



# METROLOGY for HYDROGEN VEHICLES 2

## Deliverable 8

*Report on standard test protocols concerning FC stack measurements to determine threshold limits of critical contaminants in hydrogen*

Project name: MetroHyVe 2

Grant agreement: 19ENG04

Lead partner: VTT

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Due date: 31 October 2023

Submission date: 31 October 2023

Version: 0

This project “Metrology for Hydrogen Vehicles 2” (MetroHyVe 2) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union’s Horizon 2020 research and innovation programme under Grant agreement No [19ENG04].

**EMPIR**



The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

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D8: Report on standard test protocols concerning FC measurements with stack to determine threshold limits of critical contaminants in hydrogen	
<b>Funding</b> European Metrology Program for Innovation and Research	<b>Grant agreement no:</b> 19ENG04
<b>Project name</b> Metrology for Hydrogen Vehicles 2	<b>Project short name</b> MetroHyVe 2
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<p><b>Summary</b></p> <p>The purpose of this report is to propose some standard test protocols concerning FC stack measurements to determine threshold limits of critical contaminants in hydrogen.</p> <p>This report was written as part of activity 4.5.4 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1<sup>st</sup> August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control, sampling and fuel cell stack testing). For more details about this project please visit <a href="#">website address</a>.</p>	
<b>Confidentiality</b>	Public

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# EMPIR



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## 1. Introduction

The current standard for hydrogen for transportation use (ISO 14687:2019) is still mostly based on the measurements performed in small single cells using open anode configuration. Measurements in EU-projects (HyCoRA, HYDRAITE) as well as by Matsuda et al. [1] have shown that for determining threshold limits of contaminants in hydrogen the open anode measurements are not sufficient and measurements should be preferably done at stack level, so that fuel utilisation and other operating conditions are comparable to real system operation. The effect of contaminants is strongly dependent on accumulation and diffusion effects, which can only be analysed accurately at the stack level with an integrated anode recirculation loop.

## 2. Scope

The scope of MetroHyVe2 WP4 was to provide information for harmonisation or standardisation of test protocols concerning PEMFC measurements on short stacks operating in dead-end mode with recirculation to determine threshold limits of critical contaminants in hydrogen.

The first part of the work was summarising the existing protocols and literature. The existing measurement procedures and protocols for FC stack measurements for road applications were reviewed in MetroHyVe2 project report 4.3.1 [2], which is available at MetroHyVe2 project website (<https://www.sintef.no/projectweb/metrohyve-2/downloads/>). That report is based on public guidelines that have been developed in joint work as well as in public funded European projects. After the MetroHyVe2 report 4.3.1 was prepared the HYDRAITE deliverable D2.5 was completed and published [3]. In that report EU harmonised test protocols for short stack test methods for studying hydrogen contaminants in automotive PEMFC systems were proposed. This deliverable is also publicly available at CORDIS (<https://cordis.europa.eu/project/id/779475/results>).

This report first presents a summary of report 4.3.1 and HYDRIATE deliverable D2.5 and presents and discusses the experience of performing the measurements as part of MetroHyVe2, when selected test protocols were tested by different project partners.

### 3. Review of existing single cell and stack testing protocols

An extensive review of existing public guidelines that have been developed in public funded European projects was written and reported in project report 4.3.1 by Ansorge et al. [2]. This review includes recommendations for operating conditions (temperature, pressure, humidity, stoichiometry) as well as instructions for basic procedures which should be followed when stacks are tested. These include e.g. leakage test, break-in and preconditioning. Other recommendations include load profiles, dynamic load cycles (DLC) as well as start-up and shut-down procedures.

The recommendations for start-up and shut-down are different for contaminant testing [3] compared to stack performance and durability testing [2]. For the durability testing simulating system events like start-ups and shut-downs are important, while for reversible contaminant testing the key parameter is reproducible anode catalyst surface state, meaning that all carbon monoxide and other impurities have been removed from the surface before the testing. This is also pointed out by Ansorge et al. [2]: *The development of test protocols for stack measurements depends on both the objective of the measurement as well as the possibility of implementation and reproducible realization of the tests.* This means that for stack level hydrogen contaminant studies some of the usual test procedures used for stack performance and durability studies need to be modified or omitted. In addition, some procedures should be added. These additional procedures were proposed and partially validated in HYDRAITE project.

### 4. Proposed standard procedures in HYDRAITE project

In HYDRAITE deliverable D2.5 Smith and Viitakangas [3] proposed a number of additional or modified procedures in addition to those mentioned by Ansorge et al. [2]. In most of these proposed measurements gas analysis measuring the composition of the recirculated anode gas was also active. These include:

- Measuring Loop Volume
- Measuring Anode Recirculation Rate
- Measuring Fuel Utilisation
- Start Up and shut-down
- Reference CO Poisoning
- Cyclic Voltammetry / ECSA Measurements
- Measurements with Impurity
- Measuring Influence of Parameters on Impurity Behaviour

## 5. Testing of selected standard test protocols from HYDRAITE project and additional protocols developed in MetroHyVe2

In the MetroHyVe2 project the experimental work for developing and evaluating standard test protocols (WP4 Impact on FC stack) was designed in four parts:

- Task 4.1 to study a range of different anode recirculation systems and their effect on the FC stack measurement results.
- Task 4.2 to systematically investigate the variables that may affect the integrity of the online gas analysis measurement in the anode recirculation loop.
- Task 4.3 to identify and select procedures for FC stack measurements for road applications.
- Task 4.4 to establish more reliable test protocols for reactive contaminants.

In this report the most relevant experimental results from the tasks of WP4 are gathered. Typical experimental conditions for the measurements are summarised in Table 1 though these were modified to accommodate different stacks. In gas analysis measurements OFCEAS analysers by Ap2e (ProCeas®) were used for oxygen and carbon monoxide measurements, while microGC 490 from Agilent were used for nitrogen, oxygen, methane and carbon dioxide measurements.

The choice of current density made for measurements is important. Stacks operating at higher current densities show a higher sensitivity to impurities i.e., the cell voltage is more severely impacted at higher current densities. Further, higher currents result in the impurity being delivered more quickly for the same concentration as the total gas flow is higher which makes measurements more straightforward as they can be accomplished in one working day. One challenge in operating at higher current densities is that during prolonged experiments the cell voltage may drop so low that low cell voltage alarms are triggered; this is particularly true during large transients in dynamic load cycles (DLC).

Table 1: Typical stack operating conditions in MetroHyVe2

	Property	Unit	Nominal Value
	Coolant Inlet Temperature	°C	70
	Coolant Inlet Pressure	kPag	40
	Minimum current density for stoichiometry operation	A cm <sup>2</sup> Ndm <sup>3</sup> min <sup>-1</sup>	0.3 19.4
Anode	Inlet Temp	°C	90
	Inlet Dew Point	°C	0 – humidifier bypassed
	Inlet Pressure	kPag	30
	Stoichiometry	-	1.3 or forward pressure control
	Recirculation Loop Temp	°C	90
	Fuel gas inlet humidity	% RH °C	~50 @70 °C, 1.3 bar, 1.2 A cm <sup>-2</sup> ~55
	Recirculation pump setpoint	V	Single pass stoichiometry target of 1.5 at 0.6 A cm <sup>-2</sup> .
	Fuel stoichiometry		>1.01 (99% total fuel utilisation) Enrichment factor of methane > 100
Cathode	Inlet Temp	°C	80
	Inlet Dew Point	°C	(50% at 70 °C)
	Outlet Pressure	kPag	20

## 5.1 Measurement of fuel utilisation by direct flow measurement

In the MetroHyVe2 project fuel utilisation was measured or estimated using direct measurement of flow during hydrogen purge as well as by measuring carbon dioxide, nitrogen, hydrogen or tracer gas (methane) concentrations. This type of arrangement has previously been used by Koski et al. [4]. The direct measurement of fuel utilisation proved difficult due to the required fast sampling rate. The data acquisition systems used by partners did not typically allow faster than 5-10 Hz data sampling frequency.

Despite this challenge an important observation was made. If the fuel utilisation is too high, then the average volume of the purge decreases. In addition, the fluctuation of the purge volume becomes very large. Figure 1 shows hydrogen purges during one steady state measurement where the purge frequency was 1/60 s. The estimated size of one flow purge was 0.17 Ndm<sup>3</sup>. In this set-up one 0.167 dm<sup>3</sup> purge flushes about 1/4 of the total anode gas volume, as gas volume is about 0.66 dm<sup>3</sup>, including gas sampling loop (55-60 ml) [4]. Since the pulse took place every 60 seconds this is additional hydrogen flow of 0.17 NLPM. In this measurement the total hydrogen consumption was about 8.2 LPM and the resulting fuel utilisation estimate is ~98%. However, as can be seen in Figure 1 there is clear variation in pulse volumes. Notably, the variation of pulse volume is not visible in hydrogen concentration data, as “poor” purges are randomly distributed.

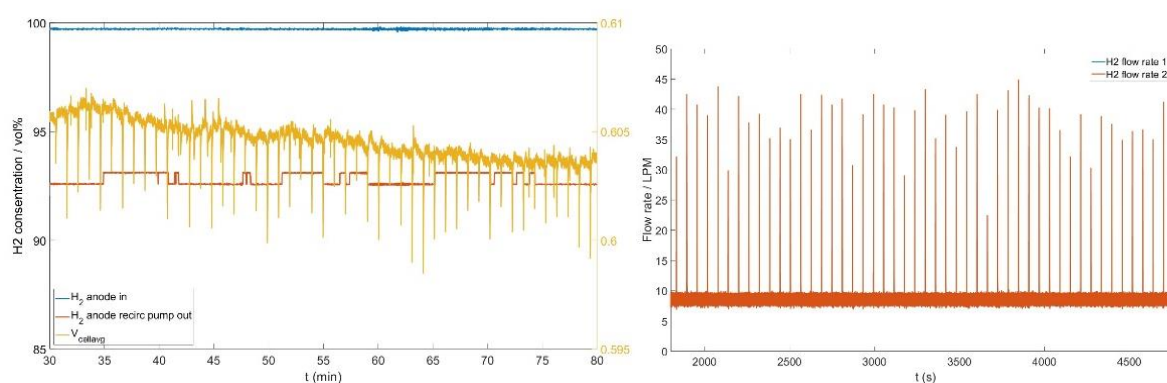


Figure 1. Left: Average cell voltage and hydrogen concentrations when purge frequency was 1/60 s. Right: Purge volumes during the same measurement.

When purge frequency was decreased to 1/400 s a much larger variation in the volume of single purges was observed. This is illustrated in Figure 2. When the purge frequency was 1/400 s, the estimated average purge volume was only about 0.05-0.07 dm<sup>3</sup>, which is 60-70% smaller compared to the measurement when purge frequency was 1/60 s. This means that by decreasing the purge frequency from 1/60 s to 1/400 s the fuel utilisation increased much more than intended, due to lower average purge volume. The smaller purge volume has two main causes. The anode gas viscosity is larger when more nitrogen has accumulated, and flow resistance is larger when more water has accumulated, with the latter being very stack dependent.



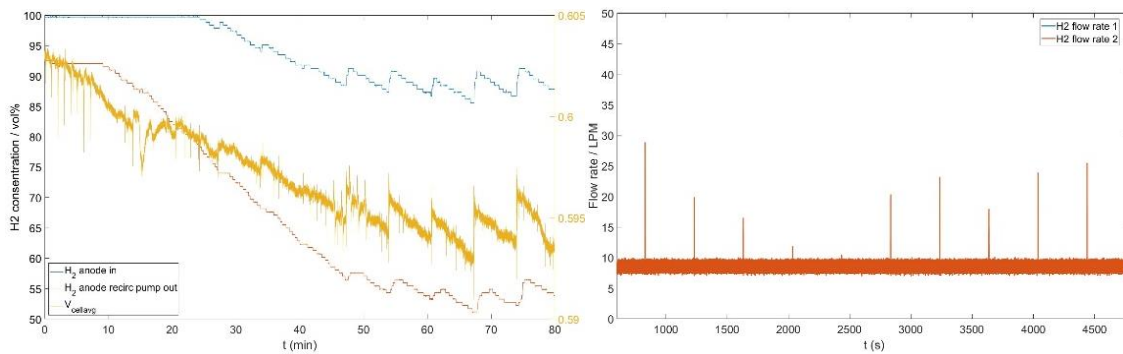


Figure 2. Left: Average cell voltage and hydrogen concentrations when purge frequency was 1/400. Right: Purge volumes during the same measurement.

It was also observed that the fuel utilisation was slightly different in measurements where carbon monoxide poisoning was applied compared to measurements with pure hydrogen, even when all experimental parameters were the same. This indicates that as the current distribution changes due to carbon dioxide poisoning, the water accumulation in the anode channels also changes, which in turn impacts the flow resistance and purge volume.

These results lead to the clear conclusion that fuel utilisation cannot be determined using purge volume from a separate measurement. If direct flow measurement during hydrogen purge is used to estimate fuel utilisation, then volumes in all purges should be measured.

### Impact of current on the fuel utilisation

When applying anode purges, approximately the same gas volume is lost during purges regardless of stack operating current. This causes an increase in fuel utilisation at higher currents. In the example in Figure 3, the fuel utilisation was assessed at 90% and 93% for the lower and higher currents respectively.

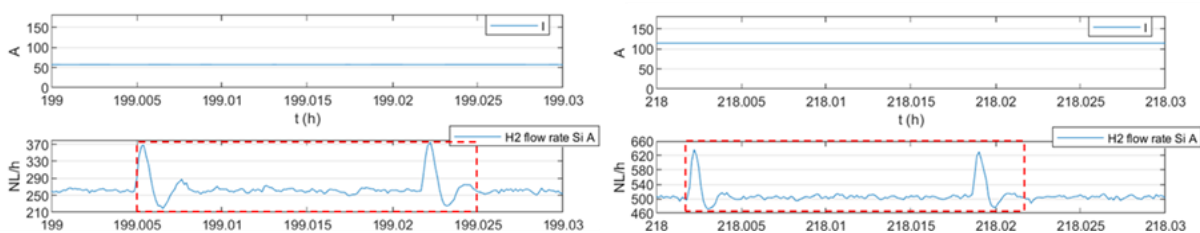


Figure 3. Anode flow rate changes during a hydrogen purge, at low and medium current operation point.

As a conclusion the direct flow measurement may be too difficult to use, even if it is accurate and the sampling can be done at a high enough frequency. The use of methane as a tracer gas is a promising method that is discussed extensively in MetroHyVe2 D7, but direct use of nitrogen accumulation (or hydrogen concentration loss) may be accurate enough if calibrated using a methane tracer [4].

## 5.2 The recommendation for use of DLC or steady-state measurements

It has been discussed in the MetroHyVe2 project report 4.3.1 [2] and also in HYDRAITE deliverable D2.5 [3] how every test bench is different. This leads to different stack behaviour when dynamic load cycles (DLC) are applied. The variations in temperature and humidity levels typical during stack measurement at one partner are illustrated in Figure 4. The stack temperature (coolant in and out) is about 4-6 °C higher than targeted at high currents, as the cooling system takes time to react. In addition, the anode inlet dew point is drops from 57-60 °C to as low as 45 °C since the recirculation rate is constant and more dry fresh hydrogen is mixed with humid hydrogen.

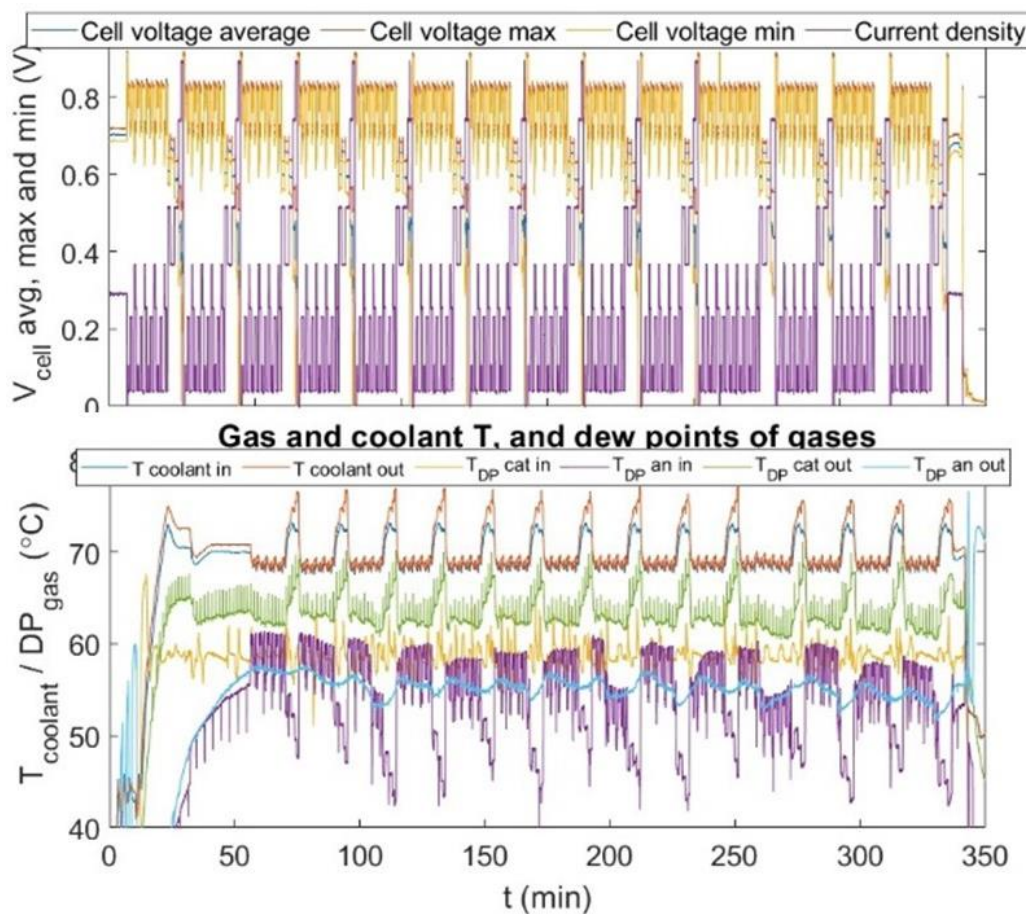


Figure 4. Top: Cell voltages and current densities during DLC. Bottom: Coolant temperatures and gas dew points.

In a real automotive PEFC system the cathode dew point would also be fluctuating due to the use of membrane humidifiers. In this data the fluctuation of cathode humidity is quite small compared to fluctuation of anode humidity. Thus, every system and stack test station is different and comparison of results from DLC measurements is very difficult not only between test stations but also between test stations and real systems.

Due to these difficulties, the difference between DLC and steady load cycle (SLC) was measured by Koski et al. [5]. In their study Koski et al. observed that the use of DLC mitigates the carbon monoxide poisoning but the effect is relatively small (< 20%) in mild (50 mV) poisoning.

These measurements were repeated in MetroHyVe2 project. When this was done with slightly different parameters, poisoning time with SLC was slightly longer than for DLC, see Figure 5. This measurement was done with DLC and SLC having  $0.25 \text{ A cm}^{-2}$  average current density while  $0.4 \text{ A cm}^{-2}$  was used in the study of Koski et al. [5].

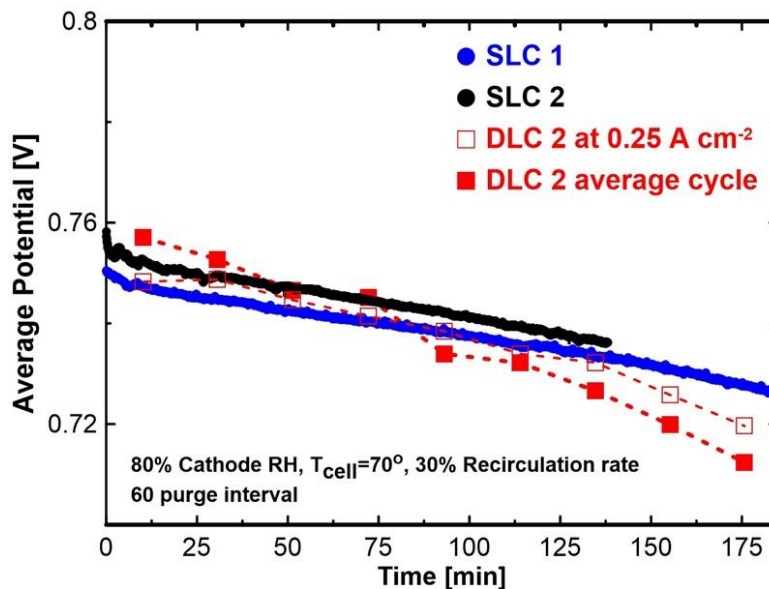


Figure 5. A comparison of average cell voltage decay rate when SLC or DLC were applied.

The difference between the results from the MetroHyVe2 study and Koski et al. [5] may be due to different fuel utilisations or small differences in the carbon monoxide levels in the hydrogen, as in DLC the control of carbon monoxide feed by MFC was not very accurate in the MetroHyVe2 project. Koski et al. used 2 ppm carbon monoxide in hydrogen pre-mix.

Despite small differences all the results indicate that the DLC has only a minor effect when carbon monoxide poisoning is mild, therefore DLC is not needed for carbon dioxide contamination work. The challenges for controlling system test benches during DLC measurement are likely to cause larger uncertainties in the results than changing from DLC to SLC. These experiences with CO indicate that DLC can be replaced by SLC and the error is acceptable. However, as this is most probably contaminant dependent, is recommended to study the effect of load cycle on contamination at single cell level before using only SLC in stack level measurements.

### 5.3 The use of steady state data to get worst case estimation for the behaviour at current levels during load cycles

In the MetroHyVe2 project, tests were conducted at different fixed currents, corresponding to current steps during load cycles. The data are collected in Figure 6. This gives some additional information to the average data. The tests were conducted with the same fuel recirculation of 10 NLPM, purges of 0.5 s every 60s with a flow limiter to reduce purge volume. A premixture of hydrogen + 1 ppm carbon monoxide was used for the poisoning. The shift was done at  $t=0$  in the figure reported here. The CO measured in the recirculation loop with the PROCEAS analyser is directly dependent on the current (or average current). In the case of these series of experiments, it could be noted that the excess concentration of carbon monoxide as well as the voltage loss measured with time after hydrogen + carbon monoxide injection presented the same behaviour, with consistent relative increase and decrease, respectively, during the 3 hours of poisoning.

When degradation during the DLC load points is compared with degradation with similar steady-state current it can be observed that degradation is much faster. Thus, the steady state data at various currents can give at least a low boundary of tolerance that can be expected when applying load cycles.

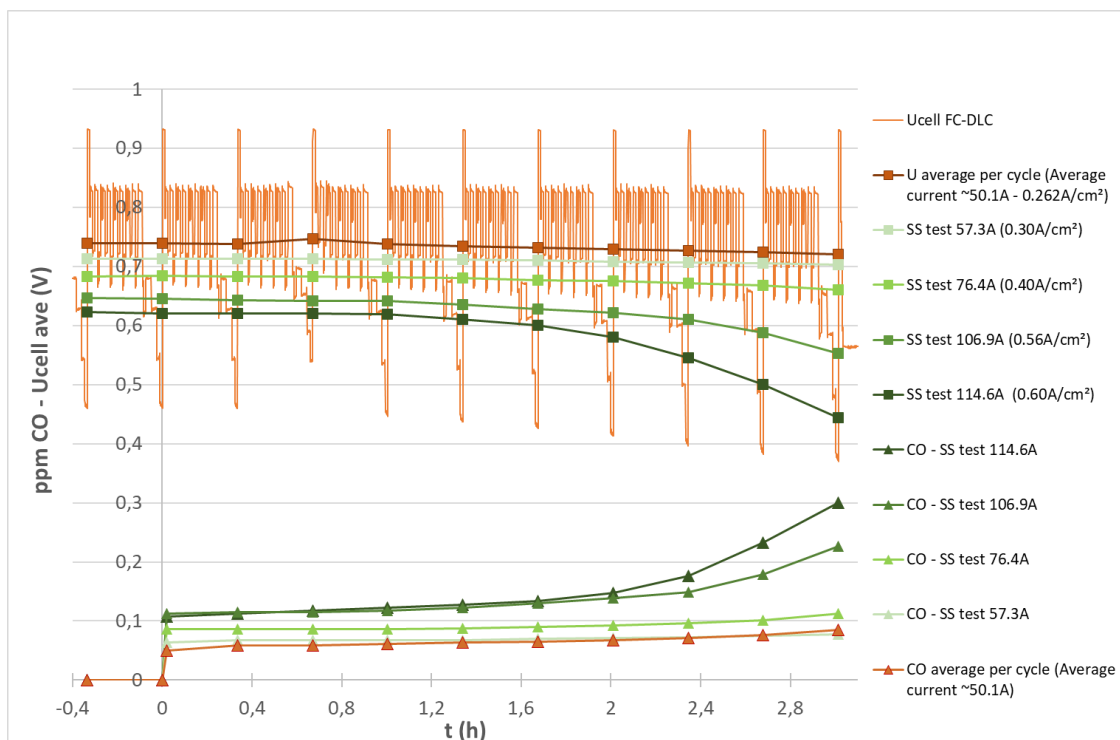


Figure 6. The data from DLC poisoning measurement with 1 ppm carbon dioxide compared with SLC measurements at load points of SLC. At  $t=0$ , hydrogen was shifted from pure to a mixture of hydrogen + 1ppm carbon dioxide.

When DLC measurements were performed OFCEAS analysers by Ap2e (ProCeas®) were used to measure recirculated anode gas. These enabled measurement of carbon monoxide and oxygen levels, when DLC was performed, see Figure 7.

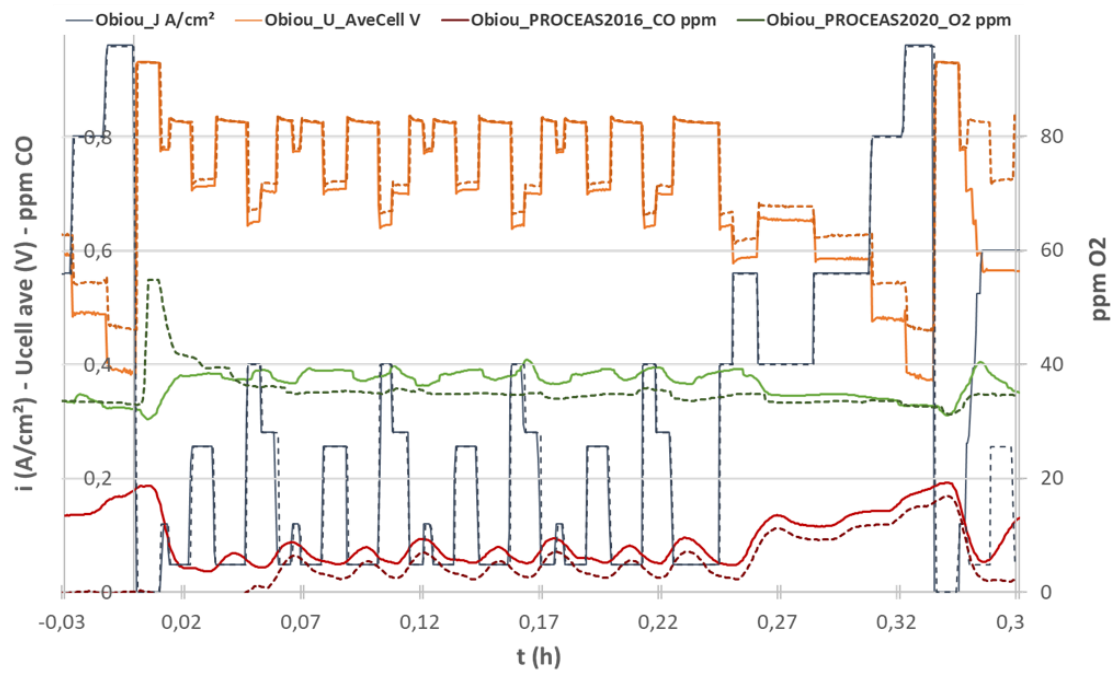


Figure 7. Details of DLC poisoning measurement from 1<sup>st</sup> and 9<sup>th</sup> cycle.

#### 5.4 Clean-up of anode catalyst using oxygen injection during shut-down

Measurement during the HyCoRA project showed that insufficient removal of carbon monoxide from the catalyst surface is an issue for reproducibility of carbon monoxide tolerance measurements. Due to this, a clean-up of the catalyst surface was proposed by Smith and Viitakangas, as shown in Figure 8 [3].

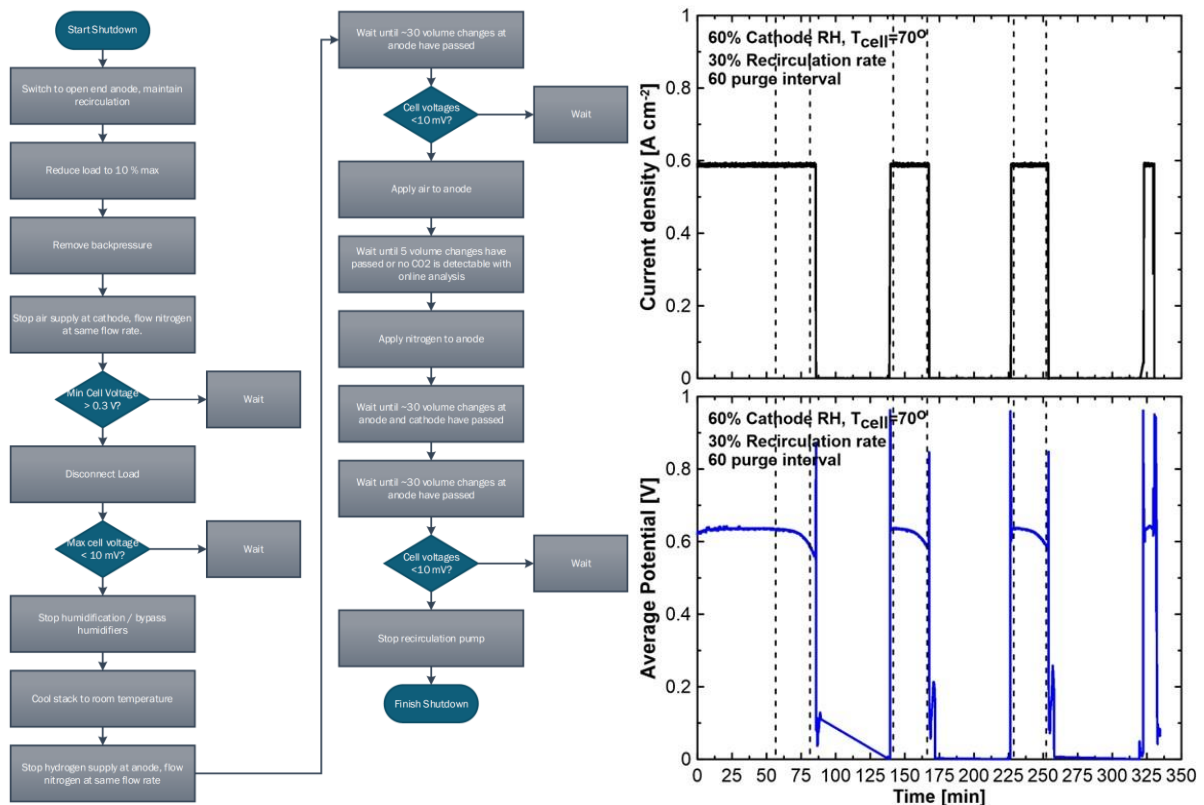


Figure 8. Left: Protocol for shutting down the stack after operation [3]. Right: Current density and average voltage during repeated CO poisoning (5 ppm CO at 0.6 Acm<sup>-2</sup>) and surface clean-up.

In the MetroHyVe2 project this clean-up procedure was tested. As seen in Figure 8 a shutdown with air purging lasting 45-60 min effectively restores the stack voltage to its pre-poisoned value (0.635 V per cell).

Employing shutdown with air purging consistently results in nearly the same duration for subsequent poisoning cycles to achieve a 50 mV potential drop as indicated in Table 2. In this case, the time required is approximately 24-26 min.

Table 2. The data from the measurements shown in Figure 8.

poisoning cycle	time start (min)	time end (min)	voltage start (V)	voltage end (V)	time (min)
1	57.375	81.767	0.635	0.585	24.392
2	140.358	166.600	0.635	0.585	26.242
3	227.100	252.667	0.635	0.585	25.567

## 5.5 Confirmed effect of un-cleaned (pre-poisoned) catalyst surface on tolerance assessment

Carbon monoxide can accumulate on the anode surface due to a small amount of carbon monoxide in the fuel or due to carbon dioxide and formation of carbon monoxide on the surface, as shown by Erbach et al. [6]. Due to this, the time delay from the measurement start to the start of carbon monoxide tolerance measurement should be kept to a minimum, as this minimises the accumulation

of carbon monoxide on the surface. The used hydrogen can have some carbon monoxide, even if the level is under the ISO 14687 limit (0.2 ppm).

A small accumulation of carbon monoxide is not visible in the cell voltage signal but can be clearly seen as reduced carbon monoxide tolerance as the following example illustrates. It was previously shown in the HYDRAITE project that 0.5 ppm carbon monoxide causes no impact on voltage even after several hours (> 5) of operation. However, as shown in Figure 9, after poisoning with 0.5 ppm carbon monoxide for about 2 hours only, the tolerance is strongly reduced, when the catalyst surface is not cleaned.

When adding 5 ppm carbon monoxide after exposure to 0.5 ppm carbon monoxide for about 2 hours (in Figure 9, left), the poisoning time was 50% shorter compared to the measurement where pure hydrogen was used before the 5 ppm carbon monoxide addition (in Figure 9, right). It can also be seen that the measured oxygen concentration in the anode recirculation loop increases faster when the surface has been pre-contaminated with carbon monoxide.

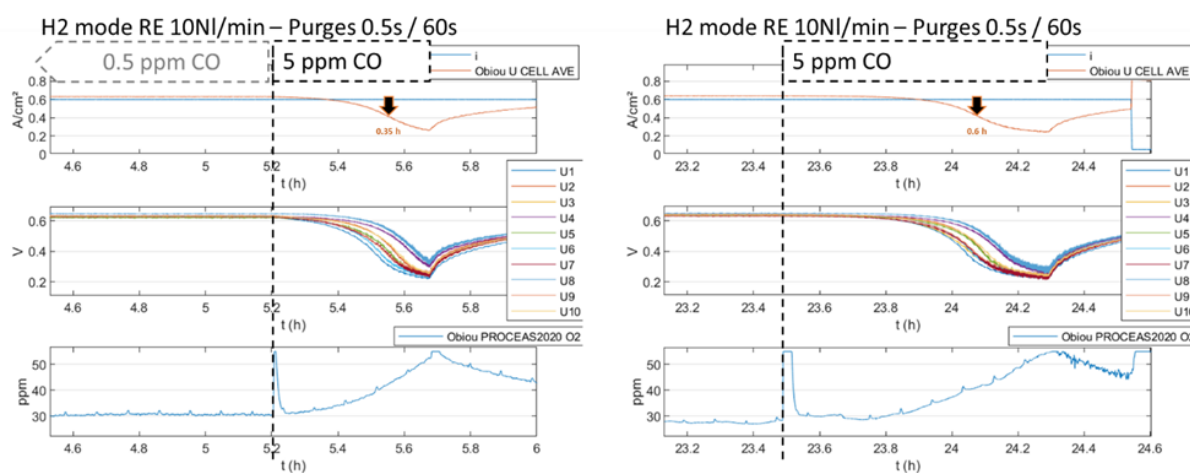


Figure 9. The effect of surface pre-contamination on fuel cell measurement.

### 5.6 Importance of fuel utilisation and fuel recirculation rate on CO poisoning

When a series of measurements were conducted with fuel utilisations of about 99.8%, 98% and 80-85% it was observed that a higher fuel utilisation decreased the poisoning time, as seen in Figure 10 and Figure 11. The poisoning time here is the time when average cell voltage decreased by 50 mV after carbon monoxide addition started.

When the recirculation rate was increased, it mitigated carbon monoxide poisoning at all purge interval times. The cathode humidity seemed to influence carbon monoxide poisoning times only when the fuel utilisation was very high. In Figure 10 and Figure 11 only the pump control value in % is shown, as accurate measurement of recirculation rate was not successful.

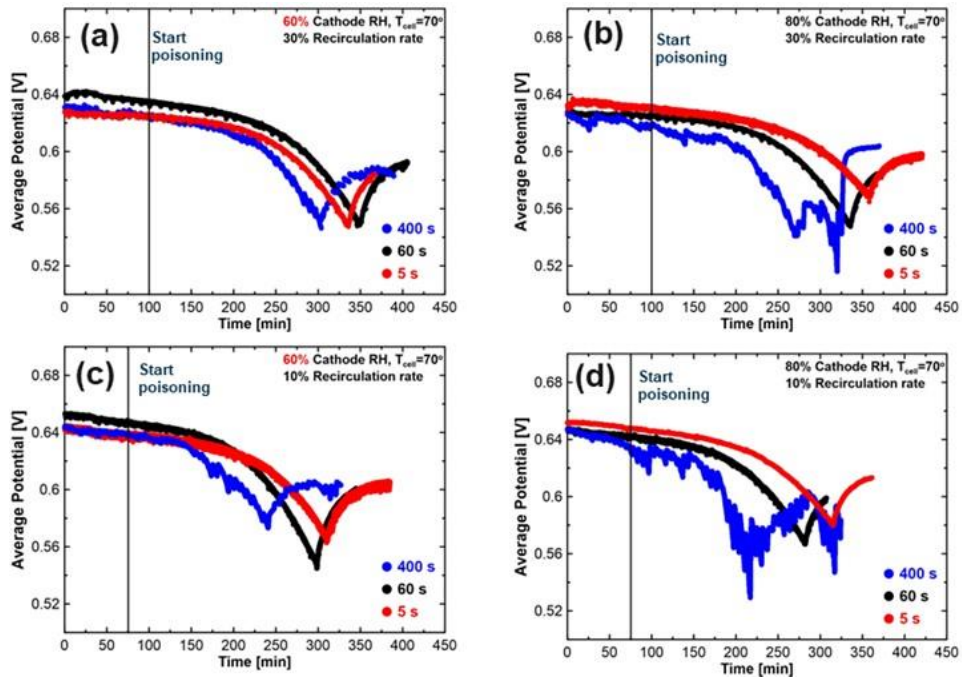


Figure 10. Poisoning times with 0.8 ppm CO concentration and 0.6 Acm<sup>-2</sup> current density. Purge frequencies 1/400 s, 1/60 s and 1/5 s correspond to FU about 99.8%, 98% and 80-85%, respectively.

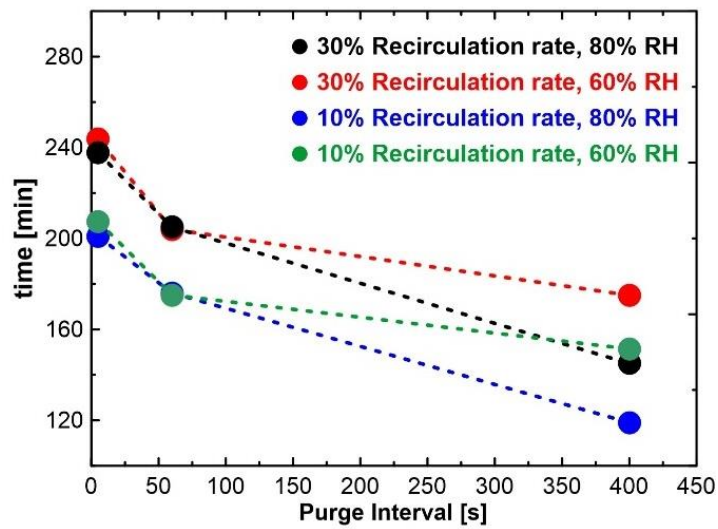


Figure 11. Collection of CO poisoning times.



## 5.7 Confirmed difference of operation between recirculation and stoichiometric mode

Matsuda et al. [1] observed a significant impact of anode gas recirculation on carbon monoxide contamination in single cell (25 cm<sup>2</sup>) measurements. The carbon monoxide tolerance was reported to be 5 times better with recirculation if compared on a carbon monoxide concentration basis. If the carbon monoxide molar amount is used, the carbon monoxide tolerance is 2.5 times better, as the fuel stoichiometry was 2.0 in their stoichiometric mode (open anode) measurements.

In the MetroHyVe2 project this type of comparative measurement was repeated at the stack level, using 5 ppm and 1 ppm carbon monoxide pre-mixtures. The results are seen in Figure 12 and Figure 13. It is clearly seen that carbon monoxide tolerance is decreased when working with stoichiometric (open anode) mode. The poisoning time with the same voltage drop is about 40% shorter. It can also be noted that individual cell voltages do not present same behaviour.

These stack level measurements confirm the beneficial effect of recirculation compared to open anode measurements, while the mitigation due to recirculation is smaller than in the single cell measurements of Matsuda et al. [1]. It should be noted that in both of these studies the anode catalyst was pure platinum and anode catalyst loadings were small (0.05 and 0.1 mgPtcm<sup>-2</sup>). The difference between stoichiometric (open anode) mode and recirculation mode can be smaller or larger with other loadings and with other catalysts. However, these stack level results confirm the observation of Matsuda that there is a risk of incorrect interpretation if operating without recirculation mode.

In these stack level measurements, there is some increase in measured oxygen level in recirculated gas, while in open anode measurements no increase can be observed. Matsuda et al. have previously measured an increase of 80 ppm in oxygen concentration even when very mild poisoning (30 mV) was taking place during 0.4 ppm carbon monoxide measurement [1].

Most of the base level oxygen concentration (about 30 ppm) in these MetroHyVe2 experiments is most probably due to sample contamination. The other partners could not measure any oxygen using microGC (with a limit of detection of 10 ppm) after elimination of sample contamination. The observed oxygen level increase in 5 ppm carbon monoxide measurement is 25 ppm while in a 1 ppm carbon monoxide measurement it was about 10 ppm, when full poisoning was achieved. These are most probably close to real levels of oxygen in the anode loop.

Therefore, the mitigating effect of recirculated oxygen was not very large in stack measurements. Previous work has shown that the oxygen concentration should be at least 100 times more than carbon monoxide level to mitigate the carbon monoxide poisoning completely [7]. The small increase in oxygen level does not explain the large difference in carbon monoxide tolerance between recirculation mode and stoichiometric mode.

In recirculation mode, the anode flow rate is significantly higher than in open anode mode. As shown in the previous chapter the recirculation rate has a mitigating effect, most probably due to more even carbon monoxide distribution on the anode catalyst surface, which slows down the accumulation of carbon monoxide on the anode Pt catalyst surface close to the inlet of the cell. This is also in line with single cell results in the literature [8].

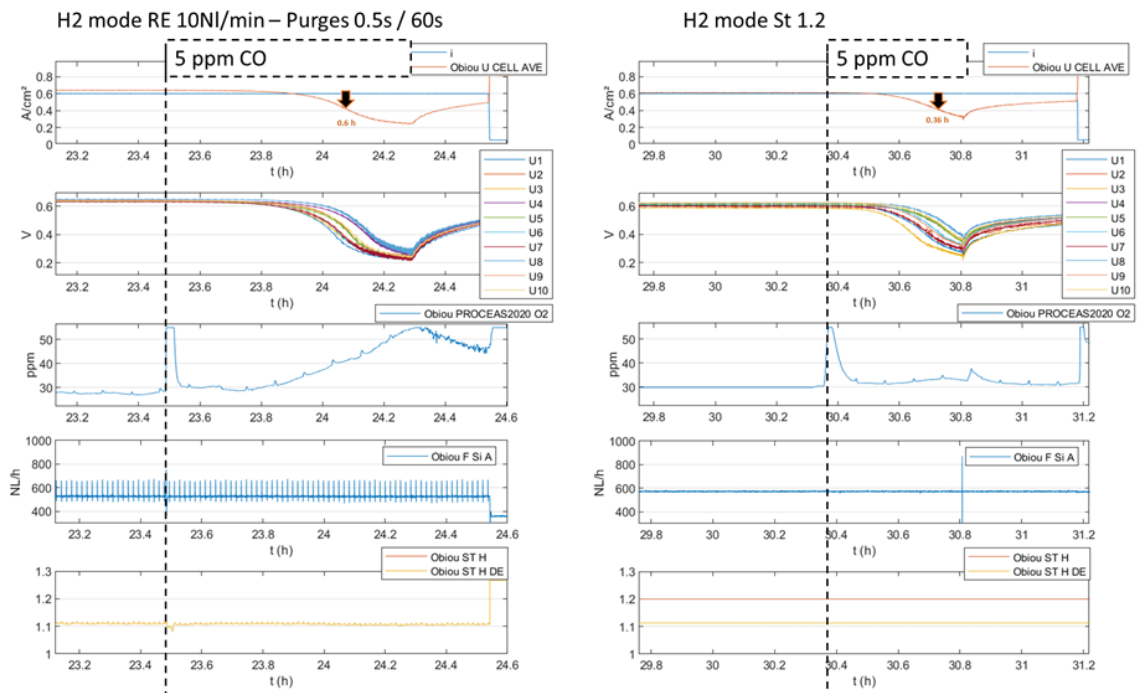


Figure 12. Poisoning with 5 ppm CO in hydrogen. Left: recirculation mode. Right: Stoichiometric anode.

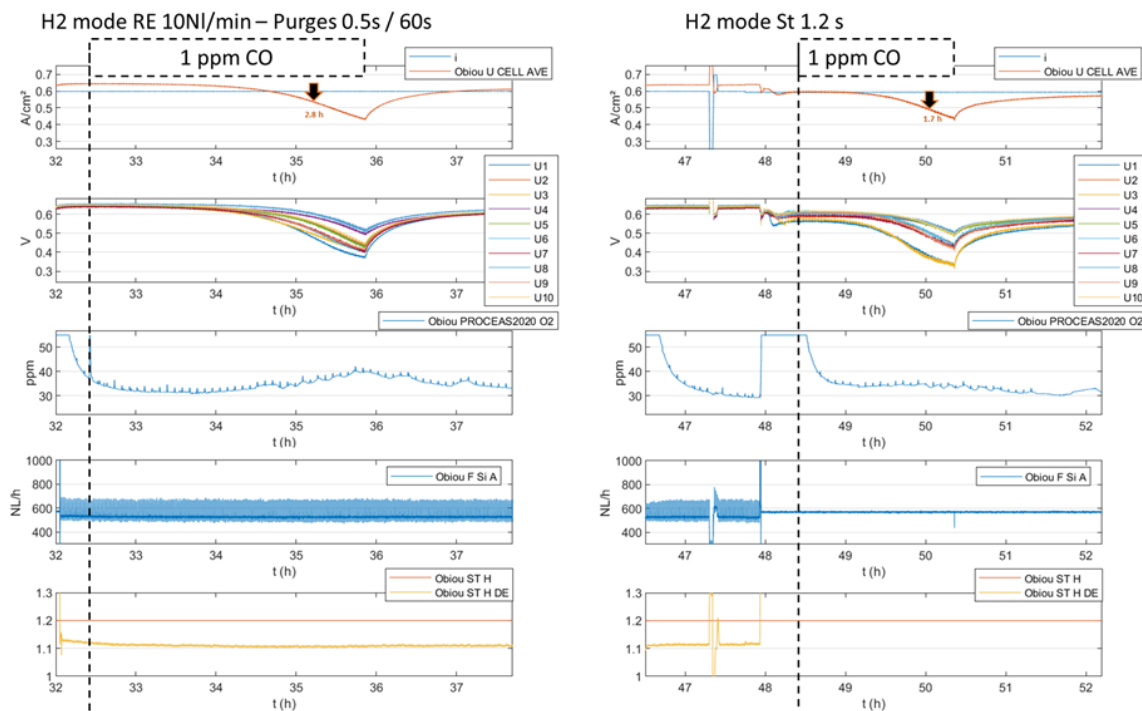


Figure 13. Poisoning with 1 ppm CO in hydrogen. Left: recirculation mode. Right: Stoichiometric anode.

The oxygen concentration in the anode recirculation loop is one key parameter for the improved carbon monoxide tolerance, when anode recirculation is applied. As shown in Figure 12 and Figure 13 there is a clear increase in oxygen level, starting from about 30 ppm, especially in the measurement with 5 ppm carbon monoxide. In measurements of the previous HYDRAITE project the lowest measured oxygen levels were under 10 ppm when similar stacks were used.

Therefore, additional measurements with more extensive poisoning were performed to verify the initial level of oxygen and increase of oxygen level during extended carbon monoxide poisoning. Figure 14 shows the result of one poisoning measurement. The increase of oxygen level over 10 ppm can only be measured when the cell voltage drop has exceeded 50 mV. The level of oxygen is a few tens of ppm, when the cell voltage drop was 300 mV. In the measurement of Matsuda et al. [1] the oxygen level was 200 ppm, when the cell voltage drop was 200 mV.

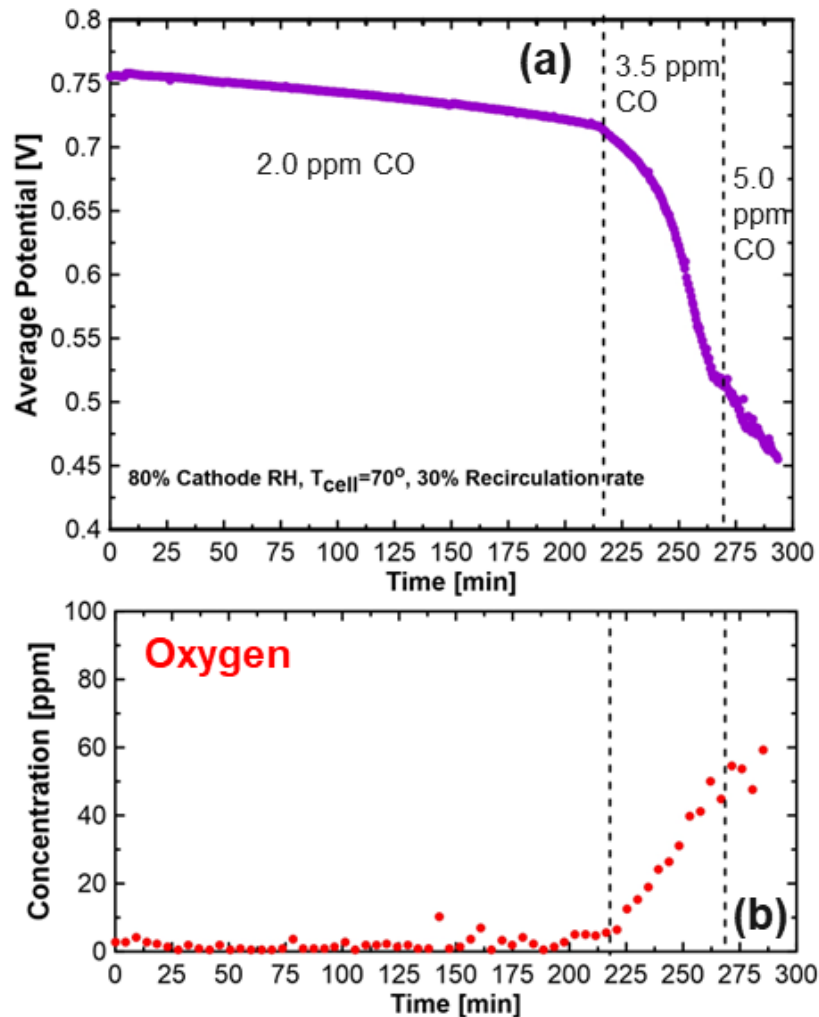


Figure 14. (a) Average potential, (b) oxygen concentration in extended CO poisoning

It can be concluded that there may be a significant increase of the oxygen concentration in the recirculation loop when carbon monoxide poisoning takes place. In the stack level measurements of the MetroHyVe2 project the increase of oxygen is much smaller than in the single cell measurements of Matsuda et al. [1]. The importance of the oxygen level in the recirculation loop can be dependent on cell and stack design as well as the stack's membrane electrode assembly. Therefore, for carbon monoxide poisoning measurements it seems that use of a recirculation loop is necessary to determine carbon monoxide tolerance accurately.

### 5.8 Measurement and elimination of O<sub>2</sub> contamination

When determining threshold limits of carbon monoxide in hydrogen one important part of the work is to eliminate additional oxygen in the anode fuel. The current limit of oxygen in the ISO standard is 5 ppm. Additional oxygen mitigates the poisoning effect of carbon monoxide and carbon monoxide

forming compounds. The measurement of small levels of oxygen in hydrogen requires elimination of all possible sources of sample contamination. A procedure to verify elimination of sample contamination should be developed and applied, before measurement of oxygen level in hydrogen gas.

### **Humidifier issue**

One well-known issue is that oxygen is dissolved in humidifier feedwater. This problem is present both in usual open anode measurements (stoichiometric mode) as well as in recirculation mode measurements if a humidifier is used. The maximum level of oxygen in anode humidifier feed water (e.g. 15 mg/kg in Helsinki area) is sufficient to increase the oxygen level in hydrogen to a few ppm, which can mitigate the effect of few tens of ppb carbon monoxide, if water is only consumed for gas humidification. This small effect is seen in carbon monoxide tolerance measurements when there is periodic refilling of humidifier.

The oxygen issue in humidifier water becomes much worse if water bleeding is applied to keep the humidifier water clean in certain types of humidifiers. The water consumed in this bleeding can be tens or even hundreds of times more than that consumed in humidification. Correspondingly, the added oxygen can mitigate carbon monoxide poisoning significantly.

In MetroHyVe2 project the bleeding effect was briefly studied and carbon monoxide levels were confirmed to be unacceptable if water bleeding was applied. Due to this, if anode humidifiers are used in carbon monoxide contamination measurements, then the water bleeding should be disabled. This should minimise the oxygen contamination effect to a level which is acceptable. However, it is recommended to measure the resulting oxygen level to confirm this.

### **Recirculation pump issue and gas permeability testing**

When anode humidification is done by using anode gas recirculation, then the issue of humidifier feedwater oxygen can be eliminated. However, in the MetroHyVe2 project it was noticed by one partner that a recirculation pump could also introduce some oxygen (20-30 ppm) which was circulated in the anode recirculation loop. This issue was only noticed, when all other sources of oxygen (sample contamination) were eliminated. This illustrates the importance of eliminating oxygen (air) contamination in gas sampling.

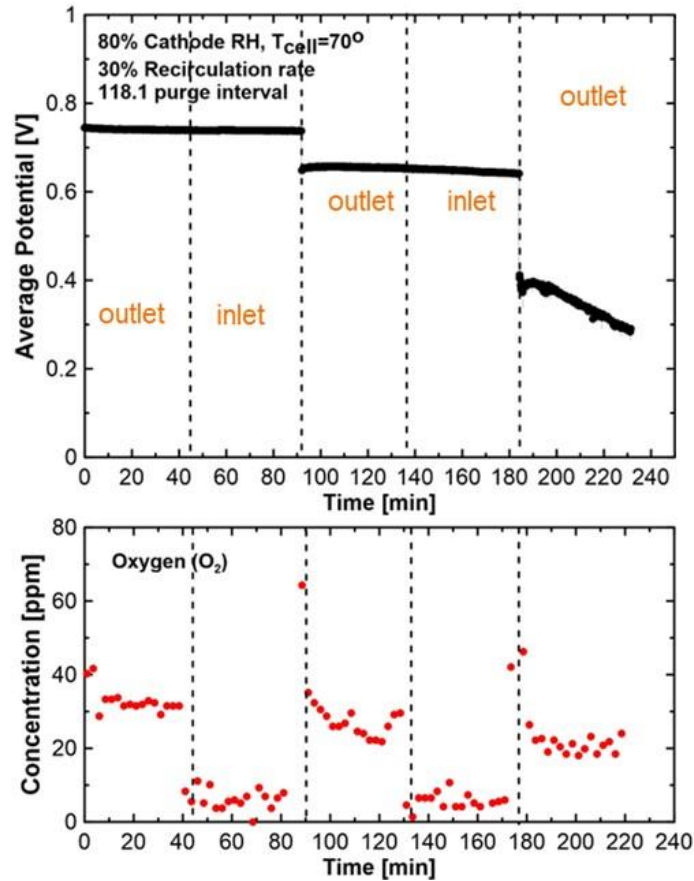


Figure 15. Average cell voltage and measurement of oxygen concentration at the inlet and outlet of the recirculation pump.

The following leak and permeability testing procedure was developed for the measurement of oxygen introduced by a pump or leak. Instead of a normal shutdown the following steps are done. 1) Anode purge valve is turned off 2) Load is set to zero and disconnected 3) nitrogen is fed to the cathode.

After these steps the anode gas contains hydrogen, nitrogen, argon, carbon dioxide and possibly tracer gas (methane) if added, while oxygen should be consumed quickly as there is no new oxygen coming from the cathode. The nitrogen concentration in the anode loop should increase while the hydrogen, argon, carbon dioxide concentrations will decrease, as shown in Figure 16. If no leak is present then these will decrease to nothing. The permeability of the gases (methane, carbon dioxide, argon) through the membrane can also be determined when the anode gas volume is known.

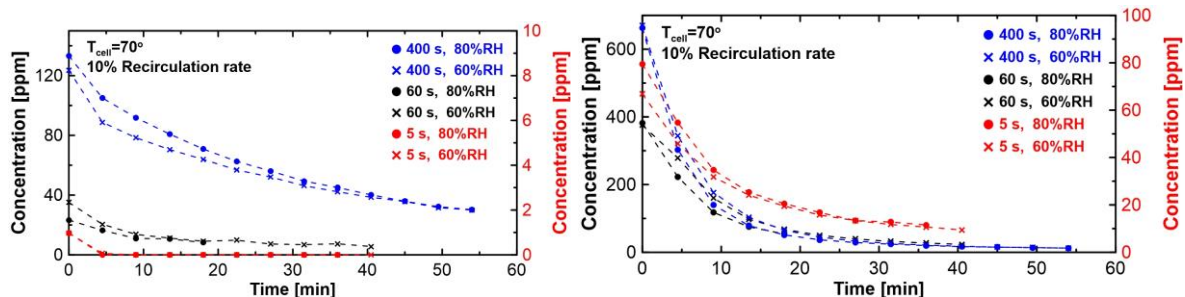


Figure 16. Decrease of concentration in the anode loop when leak and permeability testing procedure applied. Left: Methane. Right: Carbon dioxide. Data from the same measurements as in Figure 10.

## 6. Summary and conclusions

In this report some standard test protocols and practices were proposed concerning PEMFC measurements with stacks to determine threshold limits of critical contaminants in hydrogen.

When contaminant tolerance measurements are performed, anode gas recirculation should be applied, instead of operation in stoichiometric mode. This conclusion is based on the results of the MetroHyVe2 project and previous HYDRAITE project, as well as results from the literature. The recirculation rate should be realistic as the recirculation rate has an impact on contamination time.

When carbon monoxide tolerance is measured, a key parameter to monitor is oxygen content in the anode recirculation loop. The increase of oxygen concentration in the loop will mitigate the effect of carbon monoxide. A procedure to identify and eliminate sample contamination by air should be used. A procedure to measure oxygen level introduced by the humidifier and recirculation pump should be used.

In measurements the fuel utilisation rate should be kept high (> 98%) but not so high that the control of fuel utilisation becomes too complicated. The purge volume may start to fluctuate too much at very high (> 99.5%) fuel utilisation rates.

Due to variation in anode purge volume and poor accuracy of MFC dilution during DLC it is recommended to use pre-mixture bottles of impurities in hydrogen where possible, though the gas cost may be high.

Dynamic load cycling (DLC) seems to be unnecessary in all measurements and can be replaced by static load cycling (SLC). DLC should be avoided, where possible, as the operating conditions of the stack will likely be different across different stacks and test benches during dynamic operation making reproducibility exceptionally challenging. The maximum difference between DLC vs SLC should first be measured and if the difference is small and reproducible SLC can be used instead of DLC.

A procedure to clean carbon monoxide from the surface was tested and verified to be acceptable. It was also shown that any exposure to low level carbon monoxide prior to actual carbon monoxide contamination measurement will change the result. Therefore, when the surface has been cleaned the conditioning time before carbon monoxide tolerance measurement should be kept minimum.

A procedure to test anode carbon monoxide tolerance using 5 ppm CO at low or medium current density level has proven to be an easy way to monitor stack state of health and differences in test benches.

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