HyCoRA – Hydrogen Contaminant Risk Assessment
Grant agreement no: 621223
Interim progress report 4

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Summary

In this periodic activity report, the work progress of the fourth reporting period (M25-M30) of HyCoRA project is summarised. This report contains already some results for M31 and M32.

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 up to two too low. On the other hand, it seems that the main product of HCHO degradation is CO, which is a stronger poison than HCHO.

In WP1 CEA performed single cell and stack tests. A Power Cell stack has been tested to evaluate the contamination with low CO contents (1 or 2 ppm) under automotive conditions, including both stationary operation at fixed current load and Dynamic Load Cycles.

In WP2 - The work has continued according to DoW. The focus has been on pre-concentration strategies for fuel quality control. In addition, a major effort has been placed on the analysis of formaldehyde to support experimental activities in WP1.

In WP3 - A second HRS sampling campaign has been completed and hydrogen samples have been analysed. A third sampling campaign has been planned.

In WP4 The overall structure has been defined for HyCoRA model for assessing the impacts of hydrogen fuel quality control measures on the risk of degraded vehicle performance and fuel costs. The first version 1.0 of the risk model limited to consider CO as the only fuel contaminant, has been implemented in Matlab code and applied to assessment of a set of fuel quality control options to demonstrate its functioning.

In WP5 Several workshops were organised with relevance to topics addressed by this project. Also several standardisation meetings were held and presentations in relevant events were given with input from the partners.

The management WP6 has been executed as planned. Consortium has decided 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 25-30 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 5th 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 30 months of the project has been summarised mostly in deliverables D1.2, D1.3, D6.2, D6.3, D6.4 and D6.5. 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 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	un-known	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 tolerance and with CO	0.05	S2 production unit in system	1	D 1.3
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
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

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
VTT	HCHO (1.6 ppm) with 0.3 ppm CO - stack #2	Poisoning with 0.6 Acm^{-2}	0.05	S2 production unit in system	2	D 6.6 (this report)
VTT	CO (1.86 ppm)	Reference poisoning with 0.6 Acm^{-2}	0.05	S2 production unit in system	2	D 6.6 (this report)
VTT	H2 6.0	Reference with 0.6 Acm^{-2}	0.05	S2 production unit in system	1	D 6.6 (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
CEA	CO (1-2 ppm)	Constant current	0.05	Power Cell Stack in test station	~ 6	D 6.6 (this report)
CEA	CO (1-2 ppm)	FC-DLC (NEDC)	0.05	Power Cell Stack in test station	~ 3	D 6.6 (this report)
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)	Constant 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

2.1.1 Study of reversible impurities (Task 1.3)

VTT

During the period M29-M30 VTT has completed the studies of the effect of formaldehyde (HCHO) and has measured the anode electrochemical surface area (ECSA) for the S2 stacks used in the measurements.

HCHO measurements update

VTT 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 ppm HCHO in hydrogen.

Some first results of HCHO measurements were already presented in Deliverable 6.5, but since the repetition measurements were still ongoing at that time, more complete reporting is done in the present deliverable, D6.6. Further analysis is still ongoing and the results will be published in the final report and in a peer-review journal paper.

The stack measurements were performed with 10-cell Powercell S2 stacks, equipped with low anode loading MEA (0.05 mgPtcm-2). The experimental set-up has been reported in Deliverable 1.2. The operational parameters of the tests are presented in Table 2. . The tests were performed at steady state operation, with current of 0,6 A /cm^2 (117 A) drawn.

Two cylinders, of 10 l and 100 bar each, and containing 10 ppm HCHO in H2 were received from NPL. The first cylinder (#1) was utilized in measurements with aged stack, and the second cylinder (#2) with a new stack, that had not been operated prior to these measurements. Both of the stacks were Powercell's 10-cell S2 stacks, which have MEA area of 195 cm^2 in one cell.

Two runs were conducted with each stack; a 4-hour and an approx. 3-hour test run, with about 1.6 ppm HCHO (and 0.3 ppm CO) and 0.6 Acm^{-2}, Table . With each stack, the HCHO in H2 gas was utilized from one gas cylinder (referred as "green" and "pink" cylinders), therefore the length of the repetition measurements varied slightly. The fuel utilisation was 99.5-99.6%, leading to contaminant enrichment factor of 200-250. Before and after two consequent HCHO poisoning measurements, reference measurements with 1,86 ppm CO in H2 were conducted. In addition, a pure H2 reference measurement was conducted with stack #2 after all the other measurements.

From the HCHO poisoning measurements, Figure 1 a very low poisoning effect of HCHO, approx. 10 mV average voltage drop can be seen, which is in agreement with the results from earlier measurements using HCHO in H2. Approx. 10% of HCHO was found in the anode purge water that was collected during the measurements. A large methane (CH4) increase in the anode recirculation loop seem to refer that methanation of HCHO occurs in situ in anode recirculation loop. As discussed in Chapter 2.2.1 HCHO decomposes, but there is still some uncertainty whether CO is one of decomposition products.

Table 2. Experimental conditions for the HCHO poisoning and reference measurements with S2 stack

Temperatures		*Anode gas feed*		*Cathode gas feed*	
Stack inlet	80 °C	Fuel utilization	99.5-99.6%	Oxidant utilization	40 %
Stack outlet	82 °C				
		H2 flow rate 1 H2 flow rate 2 (with HCHO)	8.11 l·min^{-1} 6.49 l·min^{-1}	 Air flow rate	 49,8 l·min^{-1}
Purge f	394 s	Inlet pressure	21 kPa(g)	Inlet pressure	14 kPa(g)
Purge time	200 ms	Inlet dew point	64 °C	Inlet dew point	69-70 °C
		Inlet temperature	83 °C	Inlet temperature	73-75 °C
Current density	0,6 A·cm^{-2}	Recirc.rate	15-18 l·min^{-1}		
		HCHO in H2 measurements			
		HCHO in feed	2.0 ppm		
		Impurity flow rate HCHO in H2	 1.62 l·min^{-1}		
		H2 source purity	6.0		
		HCHO in H2 mixture	10 ppm		
		CO in H2 ref measurements			
		CO in feed	1,86 ppm		
		Impurity flow rate	8.11 l·min^{-1}		
		H2 source purity	6.0		
		CO in H2 mixture	1,86 ppm		
		pure H2 ref measurement			
		H2 source purity	6.0		

Table 3. HCHO in H2 measurement.

Test set #	Measurement	Date	Gas bottle	Duration of test [HH:mm]	Water collected [ml]	[ml]	Water analysis [mg/l]
1	1.86 ppm CO reference 1	6.5.2016		1:07	-	-	-
1	2 ppm HCHO 1	9.5.2016	green	4:00	12	± 1	38,4
1	2 ppm HCHO 2	10.5.2016	green	3:00	9	± 1	36,4
1	1.86 ppm CO reference 2	12.5.2016		1:11	-	-	-
2	1.86 CO ref 1	26.5.2016		1:30	-	-	-
2	2 ppm HCHO 1	27.5.2016	pink	4:00	10	± 1	108,9
2	2 ppm HCHO 2	2.6.2016	pink	2:37	5,5	± 0,5	121,4
2	1.86 ppm CO ref2	7.6.2016		1:12	-	-	-
2	H2 6.0 ref	8.6.2016		4:00	-	-	-

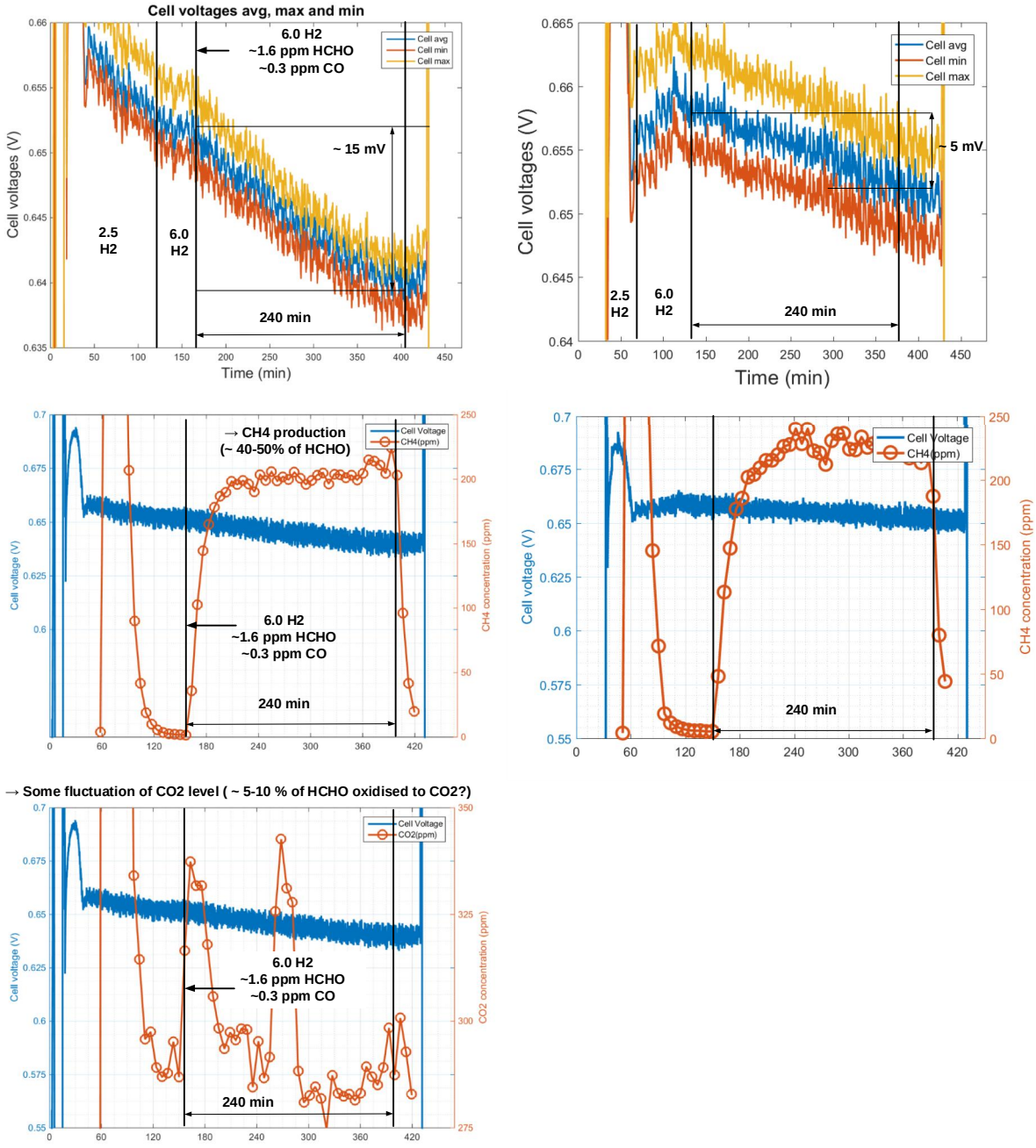


Figure 1. HCHO poisoning measurements #1 (4 hours) - cylinder #1 with an aged stack on left and cylinder #2 with a new stack on right. Cell voltages of average, max and min cells above (moving average of 18 points), CH_4 concentration in the middle, and CO_2 concentration below.

In the reference poisoning measurements with CO (1.86 ppm), Figure 2, a 50-mV drop in average cell voltage took place 55-72 minutes. With pure H2 6.0, the voltage drop due to reversible degradation was noted to be ~12 mV during a 5-hour measurement, Figure . The reference measurement with pure H2 was conducted with a new stack, stack #2 (SN040).

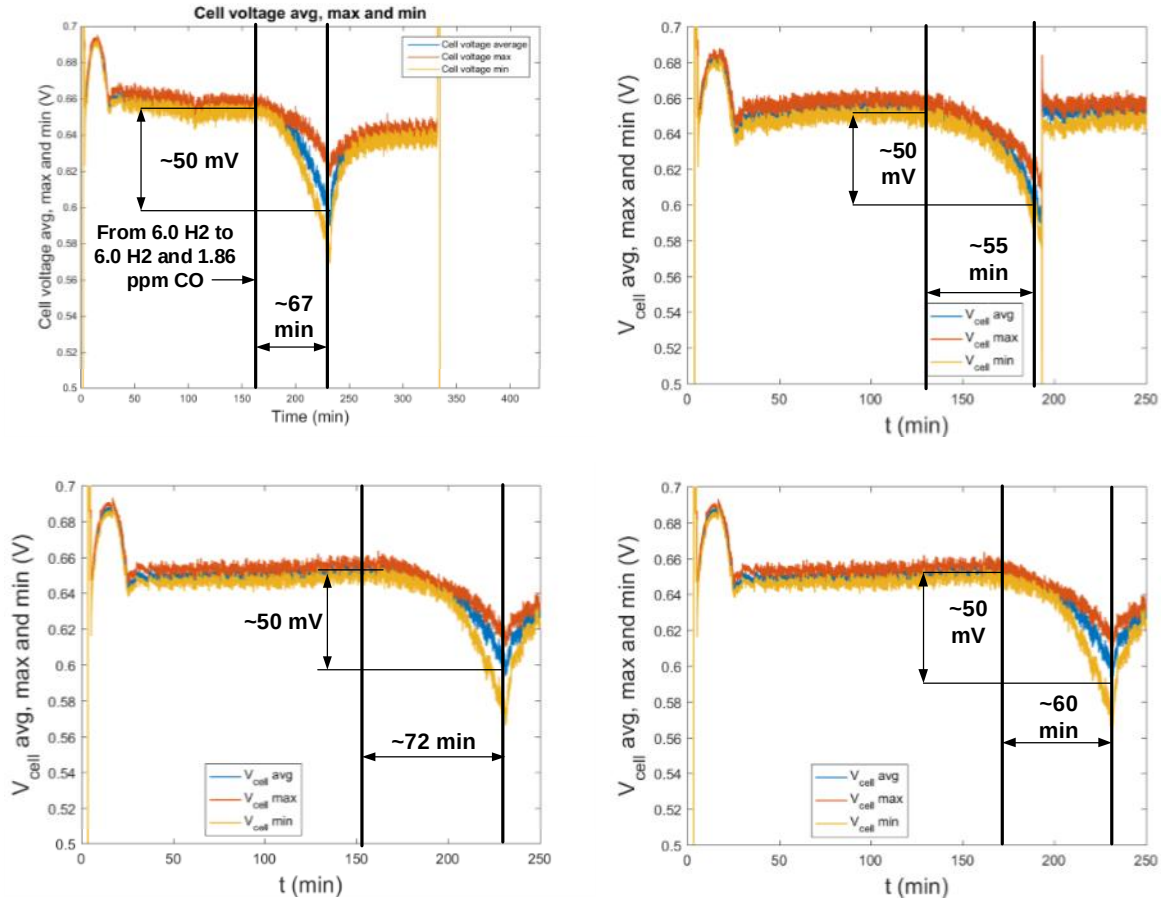


Figure 3. Reference poisonings with 1,86 ppm CO - before HCHO poisoning (figures above) and after poisoning (figures below), cylinders #1 (on left) and #2 (on right).

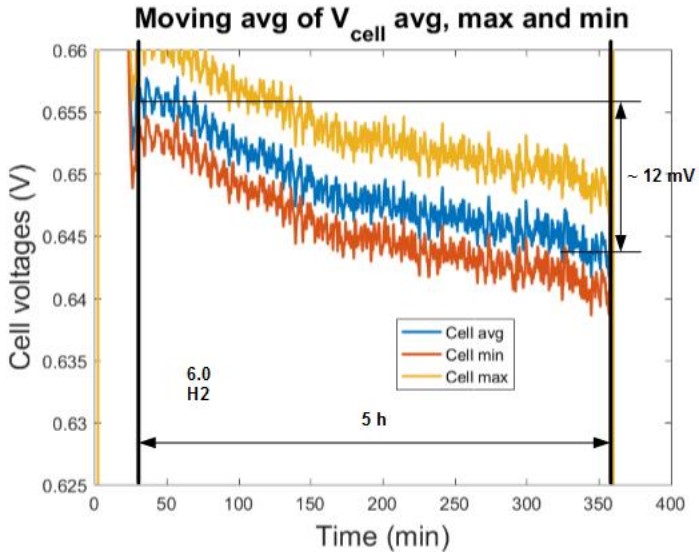


Figure 3. Voltage drop of 4-hour measurement (approx. 12 mV) - cylinder #2, new stack.

Based on these results and results conducted earlier with HCHO in N_2 (reported in Deliverable 1.3), the limit 0.01 ppm for formaldehyde in ISO 14687-2:2012 seems to be at least two orders of magnitude too low.

Anode Pt area measurements

The anode electrochemical surface area (ECSA) measurements were performed by a Master's thesis worker Florian Waeber in July and August 2016[1]. Measurements have been conducted in Greenlight G60 test station that is equipped with anode recirculation loop (reported in Deliverable 1.2. and in Master's Thesis of Waeber), and for two Powercell S2 stacks. The stacks were the same stacks, which were used for the HCHO measurements presented within this chapter above. Stack #1 was used approx. for a one year, more than hundred hours, and stack #2 only approx. 30 hours prior to the ECSA measurements.

The ECSA measurements were conducted according to work of Brightman et al.[2] and Lee et al.[3], but to PEMFC anode (instead of cathode). The measurements of anode required some adaptations to be done for the method, namely

- The potential acquisition frequency was increased from 1 Hz to 5 Hz, and
- The H_2 concentration on the anode side was decreased from 10% to 2 and 5% during the measurement.

The method is depicted in Figure 4 and described in more detail in Master's Thesis of Waeber.

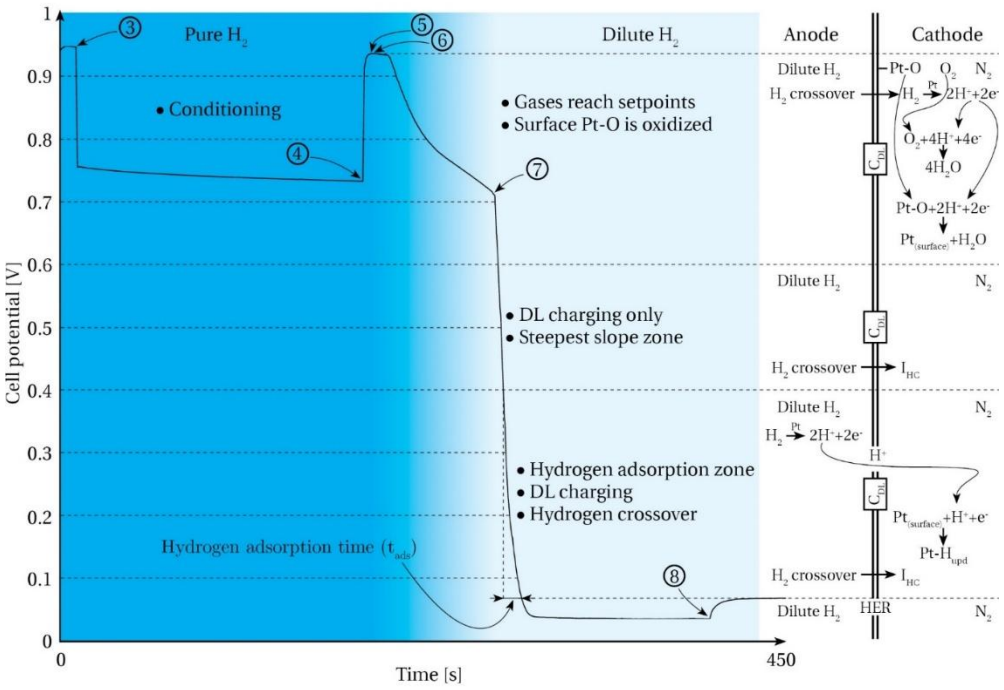


Figure 4. Adapted methodology explained with a typical experiment potential-time curve. The phenomena occurring in the different potential ranges are summarized in figure on the right. Steps in procedure: 3. Load connected 4. Load 0 A, load disconnected 5. Anode gas composition set to desired H2 concentration in N2 6. Cathode gas switched from air to N2 7. Load connected and set to desired discharge current I_{GA} 8. Load disconnected

[1] Florian Waeber. Setup and testing of an adapted galvanostatic method for measuring the electrochemically active surface area of PEMFC stacks' anodes. Master's Thesis, 2016.
[2] E. Brightman, G. Hinds, and R. O'Malley. In situ measurement of active catalyst surface area in fuel cell stacks. *Journal of Power Sources*, 242:244–254, November 2013.
[3] K.-S. Lee et al. Development of a galvanostatic analysis technique as an in-situ diagnostic tool for pemfc single cells and stacks. *International Journal of Hydrogen Energy*, 37(7):5891–5900, 2012.

The measured surface roughness factors are shown in Figure 5 and in Table 3. Two interesting observations can be done from these measurements.

Firstly, roughness factors are around 12 for older stack and 10 for newer stack. This indicates either increase of the ECSA during the measurements for the newer stack or poisoning of the catalyst for the older stack due to corrosion of recirculation pump components. The recirculation pump failed shortly after these measurements with stack #2 and it is possible that corrosion products already affected these measurements.

The second interesting observation is low catalyst area values measured for anodes. Pt loading should be 0.05 $mgcm^{-2}$. With a typical ESCA value of 50 m^2/g_{Pt} a roughness factor should be 25. The measured roughness factors for cathode are 120-130 and these are reasonable assuming a typical loading of 0.3 mg_{Pt}/cm^2. The cathode loading and catalyst type are not known here.

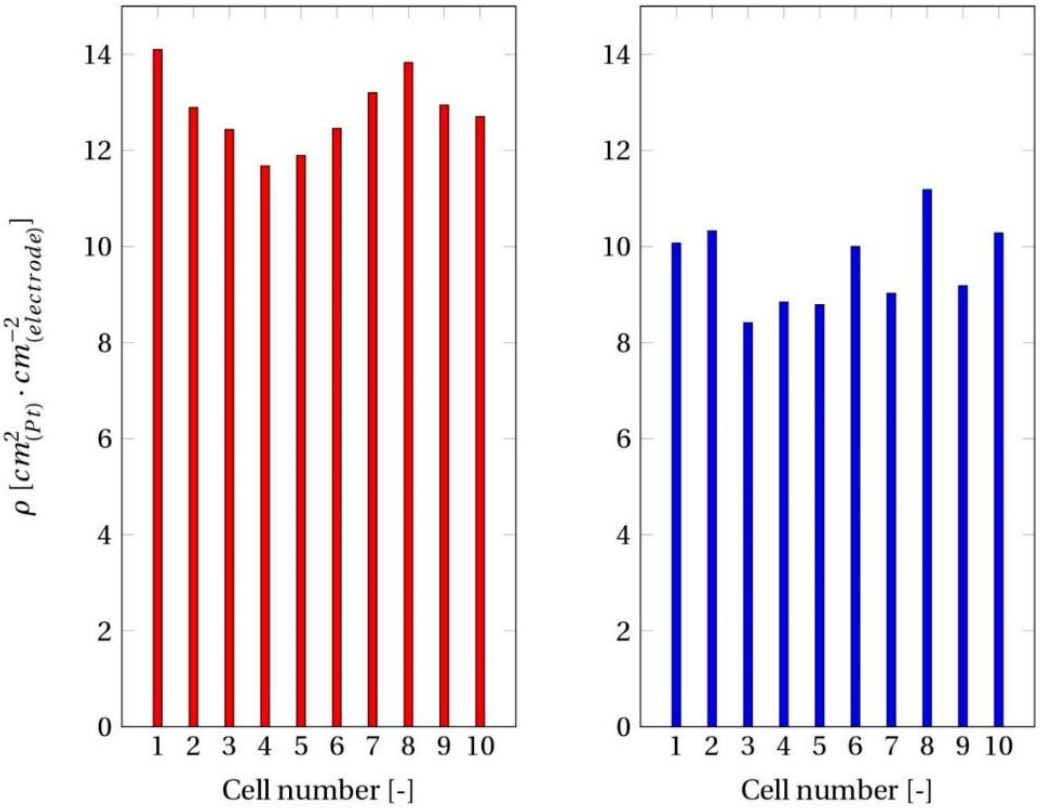


Figure 5. Roughness factors for stacks #1 and #2

Table 3. ECSA measurement results

Experiment	1	2	3	Average
Stack 1 anode ρ $[cm^2_{(Pt)} \cdot cm^2_{(electrode)}]$	13.0941	12.4601	12.8803	12.8115
Stack 2 anode ρ $[cm^2_{(Pt)} \cdot cm^2_{(electrode)}]$	9.7247	9.4466	9.6538	9.6084
Stack 1 anode average cell capacitance $[F]$	1.4606	1.5131	1.469	1.4809
Stack 2 anode average cell capacitance $[F]$	1.6727	1.5873	1.5951	1.6184
Stack 1 cathode ρ $[cm^2_{(Pt)} \cdot cm^2_{(electrode)}]$	126.5608	134.439	132.8022	131.2673
Stack 2 cathode ρ $[cm^2_{(Pt)} \cdot cm^2_{(electrode)}]$	123.8766	129.3536	127.5483	126.9262
Stack 1 cathode average cell capacitance $[F]$	6.8572	5.9586	5.9157	6.2438
Stack 2 cathode average cell capacitance $[F]$	5.8722	6.1687	5.8673	5.9694
Stack 1 average membrane H_2 crossover $[A]$	0.4205	0.3536	0.3459	0.3733
Stack 2 average membrane H_2 crossover $[A]$	0.3031	0.3392	0.3099	0.3174

CEA

Single cell:

CEA has been studying the impact of CO with 0.2 mg_{Pt}/cm^2 at the anode (homemade MEA from CEA) and low anode loading 0.05 mg_{Pt}/cm^2 (MEA from ion power. The results show a big dependence of eth impact of CO to the loading of the MEA and the anode.

In the last period of the project, CEA has prepared low loading MEA (anode: 0.05 mg_{Pt}/cm^2, cathode: 0.25 mg_{Pt}/cm^2). Electrochemical active surface area (ECSA has been measured at the BoT. The impact of 2 ppm CO has been quantified under steady state mode. Those date are very interesting to correlate the impact of Vs the anode ECSA. The next step is to do the same with aged MEA and thus feed the modelling task in WP4.

Stack test

At stack level, it has been shown that the test made using MEA with high loading at the anode (0.2 mg_{pt}/cm^2) does not enhanced the impact of CO enough to draw strong conclusion.

A SoA stack has thus been used in since July 2016. The impact of 2 ppm CO is significant under steady state current. Both anodic and cathodic ECSA has been measured.

Gas analyses

A CO and CO_2 analyser has been purchased by CEA. The calibration is ongoing in order to test tens of PPB only.

At stack level, tests have been conducted on the following PowerCell stack: SN043 / FC-S2-10-H, 10 cells of 195 cm^2.

Objectives were to evaluate under Hycora automotive conditions previously defined (80°C, 1.5 bars, 50/50%RH, st1.5/2 for fuel and Air).

Tests have been conducted starting the fuel cell under pure hydrogen for at least 1 hour, then adding 1 or 2 ppm of CO. Each test has been conducted on the short term during the working day.

The fuel provided to the stack is a mixture from 2 lines: one fed with pure H2 and the other fed with a CO containing fuel. For the latter, we first used a bottle with 2000 ppm of CO in CH4; then and mainly a bottle of % H2, %CO2, %CH4 and 1%CO.

After the contamination step, polarization curves or cyclic voltammograms have been recorded to evaluate the performance, the active area of the catalysts or to check the adsorption of CO onto the anode catalyst just after contamination.

These daily tests have been conducted at fixed load (0.5 A/cm²) or following Dynamic Load Cycles (max current density at 0.8 A/cm²).

The overall experiment including different the contamination tests is given below with the evolution of the average stack voltage, seen in Figures 6.

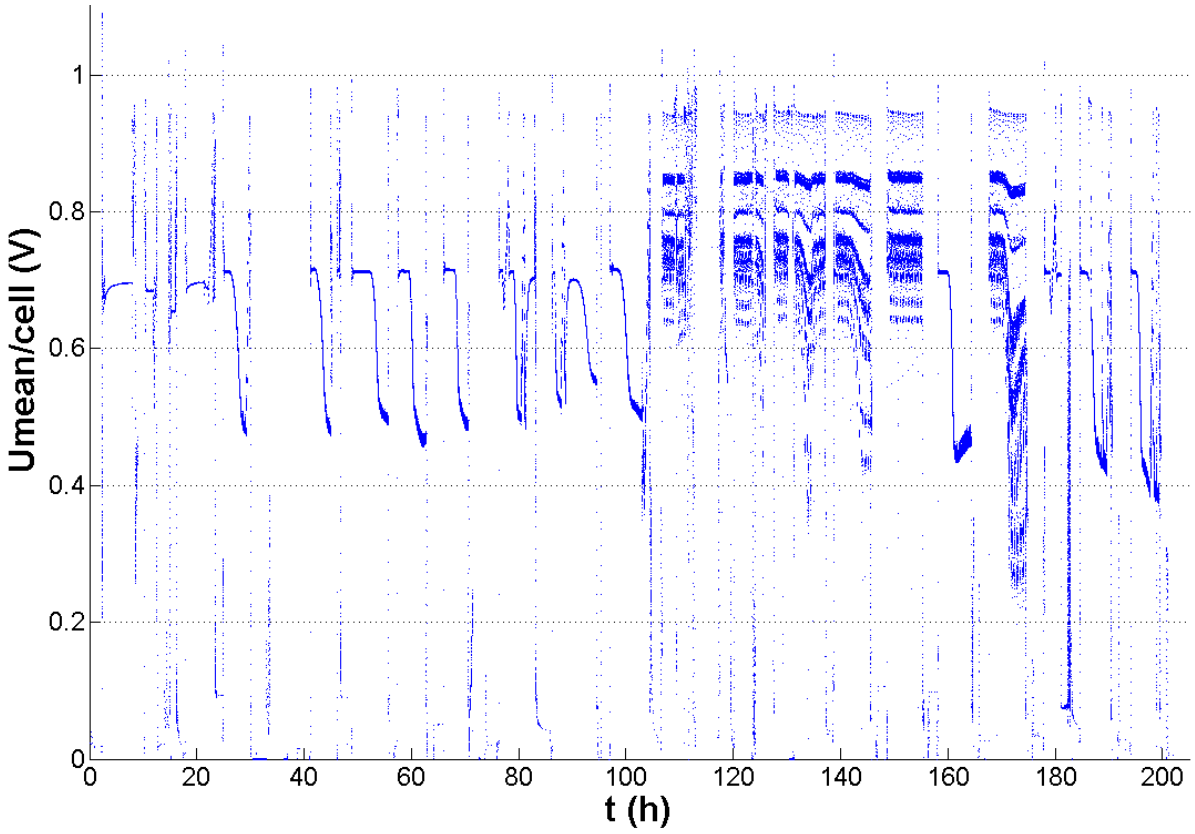


Figure 6. The overall experiment.

Polarisation curves have been recorded under pure H2 or with some CO at different moments of the whole experiment.

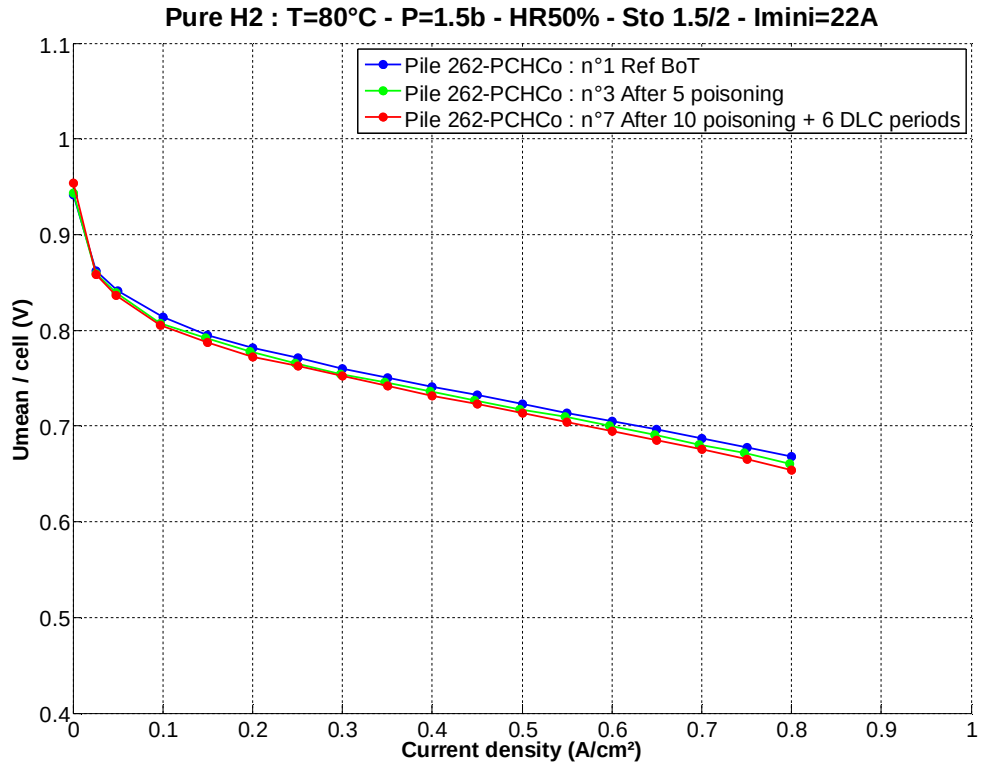


Figure 7. Polarisation curves without CO.

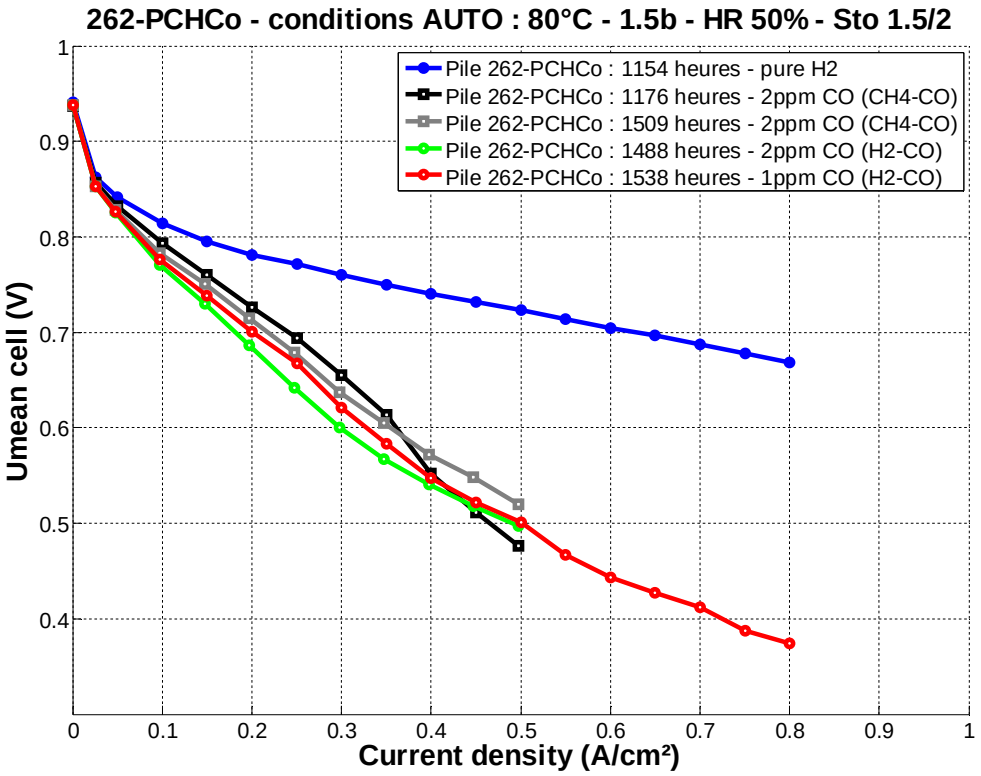
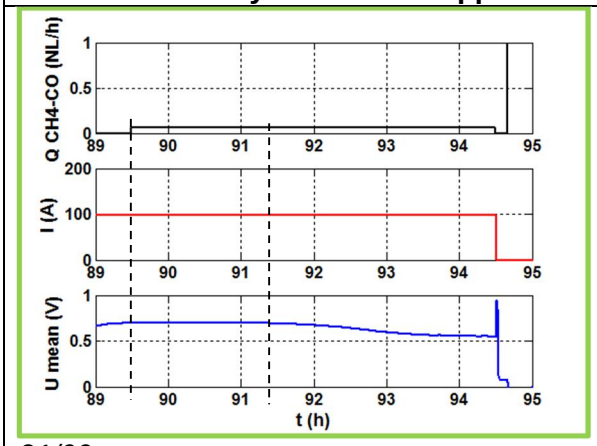
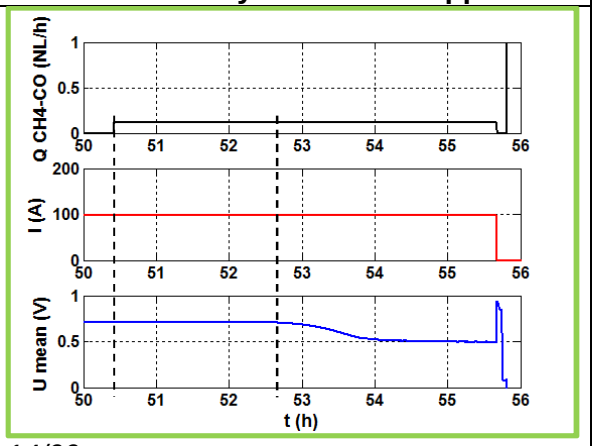


Figure 8. Polarisation curves with CO.

Concerning the daily contamination tests, the main results when adding 2 or 1 ppm of CO in the fuel are shown in Figure 9. On the figures, parameters are the contaminated fuel flow rate to show the starting of contamination, the current (98 A for 0.5 A/cm²), and the average cell voltage.

Note: for the flow rate of the contaminated fuel, the name of the parameter on the test bench is “Q CH4-CO” but the fuel here is the mixture of H2, CO2, CH4 and CO described earlier.

Contamination by addition of 1 ppm CO	**Contamination by addition of 2 ppm CO**
	
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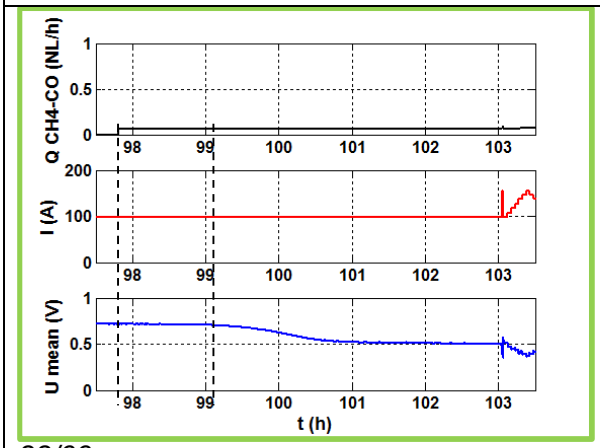	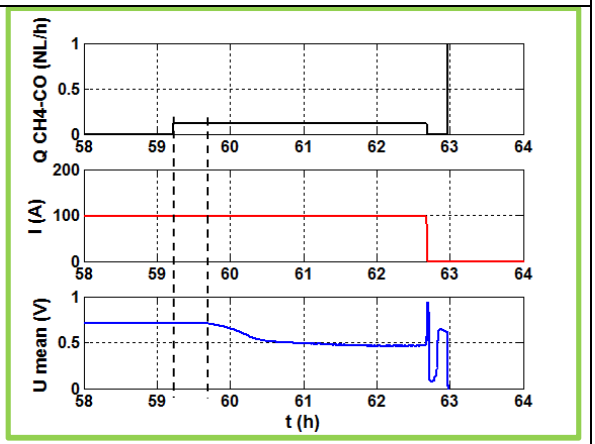
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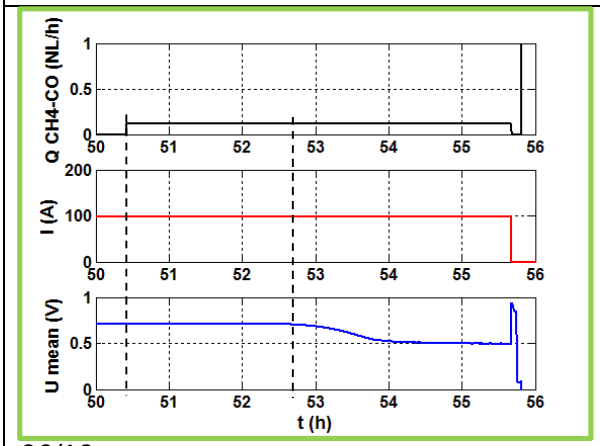	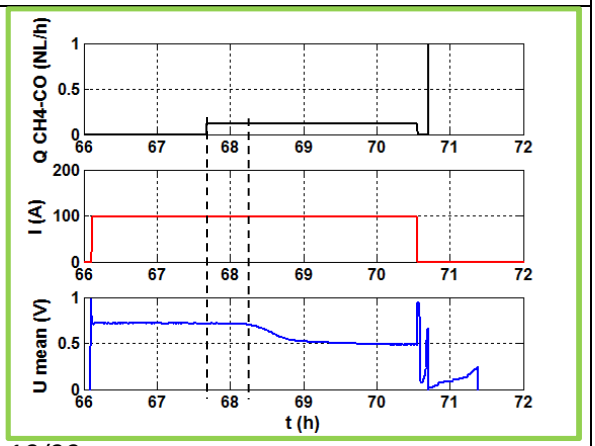
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Figure 9. The daily contamination tests.

Contamination tests have been performed several times with 1 or 2 ppm of CO.

The shortest duration before voltage decrease (~1/2 hour) was observed with 1 ppm. However, time before performance loss was between ½ hour and more than 2 hours for the 2 CO contents. Differences observed for 1 content could be due to the tests or analyses conducted just before the contamination, like time spend under pure hydrogen or recording of cyclic voltammograms. But most often the stack was stopped during at least one night before starting the contamination test and direct correlation with time under pure H2 or electrochemical diagnostic could not be demonstrated.

After stabilisation, average cell voltage at 0.5A/cm² had decreased from 0.71 V to 0.55 or 0.50 with 1 or 2 pm of CO respectively.

In spite of these low voltage reached under H2 + CO, considering the kinetics and the short periods under current densities higher than 0.5 A/cm², dynamic load cycles have been applied with 0.8 A/cm² selected as the maximum current density.

First results are presented below for H2 + 1ppm CO, pure H2 and H2 + 2ppm CO. For each test, 19 or 20 cycles (of 20 minutes each) have been applied, starting with 3 or 5 cycles under pure H2 before CO addition.

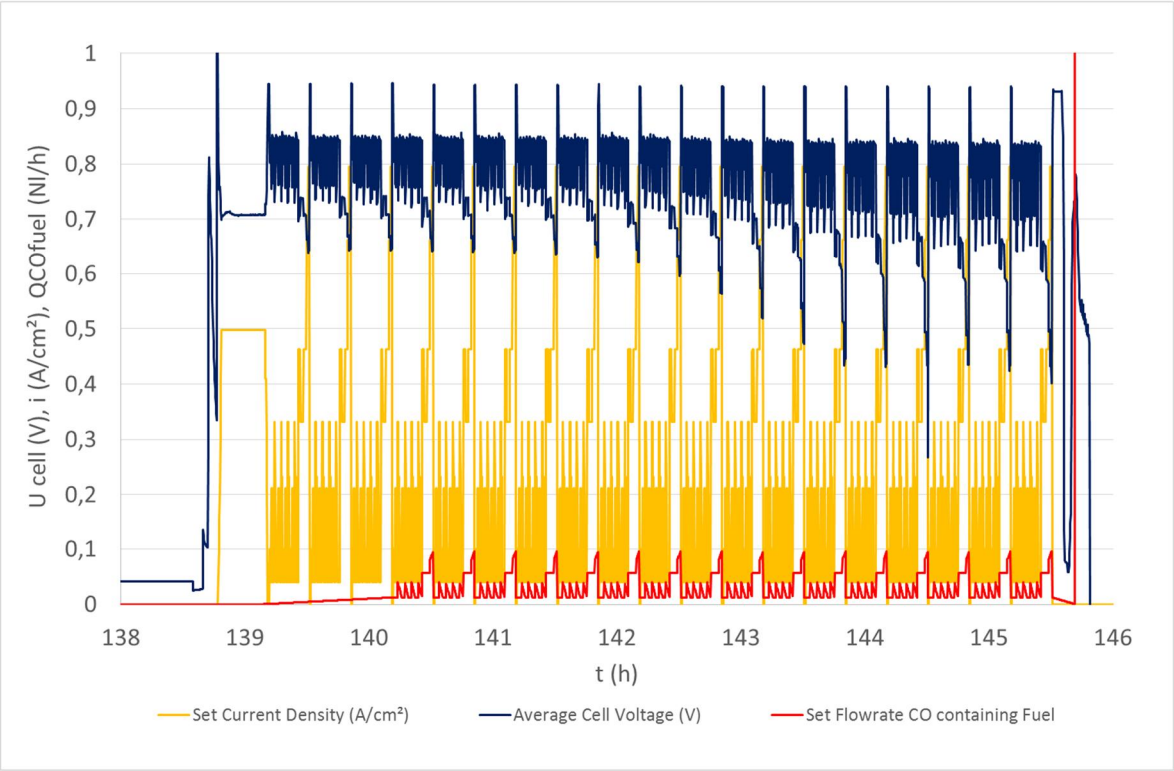

Figure 10. average cell voltage during dynamic load cycles under H2 + 1 ppm CO.

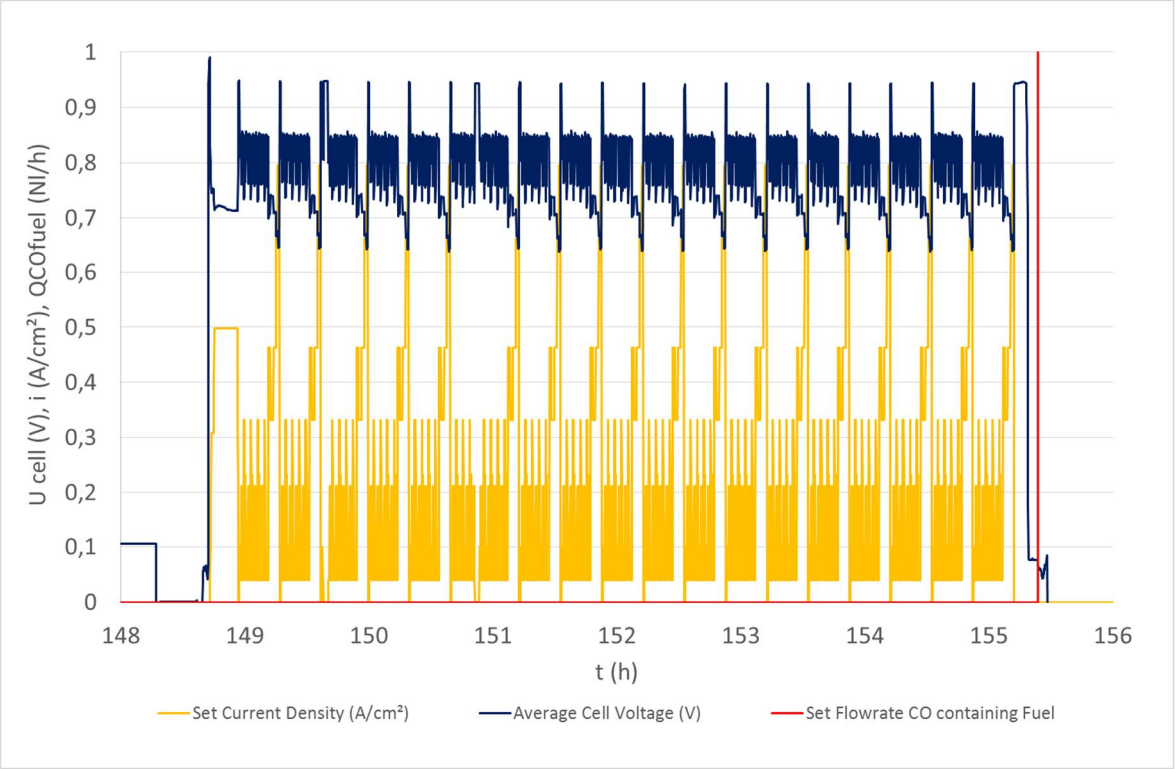

Figure 11. average cell voltage during dynamic load cycles under pure H2.

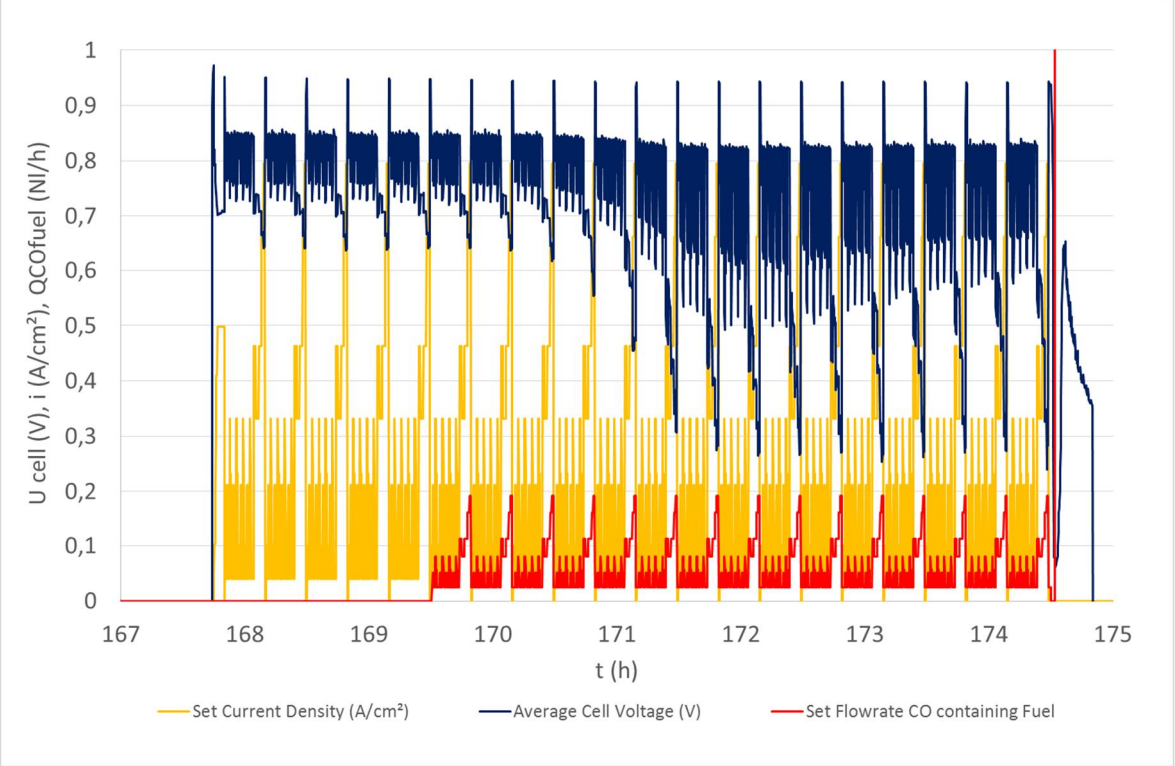

Figure 12. average cell voltage during dynamic load cycles under H2 + 2 ppm CO.

Voltages started to decrease after 7 cycles and 4 cycles for respectively 1 and 2 ppm of CO. Minimum is reached after respectively 14 and 9 cycles under CO.

Some figures about voltage losses during the load cycles under 1 ppm CO:

At 0.33A/cm², total voltage loss of 0.09V (from 0.74 to 0.65 V)

At 0.46A/cm², total voltage loss of 0.13V (from 0.71 to 0.58 V)

At 0.46A/cm², about 8 cycles to reach 50mV voltage loss.

Some figures about voltage losses during the load cycles under 2 ppm CO:

At 0.33A/cm², maximum voltage loss of 0.14V (from 0.74 to 0.50 V)

At 0.46A/cm², maximum voltage loss of 0.31V (from 0.71 to 0.40 V)

At 0.46A/cm², about 4 cycles to reach 50mV voltage loss.

During the test under 2 ppmCO, after reaching a minimum, some performance has been recovered. Voltages increased for all current densities lower than 0.46A/cm²:

At 0.33A/cm², final voltage loss was of 0.17V (from 0.74 to 0.57 V)

At 0.46A/cm², final voltage loss was of 0.25V (from 0.71 to 0.46 V)

The performance recovery is due to a gain in CO tolerance still to be explained. Repetition of the test should be done. Some internal air bleeding or self-cleaning of the anode catalyst due to the anode potential reached after important contamination level could explain this phenomenon.

To evaluate the possible adsorption of CO on the anode catalyst, cyclic voltammograms have been recorded just after the contamination tests. Few minutes under nitrogen were applied before providing hydrogen to the cathodes, here used as the counter electrodes.

CO oxidation peaks were detected after each tests, including a small peak after pure CO operation.

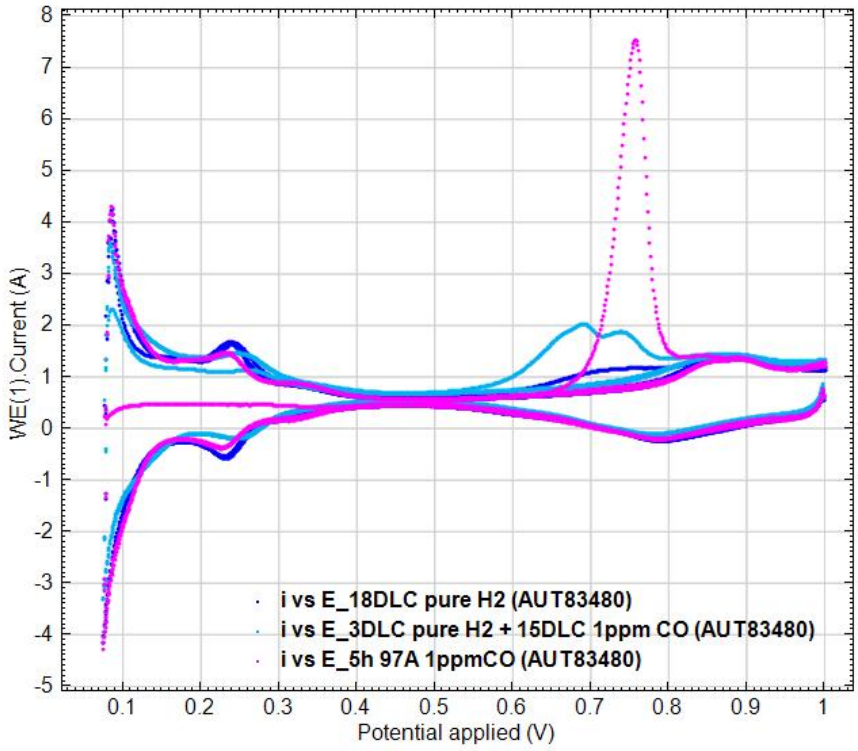

Figure 13. anode CV at 200mV/s after dynamic load cycles under H2 or H2+1 ppm or after fixed current under H2 + 1 ppm CO.

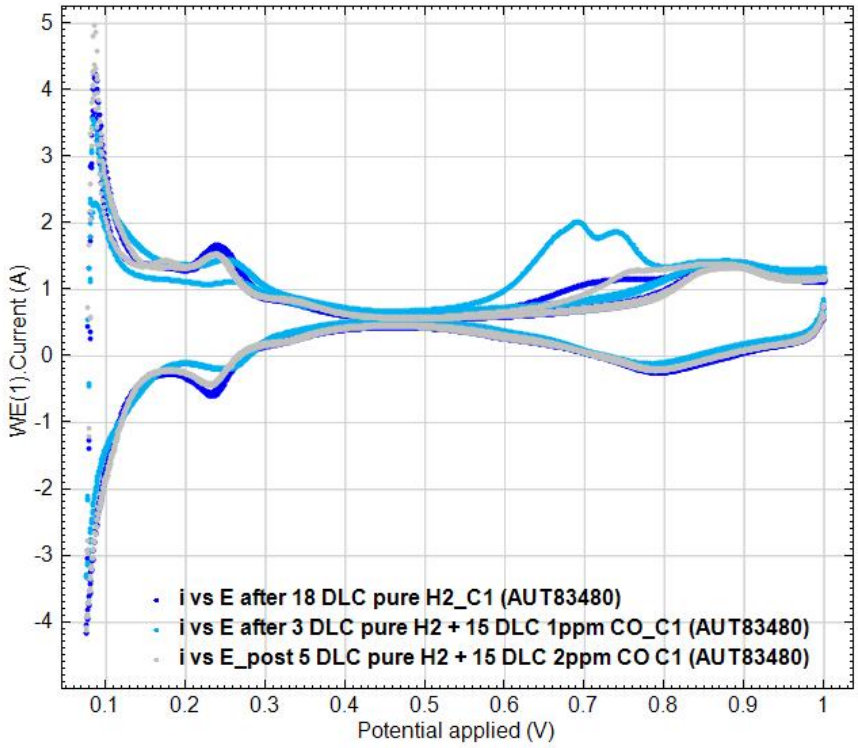

Figure 14. anode CV at 200mV/s after dynamic load cycles under H2, H2+1 ppm or H2 + 2 ppm CO.

JRC

JRC had no experimental activity during the reporting period but procured the relevant materials (^{13}CO and $^{13}CO_2$ gas mixtures) for the test campaign.

Powercell Sweden

Powercell has delivered so far 5 stacks 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

2.1.2 Study of retrievable and irreversible impurities (Task 1.4)

There have not been activities during the period M25-M30 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

Analyte pre-concentration with cryofocusing equipment

Regarding the analysis of hydrogen fuel cell impurities, especially the analysis of formaldehyde with traditional FID and TCD has been relative difficult, because of the lack of detector sensitivity[4]. For this reason, a HP 5890 Series II GC was fitted with methanator and a cryofocusing module in order to gain sensitivity towards formaldehyde as well as enhance the chromatographic resolution for detection of small concentrations (< 1 ppm).

In addition, the purpose of the cryofocusing device was to provide means of separation between impurities and other matrix constituents. The cryofocusing or cold trapping was implemented with Tekmar-3000 cryofocusing module, which enabled the sample cold trapping and analysis of methanated components with Flame Ionization Detector (FID).

The Tekmar-3000 cryofocusing module was installed on top of the GC sample inlet septum (**Error! Reference source not found.**, left). For sampling, the sample inlet flow was led through a fused silica transfer column. This transfer column went through a metal casing that was surrounded with the cryofocusing module condenser casing and heating resistor seen in Figure 15, right.

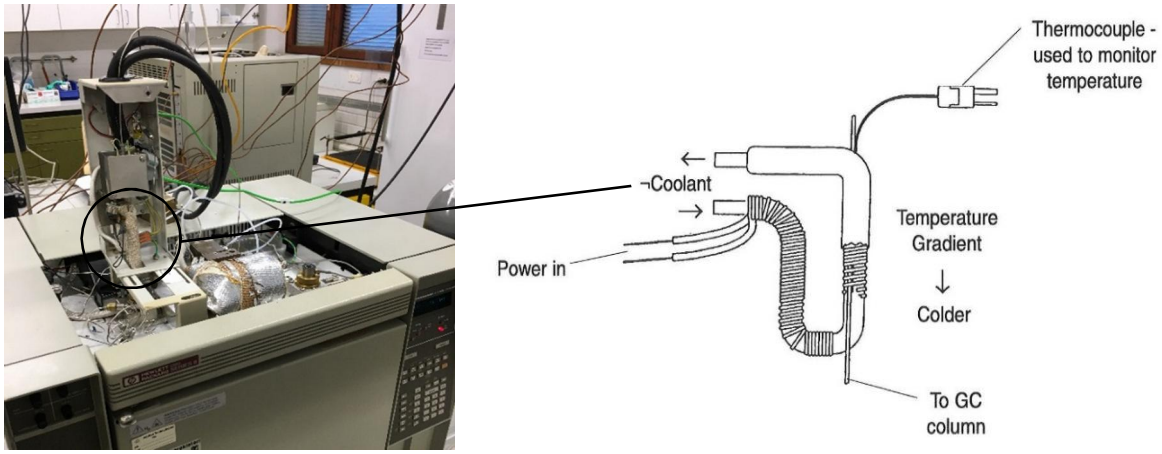

Figure 15. GC with Tekmar-3000 cryofocusing module (left) and cutaway view of the cryofocus trap (right).

Sample pre-concentration was performed by cooling the transfer column to -80°C – -180°C ±5°C with pulses of liquid nitrogen (LN_2) vapor. During the pre-concentration phase, sample

[4]Dojahn, J.G., Wentworth, W.E. & Stearns, S.D., 2001. Characterization of Formaldehyde by Gas Chromatography Using Multiple Pulsed-Discharge Photoionization Detectors and a Flame Ionization Detector. Journal of chromatographic science, 39(2), pp.54–58.

components are condensed and refocused as carrier gas passes through the cooled area. The components form into a narrow band on the first section of the trap column, while the carrier gas continues to flow through the GC system.

When the cryofocus module operation is turned from cooling to heating, the transfer/trap column is rapidly heated under a stream of carrier gas. This rapid heating causes the trapped analyte components to be injected to an analytical column. An example of CO_2 pre-concentration can be seen from the **Error! Reference source not found.**, where CO (boiling point (T_b) -191.5°C) passes through the transfer column and CO_2 (T_b -78.5°C) is trapped and refocused until released forward to analysis.

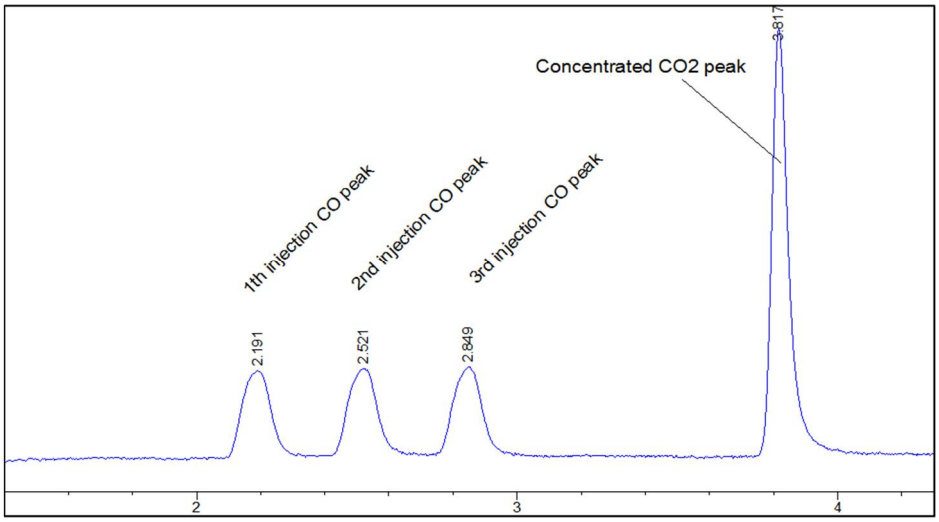

Figure 16. A chromatogram from cryofocusing of a sample (10 ppm CO + 10 ppm CO_2 in He) with 3 cycles of 15 second injection and 5 second wait time.

After this pre-concentration step, the sample is released in to the analytical column (Capillary WCOT CP Sil 5 CB, 50m x 0.32mm x 5µm) with an oven temperature of 35°C. After separation, the sample was carried to a methaniser (15% Ni), which catalytically reduces carbon monoxide (CO), carbon dioxide (CO_2) and formaldehyde (HCHO) to methane under excess hydrogen.

Cryofocusing module performance

The preliminary tests of cryofocusing module was conducted with two gas mixtures (Table 5). With these gas mixtures, the cryofocusing module performance was evaluated against the measurements performed without cold trapping.

Table 5. Gas mixture compositions

CO_2 gas mixture

Component	Concentration (ppm)	Boiling point (Celsius)
Carbon monoxide	10	-191.5
Carbon dioxide	10	-78.5
Helium	BAL	

(N_2 was used for diluting the gas to lower concentrations)

Test Gas 1 mixture

Component	Concentration (ppm)	Boiling point (Celsius)
Methane	200	-161.5
Ethylene	200	-103.7
Ethane	200	-88.5
Propylene	200	-47.6
Propane	200	-42
1-Butane	200	-1
1-Pentene	200	29.9
Nitrogen	BAL	

(N_2 was used for diluting the gas to lower concentrations)

In order to begin the cold trapping measurements, it was necessary to study the temperature behavior of each gas component. As can be seen from the Figure 17, the trapping temperature is a critical parameter when planning analysis with cold trapping equipment. With the correct cold trapping temperature, it is possible to gain selectivity for a specific gas component. With the gas components used in this experiment, the cold trapping temperature correlates strongly with the component boiling point. However, interesting behaviour can be seen with several components of Test Gas 1 mixture, where most efficient cold trapping is achieved with -150°C and further cold treatment decreases the trapped amount of a gas component. This behaviour is most likely caused by the changes to the trapping column stationary phase in temperatures under -150°C. Although undesired phenomenon, this should not pose problems to HCHO analysis, since temperatures this cold are not required.

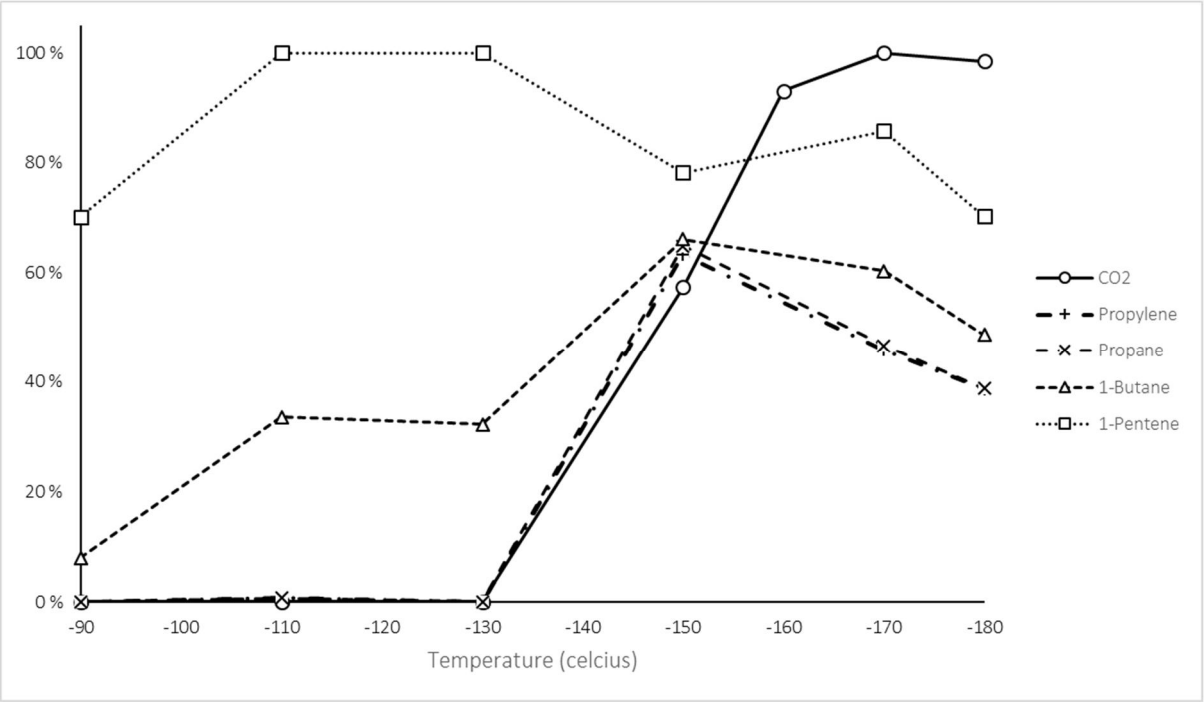

Figure 17. Cryofocusing module trapping effiency. 20 ppm CO_2 and 200 ppm Propylene, Propane, 1-Butane and 1-Pentene.

After the cold trapping profile was established for each gas component, the effect of sample pre-concentration was tested with both test gas mixtures. **Error! Reference source not found.** summarizes the results of three different measurement procedures. The first measurement procedure is a reference measurement, where cold trapping was disabled (marker dots with black outline and white fill). In the second measurement procedure (grey marker dots), three cycle pre-concentration steps were used to concentrate analyte component into the cold trap before releasing it to the analytical column and detector. The last procedure (black marker dots) used 6 pre-concentration steps for increased sensitivity in low concentration levels.

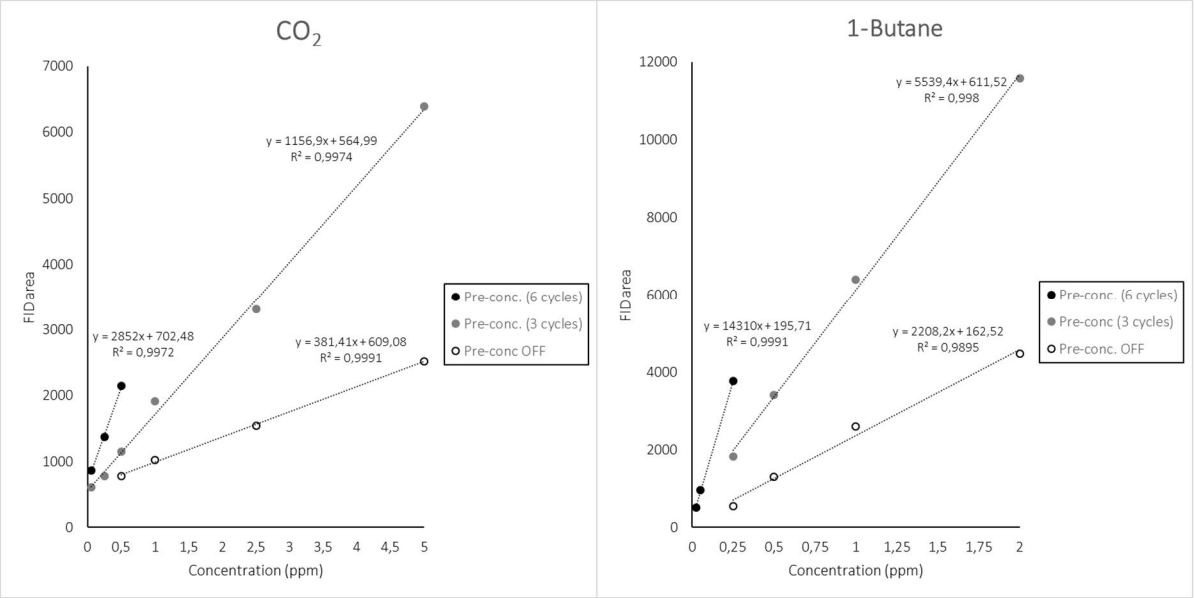

Figure 18. Linearity of concentration and measurement sensitivity

As can be seen from the Figure 17, the pre-concentration procedures were capable of trapping analytes with high linearity through the tested concentration range. In addition, the sensitivity is increased significantly with the use of cryofocusing module. With the analyte pre-concentration, the limit of detection was lowered from 250 ppb to 50 ppb (CO_2 and 1-Butane).

Re-examination of HCHO-standard cylinders NG656 and NG662

As described in the last Interim progress report 3, measurements conducted in VTT suggested that gaseous HCHO in the sample cylinders decomposes and according to the retention time of the decomposition product was thought to be CO. However, after the measurements at VTT the cylinders were returned to NPL who did not observe significant amounts of CO in the gas. The conflicting results were discussed with NPL's Thomas Bacquart by email and in a Telco on 13.9.2016. It was agreed that both VTT and Sintef shall study the possible decomposition once again using independent analysis techniques. In the first stage the same gas cylinders (NG656 and NG662) were sent back from NPL to VTT for analysis with cryofocusing, GC-MS and GC-PDD.

These gas cylinders were on their way to VTT during the writing of this report, thus the analysis results will be reported later on. A meeting between VTT, Sintef and NPL has been scheduled on 30th November at NPL in London.

By analyzing the sample cylinder gases again, VTT will identify the reasons for decomposition product detection. It was suspected that HCHO might have reacted with sample transfer line surfaces, thus in the re-experimentation this factor is removed by applying inert sample injection lines and a throughout vacuum before measurement. With these precautions, the HCHO interactions between the sample line surfaces are prohibited.

Analysis of HCOOH – methods

For preliminary analyses of HCOOH an Agilent 6890N GC was used with Pulsed Discharge Helium Ionization Detector (PDHID) and INNOWAX (Crosslinked Polyethylene Glycol) 60m x 0.25mm x 0.25 µm column. In addition, a phosphoric acid (H_3PO_4) treatment was applied to the GC injection port and analytical column. The phosphoric acid treatment was found to be a key factor in preventing the adsorption of HCOOH on sample transfer surfaces.

The phosphoric acid treatment had two separate steps, injector port (glass liner) and column treatment. A liner with wool packing was immersed in 0.3 % phosphoric acid / acetone solution for 1 minute and then dried in nitrogen gas stream. After the treated liner was installed to the GC injection port, a 100 ppm phosphoric acid / methanol solution was used to condition the column[5].

Figure 19 illustrate the effect of phosphoric acid treatment to formic acid analysis. The measured formic acid solutions consisted of 0, 10, 20, 30 ppm (v/v) HCOOH in acetone.

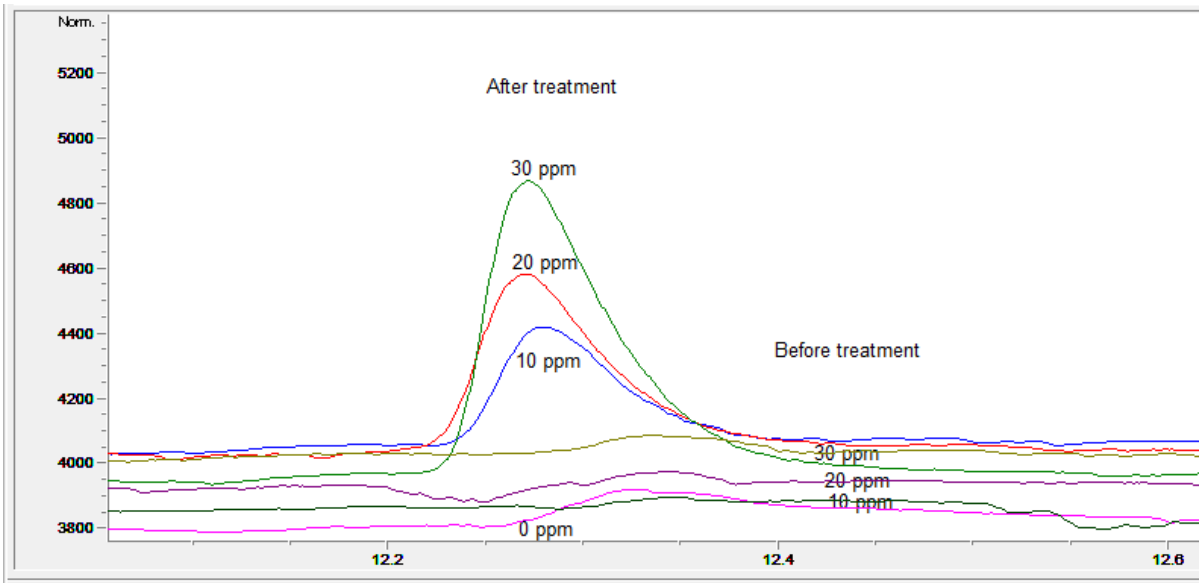

Figure 19 Chromatogram of measured HCOOH samples 0, 10, 20 and 30 ppm before and after phosphoric acid treatment.

According to these measurements, the selected GC equipment and pre-treatment procedure seem to provide methods to analyse HCOOH in low concentration levels.

Development of other analysis methods

In addition to HCHO and HCOOH work was done on the analysis of ppm-levels of oxygen and HCl.

Oxygen analysis

For the analysis of oxygen, we tested an Agilent 6890 gas chromatograph equipped with a TCD-detector, a packed 10 ft x 1/8" Supelco 13X-molecular sieve-column and a 2 ml sampling loop. Good separation and sensitivity (LOQ < 1 ppm) was achieved, Figure 20 .

[5] Shimadzu, Tracera /GC-BID) Solutions, Document Number: LAAN-B-GC004, (2015).

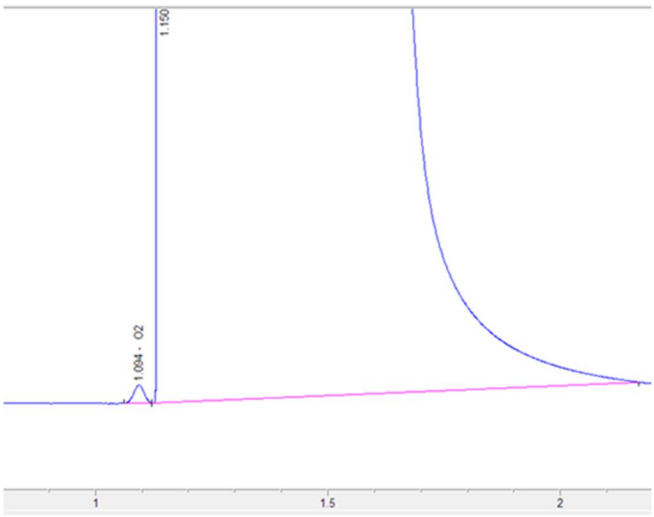

Figure 20 *10 ppm of oxygen in nitrogen.*

The oxygen analysis was developed for the measurements in WP1, as in the measurements with sub-ppm levels of CO, the oxygen level of incoming hydrogen shall be determined as well as the oxygen level of gas in the anode recirculation loop.

Analysis of HCl

The idea of converting HCl to ethylchloride over a zinc-catalyst for analysis using an ECD-detector introduced in previous reports was tested further. A pressurized reactor, Figure 21 was constructed to study the effect of reaction conditions on the conversion.

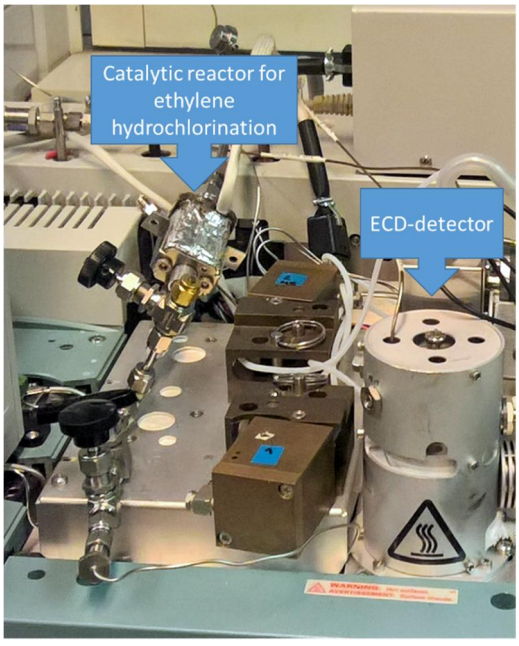

Figure 21. Analysis of HCl as ethylchloride.

Reaction of HCl with ethylene takes place but, unfortunately the repeatability of results has not been satisfactory for quantitative analysis yet.

SINTEF

SINTEF received in August a Cryotrap-4 from GL sciences. This instrument for pre-concentration is currently being installed on an Agilent 6890 GC-MS in order to pre-concentrate samples.

SINTEF is currently analyzing samples from the 2nd sampling campaign with long path FTIR. Currently, the method is being optimized for sensitivity. The results indicate very good sensitivity for CO and CO2. It is however necessary to heat the measurement cell in order to obtain good estimates for water. This is a work in progress and further analysis with be conducted with the measurement cell being heated. Some early results are shown in Table 6.

Table 6. Results from FTIR analysis by SINTEF.

Location	Country	Number	CO-ppb	CH4 ppb	CO2 ppb	H2O ppm
Bramfelder Caussee	Germany	2	2.5	200	200	5
Holmakstr - Berlin	Germany	3	< 2	< 5	200	3.5
Heerstrasse - Berlin	Germany	4	4	6	340	40
Detmoldstr - Munchen	Germany	5	< 2	< 5	430	45
Geiselwind	Germany	6	2.5	10	330	17
Kolding	Denmark	7	3	18	145	14
Århus1	Denmark	8	3	200	260	12
Århus2	Denmark	Extra				
Køge	Denmark	9	2.5	80	410	22
Gøteborg	Sweden	10	18	3300	4000	20

SINTEF has also made use of a GC-PDD configuration in PDHID mode in order to assess some of the intert gases and other constituents not covered by FTIR (ie. N_2, O_2, Ar).

SINTEF has continued the collaboration with Argonne National Laboratory with respect to pre-concentration of samples. By pre-concentration of a known mixture at various levels, it has been shown that there appears to be chemical reactions taking place on the Pd membrane surface. Methane and water is produced. The mass balances of carbon indicate that sooting might a plausible explanation to the loss of carbon. The effect appears to be more pronounced for shorter experiments and thus lower pre-concentration levels. This is consistent with findings by Power + Energy and NPL. Currently, further experiments in order to further investigate this phenomenon and to conclude if Pd membrane is a feasible approach is being investigated.

Table 7. Results form Pd-membrane pre-concentration.

Parameter	MIX	EXP1	EXP2	EXP3
CH_4	1	1.32	1.34	1.05
CO_2	1	0.591	0.446	0.753
CO	1	0.440	0.268	0.934
N_2	1			
MB C	0	0.785	0.685	0.913
MB O	0	0.935	1.06	1.01

Protea

Protea had no development activities to report during this period.

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

No activities to report during the period M25-30.

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

The 2nd sampling campaign was conducted in early June 2016. The HRS's selected were chosen with the aim of targeting as newly commissioned stations as possible. This was discussed with the HRS operators CEP in Germany, H2Logic in Denmark and Vätgas Sweden. This had to be clarified not because of assistance needed at the HRS but rather the availability of a FCHEV at each location. The list of HRS visited is shown in Table 8.

Table 8. List of HRS visited during the 2nd sampling campaign

Sample	Location	Storage	Feedstock	Technology	Operator	Commissioning
HY-2	Hamburg	Compressed	SMR	Air Products	Shell	2013
HY-3	Berlin	Liquid	SMR	Linde	Total	2015
HY-4	Berlin	Liquid	SMR	Linde	Total	2015
HY-5	Munich	CCH2	SMR	Linde	Total	2015
HY-6	Geiselwind	Liquid	SMR	Linde	Total	2015
HY-7	Kolding	Compressed	WE	H2 Logic	H2 Logic	2016
HY-8	Århus	Compressed	WE	H2 Logic	H2 Logic	2016
HY-9	Køge	Compressed	WE	H2 Logic	H2 Logic	2016
HY-10	Gothenburg	Compressed	WE	Woikoski	Vätgas SWE	2015
HY-12	Århus	Compressed	WE	H2 Logic	H2 Logic	2016

Gas samples were collected from all HRS. As for particulate sampling, a sample were initially not collected in Århus (HY-8) due to sample adapter failure. After adapter was repaired a new particulate sample was collected in addition to a new gas sample. Thus two gas samples were collected from the same HRS with the purpose of evaluating the reproducibility of the analytical results. From Gothenburg (HY-10) a particulate sample were collected, but only analyzed qualitatively due to lack of hydrogen dispension metering.

Since the first sampling campaign, no new options for analysis of samples in accordance with ISO fuel quality standard had emerged. Samples were therefore once again sent to the US for analysis by Smart Chemistry.

An overview of the results is given in Table 9.

Table 9. Analytical results from Smart Chemistry. Violation of ISO fuel quality standard is highlighted in red.

ppm mol	HY-2	HY-3	HY-4	HY-5	HY-6	HY-7	HY-8	HY-9	HY-10	HY-12	LOD
Commissioned	2013	2015	2015	2015	2015	2016	2016	2015	2015	2016	
Fuel Index	99.99396	99.99750	99.99259	99.99634	99.99371	99.99384	99.99199	99.96163	99.95574	99.99180	
H2O		1.5									1
THC (C1)	0.12	0.04	0.13	0.07	0.36	0.30	0.84	0.42	5.1	0.88	
O2	4.9	5.0	4.9	11	5.7	5.2	4.1	5.4	13	5.4	1
He			51		40						10
N2 & Ar	56	19	16	26	18	56	75	378	419	76	
N2	55	19	16	26	18	56	75	378	416	76	5
Ar	0.57								3.1		0.4
CO2									5.7		0.1
CO	0.0047	0.0011	0.0040	0.0014	0.0048	0.0032	0.0025	0.0016	0.015	0.0023	0.0005
TS	0.000026	0.000024	0.000020	0.000017	0.000032	0.000034	0.000039	0.000013	0.00011	0.00015	
HCHO											0.001
HCOOH											0.001
NH3											0.01
TH	0.00048	0.0019	0.00042	< 0.001	0.00048	0.026	0.015	0.023	0.0033	0.0049	

The results suggest that the sampling was successful; there is no indication of air contamination of the samples. The results show that two samples violate the fuel index and nitrogen levels. Additionally, the Gothenburg sample (HY-10) show too high levels of THC, CO_2 and O_2. The O2 levels are generally high in all samples. This is in contrast to previous findings. No significant levels of sulfur were found in any samples. The two samples collected from the same refuelling station showed good correlation (HY-8 and HY-12) suggesting good analytical performance by the laboratory.

The gravimetric analysis of the particulate samples is shown in Figure 22. The results indicate particulate concentrations well below the tolerance limit. An uncertainty budget was applied to the analysis, including both gravimetric analysis as well as hydrogen metering. The fairly high uncertainty sources from the conditioning of the filters: their water level before and after being measured. This is still within acceptable levels.

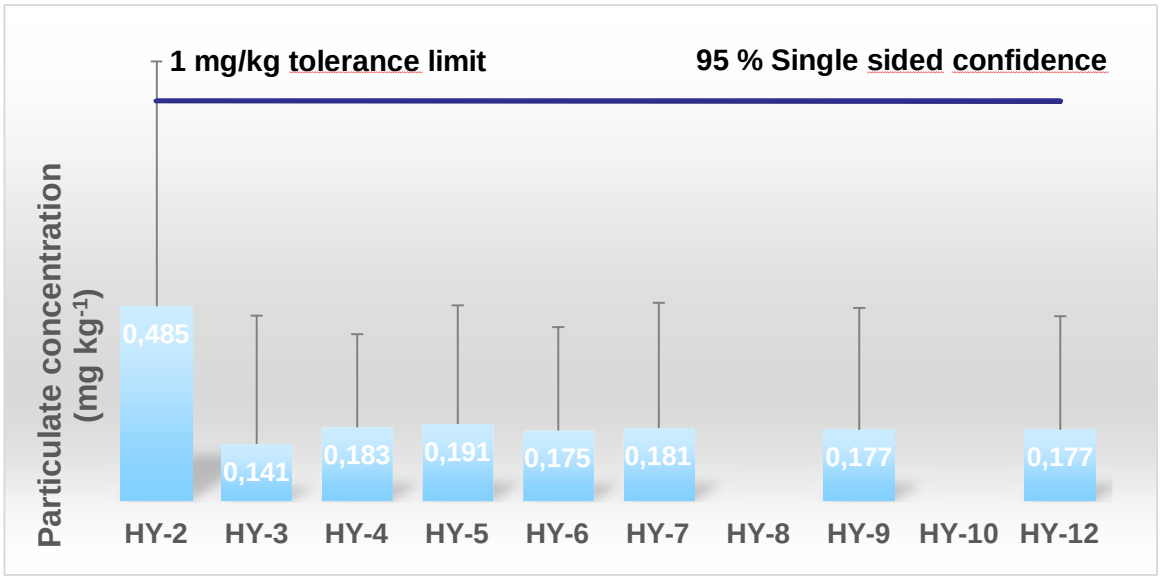

Figure 22. Results from gravimetric particulate analysis.

Qualitative assessment of the filters in SEM reveal both inorganic and organic impurities in addition to oil-like residue on some of the filters. The findings are summarized in Table 10.

Table 10. Qualitative analysis of particulate filters.

Filter	Total	Stainless steel	Ni-P	Other metals	Oxides	Organic particles	Organic residues
HY-2	medium	+	+	+	+	+	+
HY-3	low	-	-	-	+	++	-
HY-4	medium	+	++	+	+	++	++
HY-5	low	-	-	+	+	++	-
HY-6	medium	+	++	+	-	++	++
HY-7	low	+	-	+	-	++	-
HY-8	low	-	-	-	+	+	-
HY-9	low	-	++	-	+	-	+
HY-10	low	++	+	-	+	+	-
HY-12	high	+	++	-	+	+	-

In some filters, some holes were observed suggesting permeation of particulates through the 0.2 µm filter. This is currently being discussed with the manufacturer of the sampling device. A possible solution would be to use a thicker filter.

2.4 Risk model development (WP4)

The HyCoRA risk model for assessing the impacts of hydrogen fuel quality control measures on the risk of degraded FC vehicle performance caused by contaminants in the fuel, and fuel costs, has been finalised. The model applies Monte Carlo simulation to deal with and process the various sources of uncertainty involved in such assessment.

The final version of the risk model has been implemented in Matlab code and applied to assessment of a set of fuel quality control options to demonstrate its functioning. Model implementation in Matlab assures high computational power even with the very high number of simulation runs needed in order to deal properly also with events and effects having very low probability. The currently implemented model allows to carry out more than million simulations of FC stack and vehicle performance per hour. Furthermore, Matlab being a commonly used and well-known tool among experimental and modelling scientists, the Matlab implementation supports well the desired future application and further upgrading of the developed risk assessment tool beyond the HyCoRA project.

The first version 1.0 of the model code will be published and released for peer review and testing at HyCoRA www-site and in HyCoRA deliverable D4.3. Due to limitations of data on the effects of the different impurities, the first version is limited to consider CO as the only fuel contaminant posing a risk to PEMFC and vehicle performance. However, the model structure and current implementation allows other fuel contaminants to be introduced in the model later on as found relevant and sufficient data on their effect is available. Similarly, the initially assumed values for different variables and parameters in the model currently not known well can be revised in the code as better data becomes available.

The development steps of the HyCoRA risk and cost model are shown in Figure 23. Full description of the HyCoRA model and code is to be provided in HyCoRA deliverable D4.3.

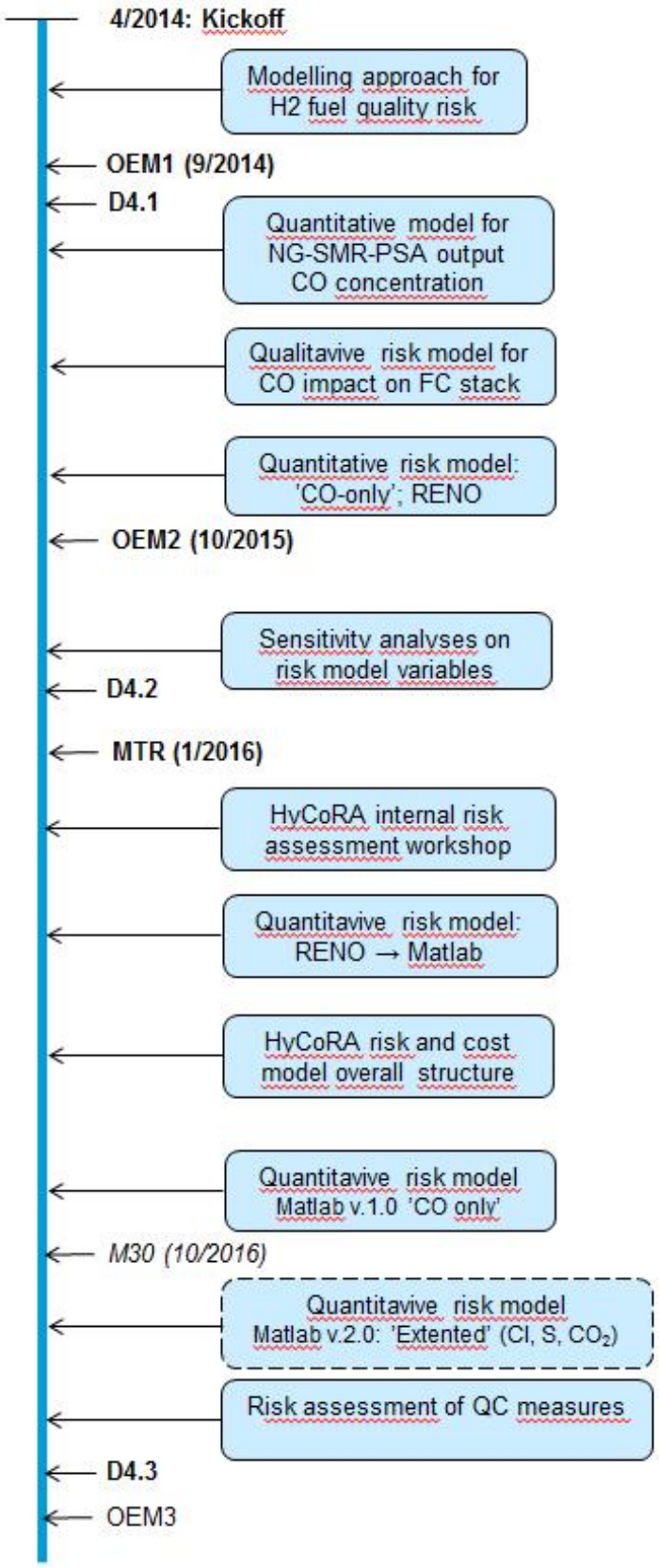

Figure 23. Development steps of the HyCoRA risk and cost model.

2.4.1 The HyCoRA model and code

The overall structure of the HyCoRA risk and cost assessment model is shown in Figure 24.

The assessment process starts with specification of the actual case to be assessed by simulation. This comprises specification of the fuel quality control measures (QC) to be considered and compared, and the specific setting in which the assessments are to be carried out. The setting for the assessment comprises selection of the vehicle type(s) and their use, and fuel production method(s) to be considered. In addition, various parameter values needed for carrying out the simulations are defined in this stage.

As the first step, the probability distributions representing the presumed variation in the concentration of different harmful impurities in the fuel as coming out from fuel production and as subsequently present in the HRS population are generated. In the current model implementation version 1.0, however, CO is the only impurity species and NG-SMR-PSA as the only fuel production method covered.

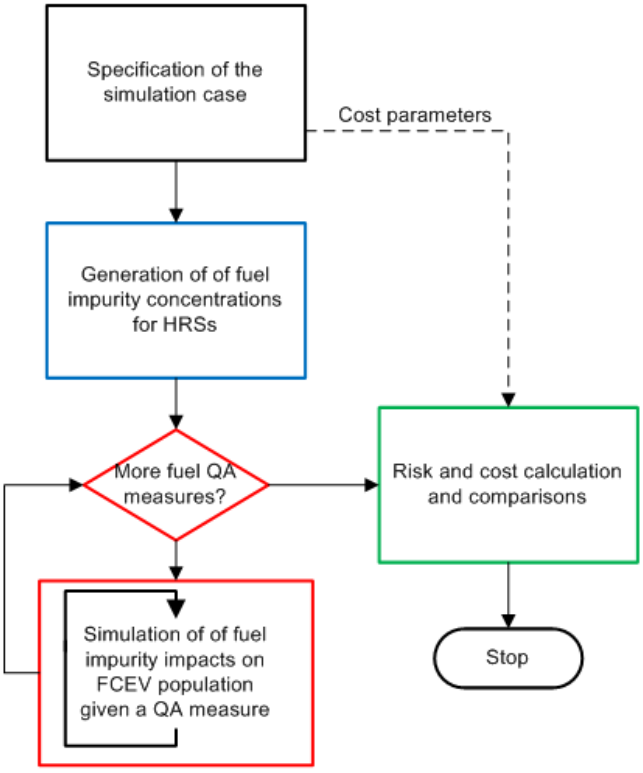

Figure 24. Flowchart presentation of the HyCoRA model for assessing the impacts of hydrogen fuel quality control measures on the risk of degraded vehicle performance and fuel costs

Once the probability distributions for the concentration of different impurities in fuel at HRSs are defined (in Risk model version 1.0 distribution available only for CO), simulation of fuel impurity impact on FCEVs can be carried out separately for each fuel quality control (QC) measure specified for the case. For this, a preselected number of simulation runs are performed, in which a vehicle is randomly selected for each simulation run from the population of the vehicle type of interest and it is exposed to impurities expected to be found in the fuel tank after refilling the vehicle in a randomly selected HRS.

The simulation produces data on performance of the specified QC measures in detecting and cutting out high impurity concentrations in the fuel dispensed at HRSs, as well as data on consequent occurrence of fuel impurity induced performance degradation incidents on FCEVs of the selected type(s). Based on these data the influence of the QC measures on the risk of having fuel impurity induced incidents on FCEVs and on the cost of hydrogen fuel can be quantified. Furthermore, the QC measure with the lowest overall cost expected can be pointed out.

Model implementation in the Matlab code consists of the main program, two sub-models/ programs called by the main program, and a number of functions defined to accomplish specific computational tasks. The main program comprises specification of the case parameters, including the quality control (QC) measures to be assessed, and performing of the risk and cost calculations regarding each QC option.

Generation of fuel impurity concentrations for HRSs is implemented as a sub-model called by the main program. The sub-model returns the distribution parameter values defining the variation of fuel CO concentration expected in the HRS population in the considered case.

Similarly, simulation of fuel impurity impacts on FC vehicles is implemented as a sub-model. In this sub-model, large number of FC vehicles selected randomly form the population of the specified vehicle type of interest are individually exposed to fuel refill on a station selected randomly from the HRS population. CO concentration of the fuel dispensed from the station is assumed to be conditioned by a particular QC measure with station specific random error reflecting the inaccuracy characteristic to the QC measure. The refilled vehicle is then exposed to daily operation following an individually determined driving and stop profile and overall duration. For the risk and cost calculation regarding the particular QC measure, the sub-model returns the number of station incidents and minor and major vehicle incidents observed in the simulation runs, the CO concentration in vehicle fuel tank associated to each vehicle incident, and the amount of fuel refilled in the vehicles over the simulation runs.

The simulation of fuel impurity impacts is repeated similarly for every QC measure specified for the case. The particular QC measure considered is assumed to be in use in all HRS stations. A ‘baseline case’ with fixed parameter values is provided as default for representing the case of having no extra QC measures added in the HRSs.

The different modules in the HyCoRA simulation model as currently implemented in the Matlab code version 1.0 will be described in more detail in the Deliverable 4.3.

The upgrades introduced to the simulation model during this reporting period are shown in red color in Figure 25.

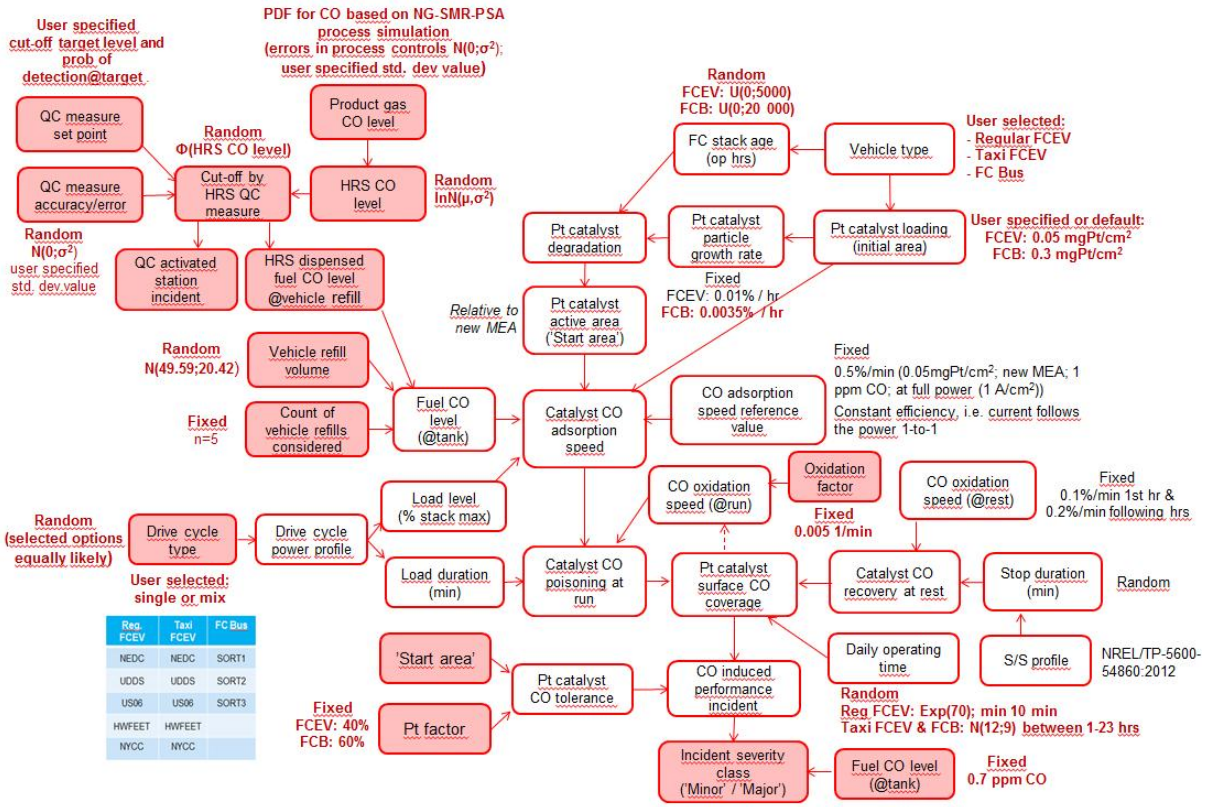

Figure 25 Upgraded HyCoRA risk and cost assessment model; 'CO only' v1.0

2.4.2 Assessment example

Some tentative example calculations have been performed to demonstrate functioning of the model and the code. In these initial calculations four QC measures with different detection capability and the base case (QC0) have been assessed in the context of the different FC vessel types. Fuel CO concentration has been assumed to follow the distribution determined for NG-SMR-PSA product gas with 1.0% stand. deviation assumed for the error in the control of the main parameters in the SMR-PSA process.

Tentative QC performance and cost parameter values based on some literature data have been applied as shown in Table 11. All QC measures have been assumed to be ideal, that is, having no inaccuracy/error in the measurement and control.

The cost penalty from 'vehicle incidents' has been assumed to be 250 €/incident for minor and 1500 €/incident for major incidents. The cost penalty emerging from 'station incidents', i.e. the QC measure rejecting dispensing of the fuel due to detected high impurity level and forcing to HR station clean-up, has not been taken into account in the calculations.

The results on Regular FCEVs are based on drive cycles FCDLC, UDDS, US06, and HWFEET, all being equally likely. Similarly, the results on Taxi FCEVs represent the outcome from drive cycles NYCC and UDDS, and the results on FC Buses drive cycles SORT 1, 2 and 3.

Table 11. Tentative performance and cost parameter values for QC measures used in the example calculations

	QC 1	QC 2	QC 3	QC 4	QC 0
CO cutoff target in hydrogen (ppm)	0.2	0.5	1.0	2.0	-
Measurement error (ppm)	0	0	0	0	-
Probability of detection at target	1	1	1	1	-
Instrument cost ($)	100 000	75 000	50 000	25 000	0
Instrument life (years)	5	5	5	5	-
Maintenance ($/year)	3000	3000	3000	3000	0

Regular FCEVs: $2*10^6$ simulations on every OC

	Measure cost (€/kg)	Minor incident cost (€/kg)	Major incident cost (€/kg)	QC cost (€/kg)
QC 1	0,084018265	0	0	0,084018265
QC 2	0,065753425	0,00027047	0	0,066023895
QC 3	0,047488584	0,003111696	0,005141064	0,055741344
QC 4	0,029223744	0,005005231	0,047887883	0,082116858
QC 0	0	0,004823209	0,139287067	0,144110276

Taxi FCEVs: $0.5*10^6$ simulations on every OC

	Measure cost (€/kg)	Minor incident cost (€/kg)	Major incident cost (€/kg)	QC cost (€/kg)
QC 1	0,084018265	0	0	0,084018265
QC 2	0,065753425	0	0	0,065753425
QC 3	0,047488584	0,000721137	0,003245114	0,051454835
QC 4	0,029223744	0,004506453	0,11464417	0,148374368
QC 0	0	0,002701924	0,248576987	0,251278911

FC Buses: $0.5*10^6$ simulations on every OC

	Measure cost (€/kg)	Minor incident cost (€/kg)	Major incident cost (€/kg)	Total cost (€/kg)
QC 1	0,084018265	0	0	0,084018265
QC 2	0,065753425	3,96668E-05	0	0,065793091
QC 3	0,047488584	0,000595087	0,001190174	0,049273845
QC 4	0,029223744	0,000793273	0,017134698	0,047151715
QC 0	0	0,000872974	0,037617256	0,038490231

Figure 25. Results of tentative cost calculations for comparing QC measure options

The cost calculation results shown in Figure 25, corresponding to HRSs with 750 kg daily fuel sales and excluding the losses from station incidents, suggest that, for FCEVs in both regular

and taxi use, QC measure number 3 with the cutoff target at 1.0 ppm CO would give the largest reduction in the fuel quality costs comprising both the costs of quality assurance and the losses foreseen to emerge from CO induced vehicle incidents. It is to be noticed, however, that even this QC option will become economically unsupported if the daily fuel sales are less than 262 kg in case of regular FCEVs or less than 144 kg in case of Taxi FCEVs.

In case of FC buses the base case with no QC measures added in the HRSs turned out to provide the lowest cost. This result can be explained by the higher tolerance to CO poisoning perceived in FC stacks in busses because of the essentially higher initial Pt loading, and the consequent low risk for vehicle incidents due to CO poisoning.

Furthermore, adding QC measure number 3 was found to suggest reduction of the likelihood of experiencing CO induced vehicle incidents from the original 3.1×10^{-4} per refuelling to 4.4×10^{-5} in case of regular FCEVs. Similarly, reduction from 4.3×10^{-4} to 1.4×10^{-5} per refuelling was suggested for FCEVs in Taxi use.

2.5 Dissemination, recommendations and communications (WP5)

JRC

JRC provided input to CEN/CENELEC SFEM (Sector Forum on Energy Management) WG H2 Energy to identify PNR (pre-normative research) and standardisation challenges & needs. The final report co-compiled by JRC is public and available at the URL www.europeanpowertogas.com.

JRC also co-organised the Workshop on Power-to-Hydrogen: key challenges and next steps held on 3-4 May 2016 in Brussels and the Putting Science into Standards Workshop: Driving Towards Decarbonisation of Transport held on 22-23 Sep 2016 in Egmond. Both workshops were attended by policy & decision makers and representatives of standards organisations.

JRC will also organise the ISO TC197 meeting & CEN H2 workshop to be held on 5-9 December 2016 in Petten & Amsterdam. The 3rd OEM workshop will be held in 2017 in Trondheim.

VTT

VTT has presented HyCoRA project and some results in " The second Materials Challenges for Fuel Cells and Hydrogen Technologies: from innovation to industry Workshop in Grenoble (France) from 19th to 21th September 2016.

CEA

CEA organized the 2nd edition of the workshop : “Material challenges for Fuel Cell and H2 economy, from research to industry “ in which a specific session on H2 quality has been hosted in the frame of HyCoRA.

SINTEF

SINTEF represented HyCoRA for the TC197 ISO meetings in Munich, hosted by Linde Gas. At the WG27 meeting, results from HyCoRA WP1 was presented as input to the discussion on tolerance limits for HCHO and HCOOH in the revision of the ISO 14687 standard. SINTEF also discussed the "total halogenate" misnomer. Based on HRS fuel quality data obtained in WP3, a discussion on the revision of the halogenate inventory was had.

In the JWG7 Meeting, the EURAMET 1220 round robin test was presented. SINTEF and CEA participated in this exercice as part of WP2. Progress in analytical methods for HyCoRA was given in the April meeting in Sacramento. In this meeting, the progress in WP2 on palladium membrane sample preconcentration strategy was given.

For the upcoming meeting of WG27, SINTEF has been asked to provide information from HyCoRA. In addition to further WP1 data on HCHO and HCOOH impurities and their decomposition, SINTEF has been asked to provide further information on halogenates as well as results from sampling of particulates.

2.6 Deviations and impact

2.6.1 VTT

VTT is still slightly lagging behind the work schedule for WP1 accepted after the mid-term review. A recirculation pump failure with a corrosion issue has required a change of pump and cleaning of the anode recirculation system.

However, since all other experimental equipment are working otherwise fine, the progress is seen as rapid and the measurement campaign, planned after the mid-term review can be completed by the end of January 2017, assuming no additional component failures.

2.6.2 CEA

At CEA, a fire destroyed the laboratory of preparation of MEA for PEMFC testing. The prepared low loaded MEA for the project has been burned. The activity to prepare new MEA could restart only in August 2016. Since September 2016, test of the impact of CO on low loaded MEA has been restarted.

Furthermore, the test station used for HyCoRA has been used in April 2016 for international round robin test of 25 cm2 single cell with Tommy Rockward from Los Alamos National Lab (US DoE). M. Tommy Rockward is the chairman of the ISO/TC197 WG12 for the standardisation of H2 quality for PEMFC application.

At stack level, a calibration of the station has been done in July 2016. This calibration has been made before the study of the impact of CO on the short stack from power cell in order to accumulate robust data.

Both single cell and short stack testing are currently (September 2016) on going.

2.6.3 JRC

Asbestos sanitization activities in the building where FC test laboratories are located caused a six week downtime for testing until beginning September 2016. Testing capability for this project will only resume during November.

The purchase of the ^{13}CO and $^{13}CO_2$ gas mixtures required in the stack testing in WP1 has taken more time than expected 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. These isotopes gas cylinders are now (September 2016) on-site at JRC.

The second recirculation pump delivery, for stack recirculation test, is expected on week 43.

2.6.4 Protea

Protea has undergone a large operational change through the last 12 months which has impacted Protea work on HyCoRA with the retirement of managing director and project LEAR, and new ownership of the company.

Whilst the new ownership is committed to HyCoRA, the immediate concern for the business has been on commercial projects and also a move in factory. This has had large effect on Protea deliverables for the project.

Now the structure of the company is secure. Protea has all the equipment to complete the tasks in HyCoRA project, and it is a matter of resourcing to achieve the goals. This will be done, but it would require a 3 month extension to ensure that the deliverables are met.

The development of Protea's low-concentration FTIR gas analyser may not see the development resulting in a field-based design by the end of the project, even with the 3 months extension, but Protea envisages a lab-based system by March 2017 thereby completing the work in task 2.1 and achieving the milestone 22.

Protea will also provide other partners a field-based combined MS-FTIR that will give a broad range of H2 impurity measurements.

2.6.5 SINTEF

SINTEF has no actual deviations. However, Data from the previous two sampling campaigns has been analysed by Smart Chemistry in the US exclusively. As Smart Chemistry did not take part in the Euramet 1220 it was in the 2nd OEM Workshop some discussion on the robustness of the results.

SINTEF, NPL and VTT has established a good working relation around the analysis of halogenates. NPL is establishing a new analytical technique that is expected to be validated early 2017. SINTEF will provide HRS fuel samples to NPL early next year in order to investigate the organohalide C4Cl4F6 found in all but one sample analysed so far by Smart Chemistry. A three month extension of the project would benefit from analytical capabilities available from samples collected in the third sampling campaign.

2.6.6 Corrective actions proposed

The work by partners CEA, JRC and Protea has been delayed and an extension for the project would be needed for them to complete their work. It has been agreed in the project management committee that 3 months extension for the project will be requested.

3. Project management during the period

3.1 Consortium management tasks and achievements

The deliverables due during the Periods 1-5, have been submitted and accepted, excluding D2.2, D6.5 and D6.6 (this report).

M30 progress meeting was held in at Powercell premises, Gothenburg, Sweden 25.10.2016.

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 issues and envisaged solutions has been listed in Chapters 2.6.1-2.6.5. As a part of the solution VTT is continuing close co-operation with JRC to develop an anode recirculation system for ^{13}CO measurements.

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

Date	Place	Title
9-10.3. 2016	Espoo (Finland)	4th semi-annual project progress meeting
20.5. 2016	www / Lync	M26 progress meeting online
7.7. 2016	www / Lync	M28 progress meeting online
12.9. 2016	www / Lync	M30 progress meeting online to prepare M30 semi-annual meeting
25.10.2016	Gothenburg, Sweden	5th semi-annual project progress meeting

3.4 Project planning and status

Project planning is progressed as expected, excluding the delay of the work and need for 3 months extension.

3.5 Impact of possible deviations from the planned milestones and deliverables

There were following deviations from the milestones and deliverables.

- D 6.6 (this report) was delayed by one month 2 month.

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.