evolution of performance for steady state condition. That shows the beneficial impact of current cycle on impurity tolerance.

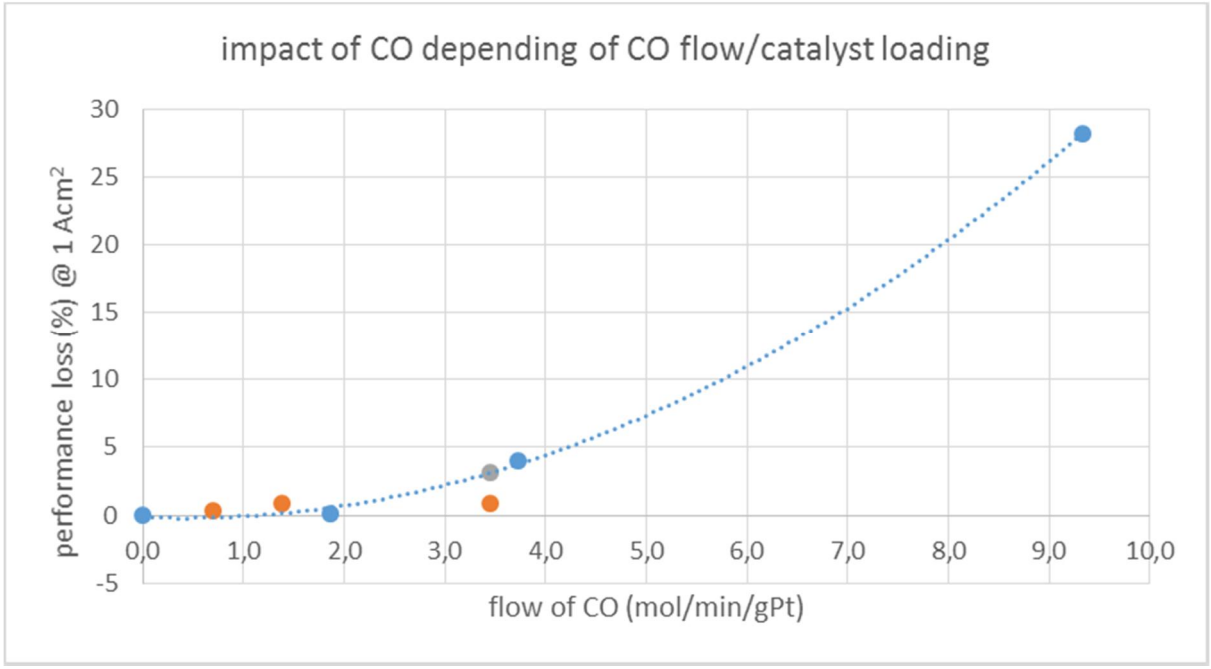


Figure 7: loss of performance as a function of the amount of CO entering the SC. Blue points are obtained by using 0, 1, 2 and 5 ppm CO at 1 A/cm^2, grey point by using 5 ppm CO at 0.37 A/cm^2, orang point by using 1,2 and 5 ppm CO/H_2 with FC-DLC (flow of H_2 corresponding to 0.37 A/cm^2 at stoichiometry 1.2).

JRC

In the WP discussions following the mid-term project review, JRC agreed with the partners on the tests to be conducted to best serve the risk model. JRC is currently in the process of ordering the various required gas mixtures with ^{13}CO. These mixtures include ^{13}CO (2000ppm in argon, 10dm^3 cylinder in 150bar), ^{13}CO (100 ppm in hydrogen, 50 dm^3 cylinder in 150bar) and $^{13}CO_2$ (200 ppm in hydrogen, 10 dm^3 cylinder in 150bar).

Also, the new test setup will be carried with support from VTT through visits by the coordinator in May 2016 and in August 2016.

Powercell Sweden

Powercell has delivered so far 5 stack in the HyCoRA project. These are listed in table 4.

Table 4. Powercell stack delivered to partners in HyCoRA project.

Serial no	Assembled	Model code	Cells	Customer
SN025	2015-05-07	FC-S2-10-H	10	VTT - Hycora
SN040	2015-09-04	FC-S2-10-H	10	VTT - Hycora
SN043	2015-09-14	FC-S2-10-H	10	CEA - Hycora
SN049	2015-10-15	FC-S2-5-H	5	JRC - HyCora
SN067	2016-04-07	FC-S2-10-H	10	VTT – HyCoRA

Polarization curves for the stacks with serial numbers SN049 and SN067 were recorded and distributed to the partners receiving the fuel cell stacks. Examples of polarization curves for SN067 are shown in Figure 8 and Figure 9.

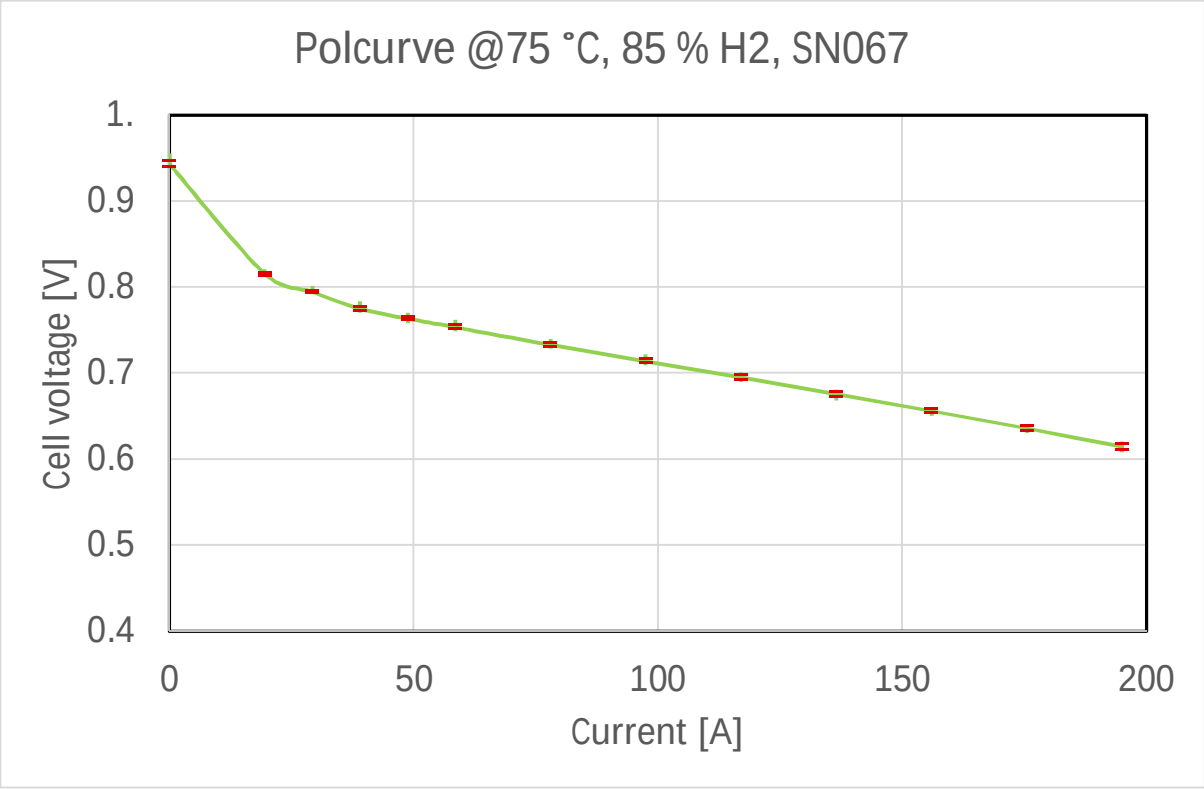


Figure 8. Reference polarization curve SN067, 75 °C

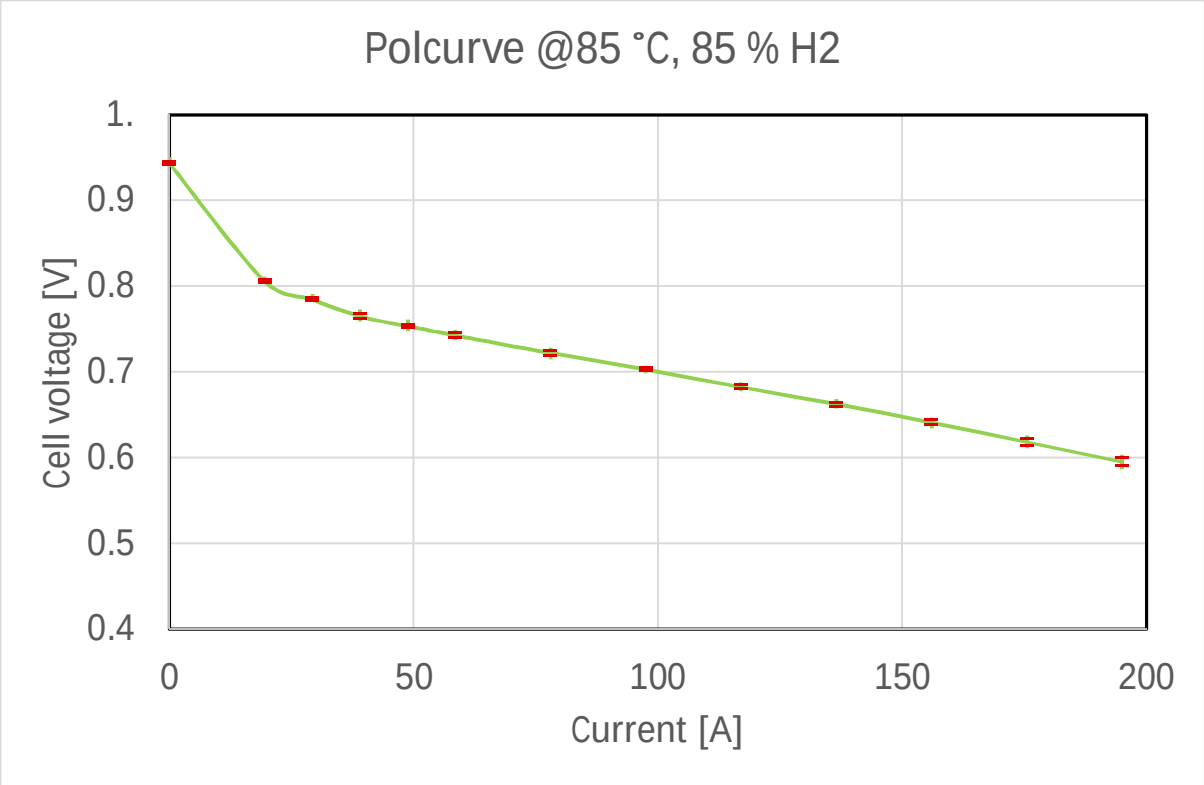


Figure 9. Reference polarization curve SN067, 85 °C

2.1.2 Study of retrievable and irreversible impurities (Task 1.4)

There have not been activities during the period M19-M24 in Task 1.4, excluding purchasing of necessary gases and components for the sulphur contamination measurements.

2.2 Development and validation of novel analytical methods for hydrogen quality assurance (WP2)

2.2.1 Development and validation of novel and traceable accurate methods for hydrogen purity analysis (Task 2.1)

VTT

Analysis of HCHO – literature and methods

A literature survey on the GC analysis of formaldehyde was carried out. Several types of columns including PLOT- (Poraplot-Q and Poraplot-U) and WCOT-columns with different polarities and phase thicknesses have been tested in the analysis of HCHO. The experiences could be summarised as:

- PLOT-columns: often lead to bad peak symmetry and irreproducible results, high temperature needed for symmetric peaks which results to bad separation
- WCOT-columns: Increasing polarity resulted in the loss of symmetry. Highly polar columns like DB-WAX absorbed formaldehyde completely[3].

Some plausible explanations for these observations are hydrogen bonding of the aldehydes to the surface of the stationary phase, interactions between the aldehydes and the stationary phase/column inner surface or interactions between the aldehydes and residual active sites on the stationary phase itself.

With polar columns increasing film thickness resulted to loss of symmetry, especially formaldehyde, however, with non-polar CP Sil 5 CB (100 % dimethyl siloxane) excellent resolution and good peak shape was obtained with 50 m, 0.32 mm, 5 µm column. At 35°C H_2, CO, CO_2 and HCHO were found to separate nicely.

Based on these findings two columns were selected for the analysis:

- Packed Carboxen-1000 (1/8”, 1,5 m)
- Capillary WCOT-column CP Sil 5 CB (50 m, 0.32 mm, 5 µm)

Helium was used as the carrier gas (20 ml/min for the packed column; 2 ml/min, split-ratio 10:1 for the capillary column).

As flame ionisation detector (FID) is not sensitive to formaldehyde a methanizer is used in front of the detector to convert oxidised products to methane. Three different methanizers were constructed at VTT and tested with an ordinary FID:

- “Conventional” methanizer using a Ni-catalyst (BASF 15 % Ni)
- A methanizer using a self-made ruthenium-based precious metal catalyst[4]

[3] J. Luong, L. Sieben and M. Fairhurst, Determination of low levels of formaldehyde and acetaldehyde by gas chromatography/flame ionization detection with a nickel catalyst, J. High Resol. Chromatogr. 19 (1996), 591.
[4] M. Colket, D. Naegeli, F. Dryer and l. Glassman, Flame Ionization Detection of Carbon Oxides and Hydrocarbon Oxygenates, Environ. Sci. & Techn. 8 (1974), 43.

- A methanizer using a commercial precious metal catalyst (Johnson Matthey Reformax)

Both methanizers using a precious metal catalyst performed quite similarly to the nickel catalyst. However the catalyst temperature could be lowered to 300-320 °C without affecting the complete conversion of CO and CO_2. However, that 100% conversion of HCHO to CH_4 could not be achieved with direct methanization using any of the catalysts or temperatures.

As one more alternative a fourth methanizer consisting of an oxidizing catalyst (Pd) and a hydrogenation catalyst (Ni) was constructed[5] . In the first step compounds eluting from the column are oxidized with synthetic air. Carbon oxides are then reduced to methane in the second step with hydrogen.

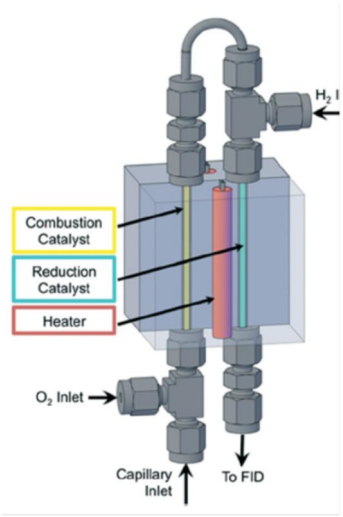


Figure 10. Oxidizer/methanizer combination[5].

Initially this catalyst worked well but the Pd-catalyst was coking fast. Accordingly, a Ni-based methanizer was selected for use with a FID.

As an alternative to a methanizer-FID a pulsed discharge photoionization detector can be used for the analysis of HCHO. VTT already tested the use of a VICI-Valco PD-PID in Helium-discharge mode (reported in 2nd Periodic Activity Report, Deliverable 6.3). It was observed that the sensitivity of the detector (about 5 ppm of HCHO) was not adequate. One of the reasons for this was that in He-discharge mode this detector is sensitive also to hydrogen causing detector saturation and loss of resolution making the analysis of impurities difficult.

According to literature[6] for formaldehyde, the Ar-PDPID is more sensitive as well as more selective than He-PDPID because N_2 or H_2 should not be detected. This will be tested at VTT in the next reporting period.

[5] S. Maduskar, A. Teixeira, A. Paulsen, C. Krumm, T. Mountziaris, W. Fa and P. Dauenhauer, Quantitative carbon detector (QCD) for calibration-free, high-resolution characterization of complex mixtures, Lab Chip, 15 (2015), 440.
[6] 4.J.G. Dojahn, W.E.Wentworth and S.D. Stearns, Characterization of Formaldehyde By Gas Chromatography Using Multiple Pulsed-Discharge Photoionization Detectors and a Flame Ionization Detector, J. Chromatog. Sci. 39 (2001), 55.

Results on decomposition of HCHO-standards

HCHO-standard cylinders NG656 and NG662 were calibrated at NPL on 5-7. April 2016 as 9,8 +/- 1,4 ppm HCHO in hydrogen. After delivered to VTT, the cylinders were analysed again about one month later. The analysis was done using an Agilent-5890 gas chromatograph equipped with a packed Carboxen-1000-column, Ni-catalyst and 2 ml injection. The results are listed in Table .

Table 5. Analysis of NPL HCHO-cylinders at VTT.

Sample cylinder	Analysis date	HCHO / ppm	CO / ppm
NG656	3.5.2016	8,5	1,2
NG622	13.5.2016	7,9	1,6

An example of a gas chromatograph (NG622) is shown in Figure 11.

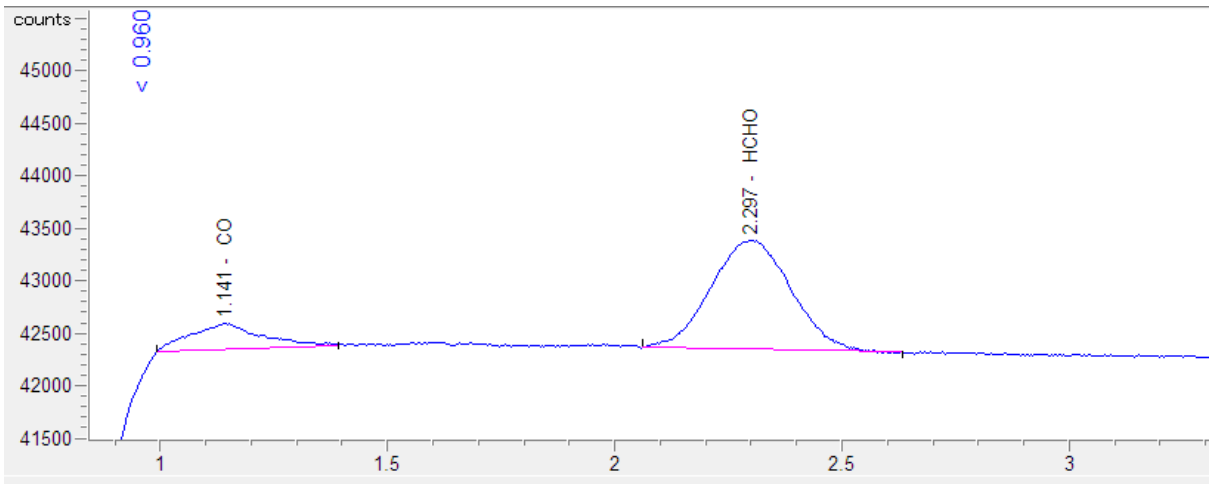


Figure 11. Decomposition of HCHO in hydrogen.

It was evident that HCHO had started to decompose in both sample cylinders. Similar behaviour was observed earlier with a 20 ppm HCOOH/N_2 calibration gas prepared by Air Liquide. The cylinder was analysed using a CP Sil 5 CB (50 m, 0.32 mm, 5 µm) column on 3.2.2016, see Figure .

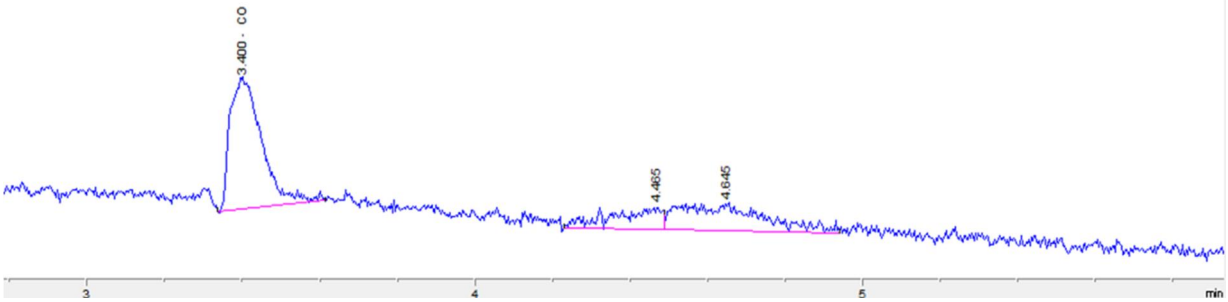


Figure 12. Decomposition of 20 ppm HCHO/N_2 in about 12 months.

The measured CO contents was 5.2 ppm whereas no sharp peak was found for free HCHO. It seems that HCHO had both decomposed and started to polymerize during storage.

The instability of hydrogen impurities must be taken into account when studying their poisoning effect. In addition to formaldehyde, VTT has observed earlier that also formic acid decomposes in the course of time, see Figure 13. The measured contents of CO and CO_2 were 3.8 ppm and 2.8 ppm, respectively.

The previous measurement with formaldehyde as contaminant (Deliverable 1.3, Figures 50-51) was performed 3 months after the gas mixture was received. Based on these new results, it can be concluded that in these earlier measurements, the level of formaldehyde in nitrogen mixture was most probably not at the original level and the mixture may have contained significant amount of CO.

It is now obvious that when the contaminant measurements are performed, the gas quality must be monitored frequently, if there is any suspicion that the studied contaminant is not stable in the gas mixture. It may also be, as in the case of formaldehyde, that the decomposition product has actually stronger poisoning effect than the studied component.

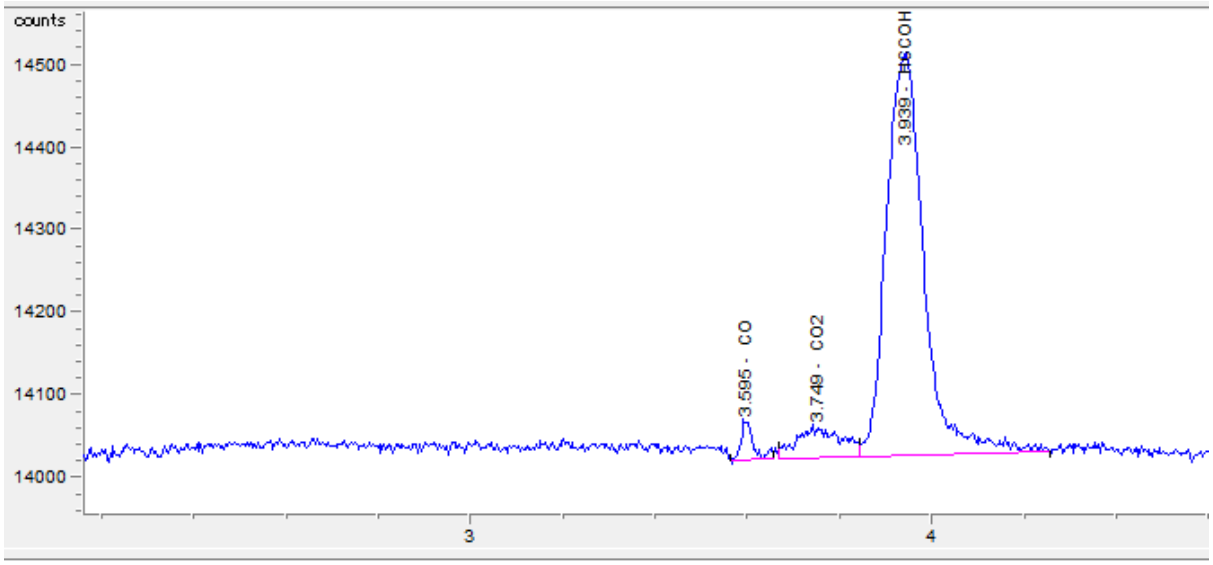


Figure 13. Decomposition of 100 ppm HCOOH/N_2 in about 12 months.

Both packed and capillary columns can be used for the analysis of HCHO in ppm levels. For acids capillary column provides a better peak shape. Packed columns allow for larger sampling volumes. VTT has just acquired a Tekmar-3000 series cryo-focusing device that will be used with a capillary column to increase sensitivity while maintaining good resolution.

SINTEF

SINTEF has in this period mainly focused on pre-concentration strategies for fuel quality control.

The results from the Pd-membrane pre-concentration effort, with instrumentation rented from Argonne National Laboratory, has previously been difficult to interpret. The reason for this has been that analysis of pre-concentrated samples analyzed by SINTEF has been compared with analytical results of the original HRS samples analyzed by Smart Chemistry.

The results indicated that pre-concentration was not consistent for all species and, after a meeting with Argonne National Laboratory held in Oslo, it was decided to pre-concentrate a known gas mixture, and at a higher concentration level in order to be able to evaluate the mass balances of relevant gas constituents.

The result from the pre-concentration is shown in Table 6.

Table 6. Pd-membrane pre-concentration of sample with factor 21. Analysis was performed with FTIR. N_2 analysis is pending (GC-TCD)

Gas species	Original	After concentration
CH_4	10 ppm	280 ±10 ppm
CO_2	10 ppm	125 ±5 ppm
CO	10 ppm	93 ±3 ppm
N_2	10 ppm	Not yet analyzed
Water	-	2-300 ppm

With a pre-concentration factor of 21, it appears that methane is formed from CO and CO_2. The following mechanisms are proposed[7]:

$$CO + 3H_2 = CH_4 + H_2O$$

$$CO_2 + 4H_2 = CH_4 + 2H_2O$$

Analysis of water of the pre-concentrated sample revealed a level between 2-300 ppm mol (water is difficult to assess). This supports the fact that these or similar reactions are likely to have taken place in the reactor.

A suspected intermediate in these reactions could be HCHO, but this species could not be found in the samples. The assumed sensitivity of analysis was low ppb level.

After pre-concentration, the Pd membrane was regenerated at elevated temperature while exposed to air. In addition to CO and CO_2, an unknown peak was observed. This signature is likely organic and maybe comprised of several constituents. The peak is shown in Figure 14.

[7] Ahmed, S., Lee, S.H.D and Papadias, D.D, Int. J. Hydrogen Energy 35 (2010) 12480-12490.

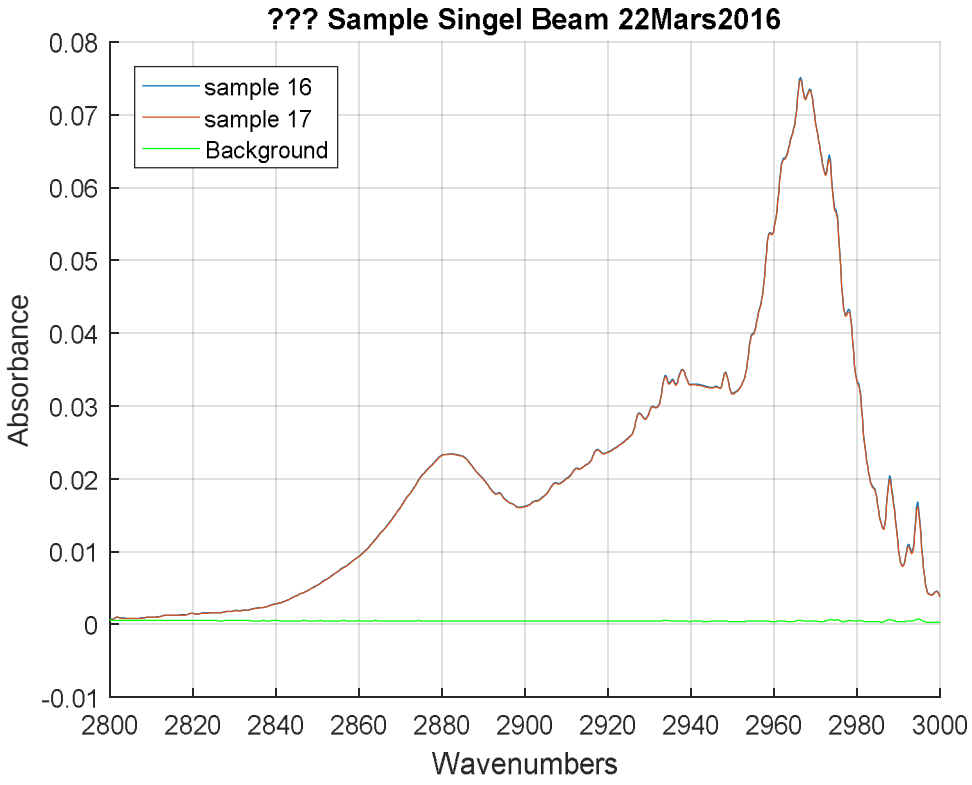


Figure 14 Unknown gas constituent from membrane regeneration.

Regeneration of membrane gives indication of interaction between gas phase constituents and with palladium possibly acting as a catalyst. Although coking reactions routes is possible, carbon in condensed form has not been observed:

$$CO + H_2 = C + H_2O$$

$$CO_2 + 2H_2 = C + 2H_2O$$

Further work would be to evaluate the stability of the gas with respect to palladium membrane temperature, exposure duration and pre-concentration factor.

SINTEF has tested two other approaches to pre-concentration of samples. Thermal adsorption applies a cold adsorbent followed by a rapid temperature increase. The sensitivity is typically in the ppt range. Analysis of samples from the first sampling campaign (HY-2, HY-3) revealed the presence of benzene, toluene, acetone. A signal assumed to be H_2S was also observed. As one of the major lines of H_2S, m/z 32, was interfered by air (O_2 also at m/z 32), the qualification is still not verified.

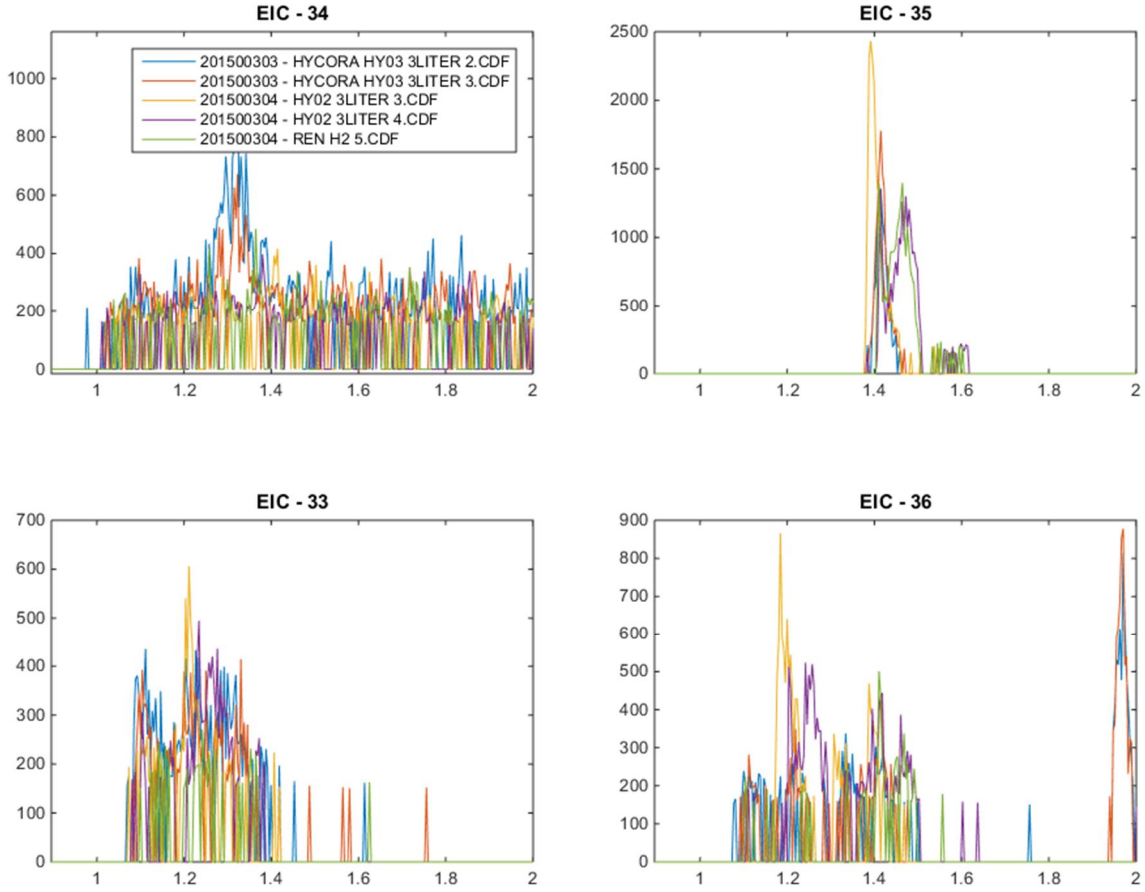


Figure 15. TD-GC-MS intensity vs time spectra for m/z 33-36.

The signal intensities for these masses are much higher for HY-3. From the Smart Chemistry analytical results, HY-3 and HY-2 contain 23 and 19 ppb mol H_2S respectively. The total S concentrations are however 98 and 51 ppt respectively, where COS and CS_2 add to the sulfur inventory.

Interestingly, SO_2 is found in these samples. Although a background value is observed due to a previous 100 ppm standard run, the signal is clearly distinguishable from the pure hydrogen. The relevant m/z for SO_2 is shown in Figure 16.

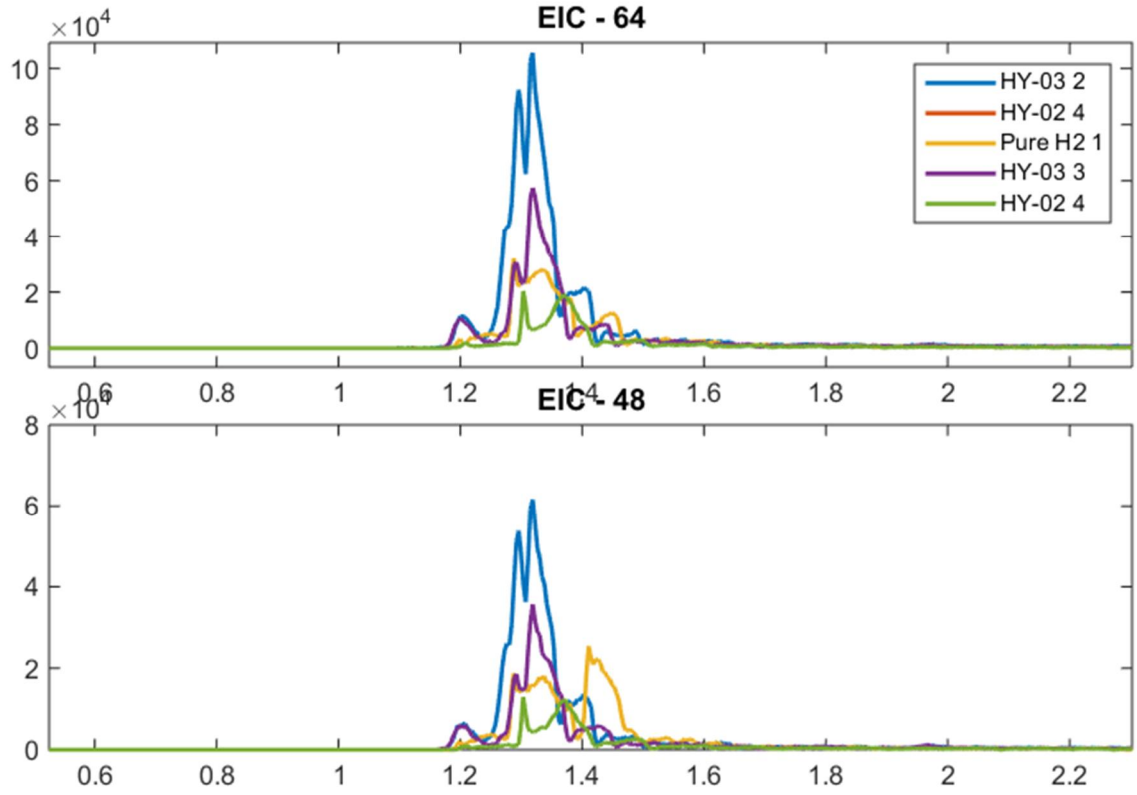


Figure 16. M/z signature for SO_2.

Interestingly, analysis by Smart Chemistry has not reported this gas species.

Another approach to pre-concetration is cryo-focusing. By application of liquid nitrogen, the sample was trapped onto an 1/8" silonite coated tube filled with glass beads. After trapping, the sample is rapidly heated before injection into the GC column.

As with the thermal desorption effort, the sensitivity of the cryo-focusing is very good. With the exception of acetone and H_2S, the same organic species and SO_2 are found by this method.

It is very interesting to observe that SO_2 is detected also in the sample HY-6 analysed with this strategy. As seen in Figure 17 the background signal from the carrier gas is very low thus indicating no history of SO_2 in the analyzer. A slight difference in elution time is observed between the samples, but the HP-5 column does not retain sulfur species well and so some variance could be observed.

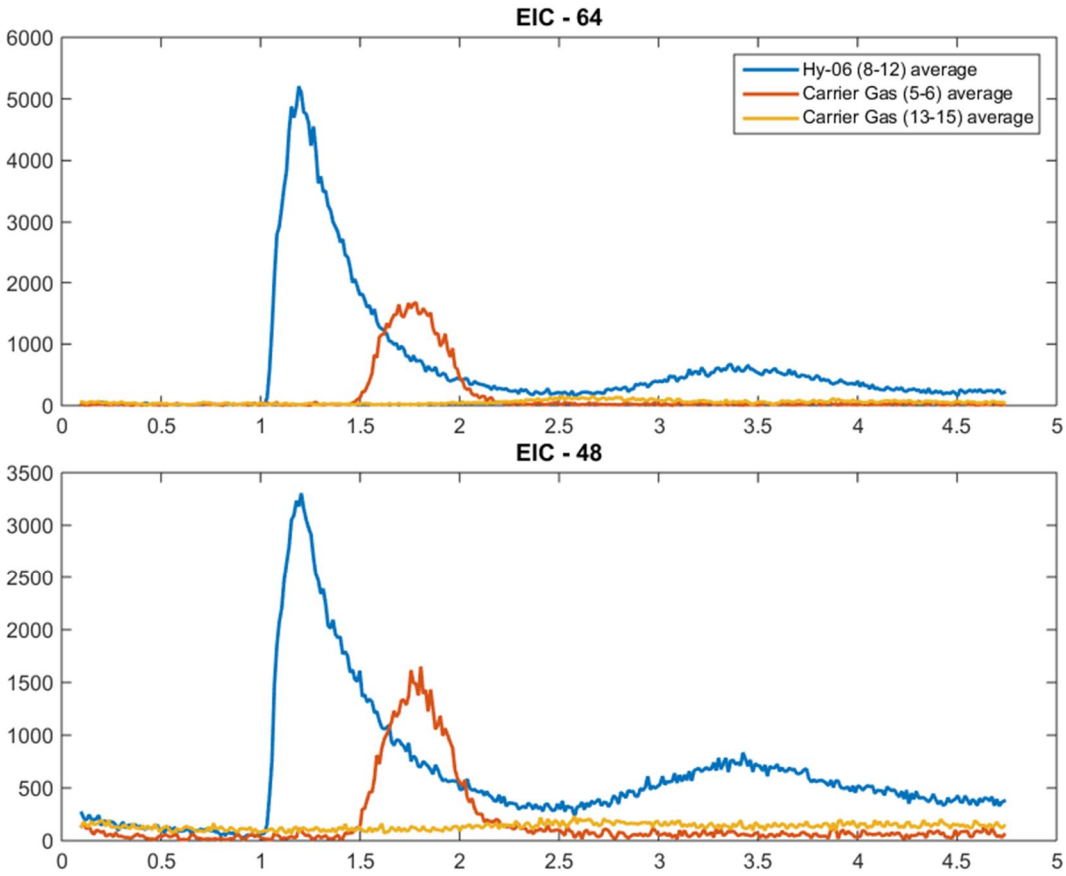


Figure 17. SO_2 signal from GC-MS by cryo-focusing preconcentration.

A summary of the results from pre-concentration is shown in Table 7.

Table 7. Pre-concentration efforts summary.

Sample	Strategy	Benzene	Toulene	Acetone	H_2S	SO_2
HY-2	TD	V	V	V	V	V
HY-3	TD	V	V	V	V	V
HY-6	Cryo	V	V	_	_	V

The work done so far gives indication of excellent sensitivity for the pre-concentration strategies conducted. The challenge appears to be the quantification at these low concentrations. Attempts to add standard gases at low levels will be conducted. Further, tuning of the analytical parameters will be done. A few actions are summarized:

- Switch to new GC-MSD system with higher MSD sensitivity
- Change to GASPRO column for better separation of gas species
- Change to hydrogen as carrier gas
- Tuning of thermal desorption parameteres (dT, trap / adsorbent)
- Cryo focusing without glass beads

SINTEF will purchase a commercial cryofocusing unit for installation on the new GC-MSD system. The automation of cooling and heating profiles should improve analytical performance.

Smart chemistry has determined that $C_4Cl_4F_6$ is present in all samples from Sampling Campaign 1 at levels between 13-28 ppbv. SINTEF has previously scanned for this species by FTIR and with pre-concentration strategies without success. An GC-ECD in operation was recently used to test for this Freon gas. From the detector response seen in Figure 18 there is no indication of Freon. The signal drop observed during elution is due to the He carrier gas and is not optimal. A new attempt on analysis will be performed if a switch to Hydrogen carrier gas is possible.

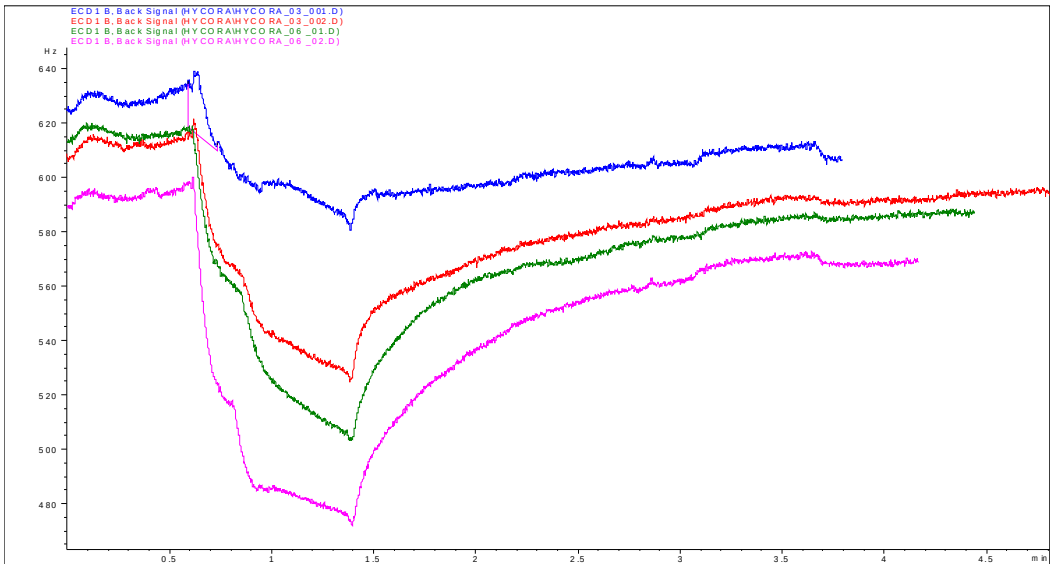
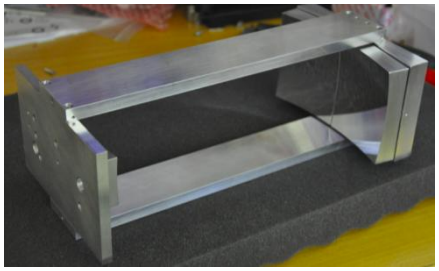


Figure 18. GC-ECD response for two HyCoRA samples (HY-3 and HY-6)

Protea

The novel design of FTIR gas cell mirrors have been manufactured, aligned and tested. The parts are with sub-contractors for specialist coating for measurement of low-concentration impurities in H2.



Protea's development mass spectrometer for this project has suffered two catastrophic failures since 01/16 requiring off-site repair another failure in electronics and is still we repaired. This was due, in part, to the prototyping of a constant temperature bake-out to remove background levels of H_2O to gain lowest possible detection.

2.2.2 Testing and validation of new analysers for measuring multiple impurities (Task 2.2)

PT

Data collection for mass spectrometer was to be completed, but failure in components has delayed this.

Validation of combined FTIR-MS system is still scheduled for 08-09/16 and we will be ready for outside lab tests from 10/16 onwards to end of the project.

2.3 Assessment of hydrogen quality variation in hydrogen refuelling stations (WP3)

The planning of the second measurement campaign has been in progress since the mid-term review. The focus of the sampling campaign has been to sample from newly commissioned refuelling stations. It is expected that this will provide information about contamination of fuel downstream hydrogen production and transportation where appropriate. Fuel quality data published suggests that Nitrogen, particulate and Freon contamination are more prominent for newly commissioned refuelling stations[8].

An initial plan for the campaign has been set up. This plan is shown in Table 8.

Table 8. Sampling campaign 2 tentative plan.

Date	City	Contact	Commissioned
02.06	Hamburg (Schnackenburgalle)	CEP	2014
02.06	Hamburg	CEP	< 2014
03.06	Helmond	Waterstofnet	2013
03.06	Flanders	Waterstofnet	2012
06.06	London	ITM Power	2016
06.06	Teddington (NPL)	ITM Power	2016
08.06	Kolding	H2Logic	2016
09.06	Aarhus	H2Logic	2016
10.06	Køge	H2Logic	2016
11.06	Gothenburg	Vätgas Sweden	2015

The sampling in Hamburg was chosen as to provide a comparison with the previous sampling campaign.

[8] J.P. Hsu, Int. J. Hydrogen Energy 37 (2012) 1770-1780.

The sampling in UK was strategically chosen. It is part of the HyCoRA workplan to have NPL analyse samples for total sulfur and total halogenates in order to have comparable analysis with the contract laboratory used (Smart Chemistry). NPL does not have sampling equipment so the stop at NPL would serve several purposes.

Since the setup of the plan, some questions regarding anonymization of data have arisen:

- ITM Power requires their HRS data to be anonymized. A request for alternatives in London is pending (Air Products, BOC and HyFive)

- Waterstofnet might require their data to be anonymized. Their HRS's are not recently commissioned so they should not be prioritized. The newly commissioned Air Liquide refuelling station in Zaventem City is pending a request to sample hydrogen and to publish data from analysis.

It appears that CEP in Germany has several good alternatives: refuelling stations in Karlsruhe, Stuttgart, Munich and Freiburg has opened in 2016. Discussion with CEP regarding sampling ongoing; CEP policy is good but there is a requirement of an empty FCHEV at every sampling location.

10 samples will be collected for this campaign. Samples will be split off for analysis by Smart Chemistry in the US. Additionally, SINTEF and NPL will analyse for selected impurity constituents for comparison.

Particulate sampling from 10 HRS will also be conducted. The particulate load and size will be analyzed by SINTEF. A portable glove box will be used for installation and removal of filters. In order to check for significance between using glove box and a clean-room, an agreement has been setup with the sampler manufacturer HYDAC to meet at at least one location in order to compare analytical results.

2.4 Risk model development (WP4)

2.4.1 Progress in the risk model development in M19-M24

Following the recommendations of the Mid-Term Review of better integration of the work in the different WPs, ***an internal risk assessment workshop*** was arranged in connection to M24 progress meeting 9th of March 2016. In the workshop, the existing quantitative risk model version for CO (see Figure 19) was presented and reviewed, and the needs regarding further development of the risk model and the input data were discussed. Based on this discussion, expectations for the quantitative data and the work to be carried out in the other WPs were listed and agreed so that these can be integrated in the individual WP plans.

Based on simulation results produced with the risk model, development needs on the initial risk model version have been identified together with some initial suggestions and plans for their resolution.

In addition, decision has been made to transfer the HyCoRA quantitative risk model to Matlab software environment. This is done in order to have sufficient computational power for the simulations, as well as to facilitate the future use and development of the risk model by interesting parties.

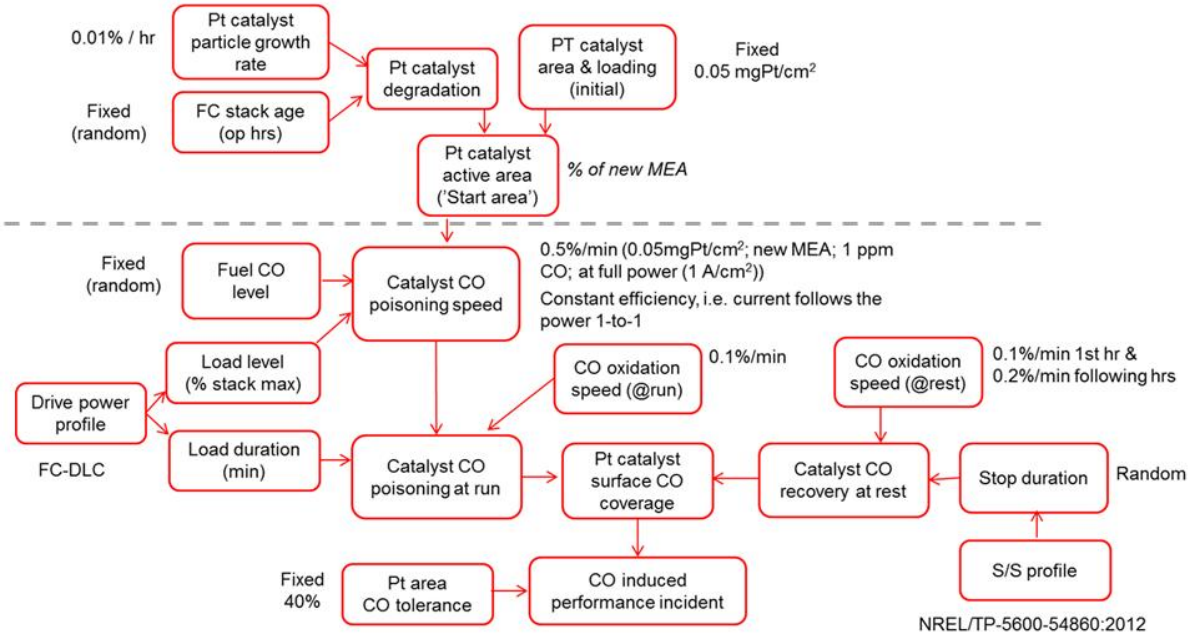


Figure 19. Impurity impact risk model; CO-only, version 1.0

2.4.2 Further guidance for the work in WP1, WP2 and WP3

The first version of quantitative risk model considers the impact of CO on the active catalyst surface area on anode taking into account the slow loss of electro-chemically active Pt surface area over time due to particle growth, and the active surface area getting covered by CO during vehicle use in a single day. To account for the lack of detailed knowledge, simplifying assumptions have been introduced regarding various model parameters (see Figure 19).

In the final year of the project the HyCoRA risk model will be developed further so that in the final risk model version:

- the slow loss of electro-chemically active Pt surface area also includes sulphur (S) adsorption and desorption and the effect of chlorine (Cl^-);
- the combined effects of CO and CO_2, CO and HCHO and CO and HCOOH are taken into account in the active surface area poisoning; and
- the most important initial assumptions and simplifications in the model are resolved.

In order to do this, quantitative data produced in WP1, WP2 and WP3 is needed on:

1. The CO cleaning effect due to the internal air bleed. This is of crucial importance for the bus application where fuel cell system is used for a long time with low average power and without stoppage. Without accurate data on the internal air bleed effect, the model cannot be used for buses and other fleet applications.
2. The mitigating effect of FC-DLC at the stack and miniature automotive system level. This may change the level of CO surface coverage needed for causing a critical drop in stack output voltage leading to an ‘incident’.
3. The CO cleaning effect of start and stop with real automotive gas volumes and operation during the stop. This may change radically the time needed for the CO oxidation from the surface.
4. The sensitivity of CO surface coverage for Pt area (aging). It may be that with aged catalyst lower surface coverage is needed for a critical voltage drop.
5. Quantitative information about the sulphur desorption after a sulphur poisoning incident.
6. The effect of chlorine on the Pt catalyst particle growth rate.

2.5 Dissemination, recommendations and communications (WP5)

JRC

Jointly with US DoE (USA), NOW (Germany) and NEDO (Japan) JRC organises the "4th International Workshop on Hydrogen Infrastructure & Transportation" aiming at generating an exchange of international experience and knowledge to discuss current challenges and develop new strategies to further integrate hydrogen and fuel cell technologies into the global energy portfolio with a special focus on the transportation sector. It is held on 24-25 May 2016 with a scope to accelerate the deployment of Hydrogen Refuelling Infrastructure by addressing among others the key issue of hydrogen fuel quality.

In this workshop, two presentations will be made on and with input from the HyCoRa project.

1) Hydrogen Fuelling,

2) Hydrogen Quality,

VTT

VTT has presented HyCoRA project and some results in "4th International Workshop on Hydrogen Infrastructure & Transportation" Hotel Zuiderduin – Egmond aan Zee, Netherlands, May 24 -25, 2016.

HyCoRA project was presented by poster in FCH JU program review days in Brussels 18.-19.11. 2015

CEA

CEA is organising a works shop on the 19-21 September: “Material Challenges for H2 and Fuel cell technologies”. A specific session dealing with the impact of pollutants and impurities is attached to HyCoRA.

CEA is participating to an international round robin test which organized by Tommy Rockward (LANL, US DoE) who is the chairman of the ISO TC197 WG 12.

Results obtained on H2S impact on single cell test in the frame of a visit of T. Rockward at CEA will be presented in the US DoE annual merit review (June 2016).

SINTEF

SINTEF has presented its work at the ISO TC 197 WG24 meeting in Torrance, CA (Nov 2015) but also at the following meeting in Sacramento (April 2016). SINTEF has worked with US and Japanese groups in order to provide an Annex I (Sampling Procedures and Hardware for Hydrogen Fuel Quality Analysis) to the ISO/CD 19980-1 standard for HRS.

SINTEF has also presented HyCoRA WP2 work for the ISO TC 158 JWG7 (also in Sacramento April 2016). The analytical methods and requirements for hydrogen quality control has been discussed.

2.6 Deviations and impact

2.6.1 VTT

VTT is slightly lagging behind the work schedule for WP1 accepted after the mid-term review. However, since all experimental equipment is working now well, the progress is rapid and the overall time schedule is not in danger.

2.6.2 CEA

The initially single cell test has been shifted to 2 months in order to proceed to the international round robin test. The impact of CO under EU-harmonized conditions will be start in June. No problematic deviation for the stack test.

2.6.3 JRC

The purchase of the ^{13}CO and $^{13}CO_2$ gas mixtures required in the stack testing in WP1 is still ongoing due to unexpected difficulties with the intended supplier. This will cause a several months delay for starting the measurements. This has caused a further delay for the work of JRC.

2.6.4 Protea

Protea is moving office locations in 06/16. This will have some effects on project due to the time to re-locate and install H2 calibration gas standards to new laboratory area.

2.6.5 Corrective actions proposed – 3 months extension for the project

Due to encountered difficulties to reach agreement with the intended supplier stemming from changes in the procedures to increases transparency the purchase of the ^{13}CO gas mixtures required in the stack testing is still ongoing. This has impacted on the continuation of the experimental activities at JRC by about the same period as requested in the project extension.

The 3 months extension would also help the other partners to complete their work with improved quality.

3. Project management during the period

3.1 Consortium management tasks and achievements

The deliverables due during the Period 1, Period 2 and Period 3 have been submitted and accepted.

Mid-term review meeting was held in Brussels 14.1.2016. After the mid-term review a number of recommendations and requirements for the continuation of the project were received form FCH JU. These have been addressed successfully.

The overall progress of the project has been monitored by bimonthly progress meetings. Work package leaders have had online meetings within WP members and/or with coordinator when considered necessary.

3.2 Problems which have occurred and envisaged solutions

The main issues of the project have been the slow progress of WP1 and poor integration of WP1-WP3 to WP4 risk model work. Management has been strengthened with coordinator visits to WP partners. As discussed in Chapter 2.4.1, an internal risk assessment workshop was arranged to improve the integration of WP1-WP3 work to WP4 risk model work

3.3 List of project meetings, dates and venues related to reporting period

Date	Place	Title
17.11. 2015	Brussels (Belgium)	3rd semi-annual project progress meeting
18.12.2015	on-line	M20 progress meeting
14.1.2016	Brussels (Belgium)	Mid-term review meeting
22.1.2016	on-line	WP1 M22 progress meeting
9-10.3. 2016	Espoo (Finland)	4th semi-annual project progress meeting

3.4 Project planning and status

Project planning is progressed as expected. The recommendations received from and after mid-term review meeting have been taken into account when project planning has been continued.

3.5 Impact of possible deviations from the planned milestones and deliverables

There were following deviations from the milestones and deliverables.

- D 2.2 was delayed by 2 months.
- D 6.5 (this report) was delayed by 2 months.

These will not affect the overall progress of the project.

3.6 Project website

The public web-site for the project is in http://hycora.eu/. The public deliverables have been added there when they have been accepted by project officer.