METROLOGY for HYDROGEN VEHICLES

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Fuel cell impurity measurements

Jari Ihonen (VTT)

Workshop on hydrogen quality and flow metering for hydrogen fuel cell vehicles
11-12 September 2019, Delft (NL)

EMPIR EURAMET FCH

Overview

- In this presentation measurement challenges related to fuel cell impurity measurements in ISO 14687-2:2012 standard are reviewed.

- These measurement challenges have determined the measurements methods and equipment, which are used in HYDRAITE project.

- The solutions for measurement challenges are presented as well as examples of experimental set-ups from two HYDRAITE partners

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The objectives of fuel cell impurity measurements in HYDRAITE project

- To provide recommendations for revision of ISO standards, governing threshold contaminant levels in hydrogen for automotive fuel cell applications, including existing contaminants and contaminants introduced by HRS components and operation and maintenance practices.

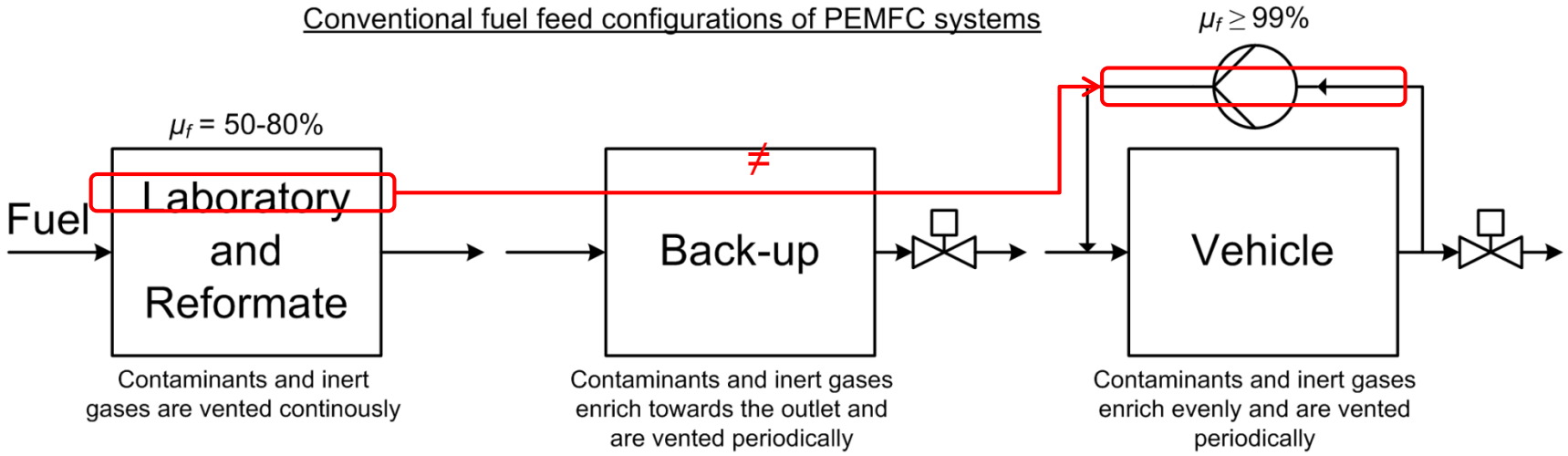
- To develop recommendations for conducting fuel cell contaminant measurements at stack level in automotive type operation.

Measurement challenge

- The general challenges for determining limit for contaminants in hydrogen for ISO 14687-2:2012 standard – a need for high fuel utilisation and stack level measurements
- The challenge of oxygen
- The challenge of CO2 effect
- The challenge of right shut-down / start –up procedure

General challenges

Open anode, back-up and automotive systems



- In automotive PEMFC, fuel utilization is up to 99.5-99.8% (lower with thinner MEA)
  - Contaminants and inert gases can enrich up to 200-500 times in anode.
  - In laboratory test station (with open anode) enrichment is 2-5 times.

- In automotive PEMFC N_2 is enriched up to 10-30%, even higher.
  - This is possible partially due to purge operation – removes water

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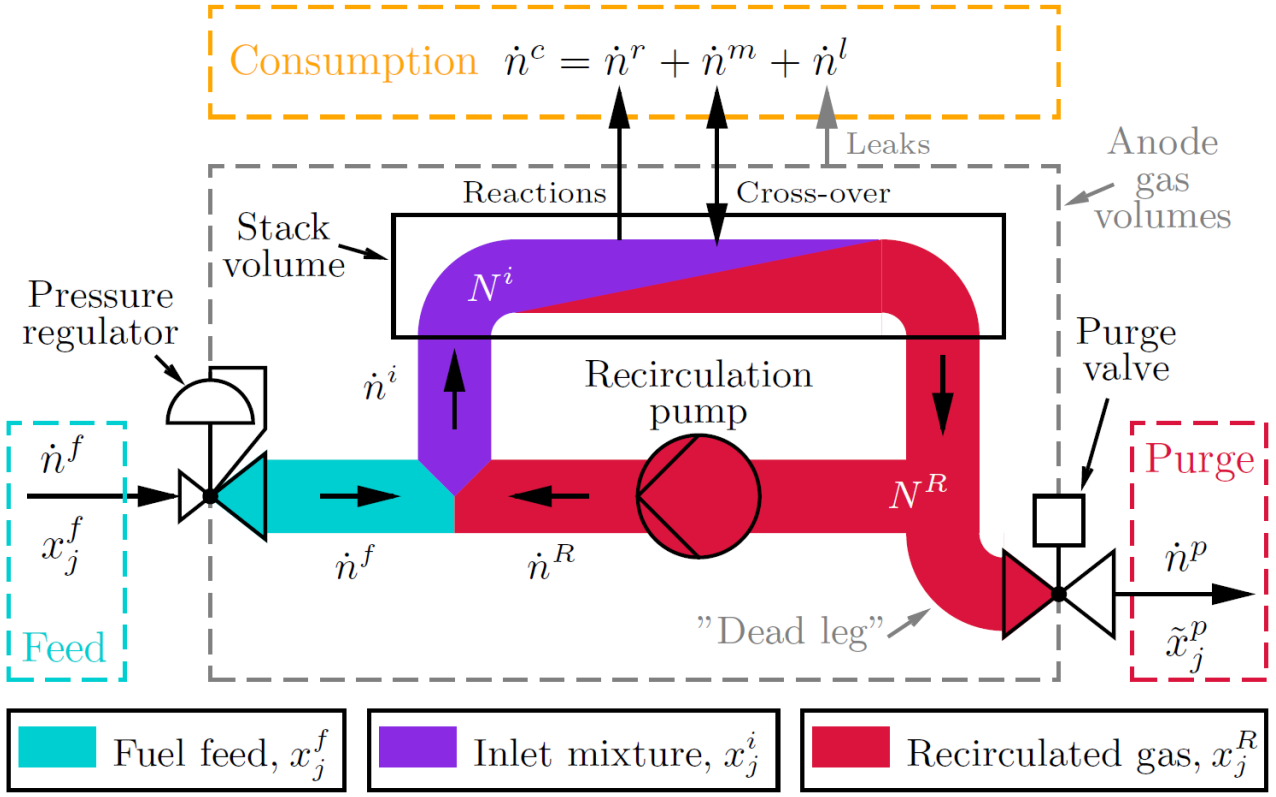
PEMFC with recirculation system - details

- 99-99.8 % of H2 is typically consumed
  - The lower the current the lower the uf
  - The thinner the membrane the lower the uf
- Most of N2, CO2 come from the cathode
- Purge gas may contain ”fresh fuel” if purge is too long
- Humid is kept in the loop and anode is humidified by recicylated anode gas
- Purge gas composition may differ slightly from recirculated gas due to ”dead leg”



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Enrichment of impurities in anode recirculation loop

- Impurities can be enriched in the anode gas recirculation loop – if not adsorbed or converted to other molecules (e.g. CO $\Rightarrow$ CO_2)
  - Matsuda, et al. Review of Automotive Engineering 30:167-72.
  - Hashimasa et al. ECS Transactions, 26 (1) 131-142 (2010)
- The importance of enrichment depends on the contaminant and system studied
- For some contaminants (HCHO, HCOOH) enrichment and/or conversion was unknown and conservative assumptions were applied in ISO 14687-2:2012 due to lack of data – this is changing now (HyCoRA, JARI results)
- Contaminants from LOHC (toluene/MCH, Benzene/CH) can be a new topic of interest

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Oxygen issue

“New” issue in 2016:
Oxygen permeation through the membrane

Journal of Power Sources 318 (2016) 1–8

Adsorption behavior of low concentration carbon monoxide on polymer electrolyte fuel cell anodes for automotive applications

Yoshiyuki Matsuda [a, b, *], Takahiro Shimizu [a], Shigenori Mitsushima [b, c]

H I G H L I G H T S

- CO, CO_2 and O_2 in the anode exhaust were measured during the PEFC operation.
- CO coverage was estimated from gas analysis and CO stripping voltammetry.
- The CO coverage at low CO concentration followed a Temkin-type isotherm.
- The CO coverage was 0.6 at 0.2 ppm CO and 0.11 mg cm^{-2} anode loading at 60 °C.
- Permeated O_2 should have an important role for CO oxidation at low CO concentration.

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Oxygen detected at the exit of the PEMFC

- 30-75 ppm oxygen is detected at the anode exit, depending on CO poisoning level. 5 ppm in standard.
  - The amount of O2 at the anode exit can be tens of times (30-100) more than CO at the inlet

- The result is valid for 60° C, atmospheric pressure, 1 Acm^{-2} and 0.11 $mgcm^{-2}$ Pt loading

- How in other conditions?

dV = 46 mV

dV = 200 mV

dV = 29 mV

~ 75 ppm O_2

~ 30 ppm O_2

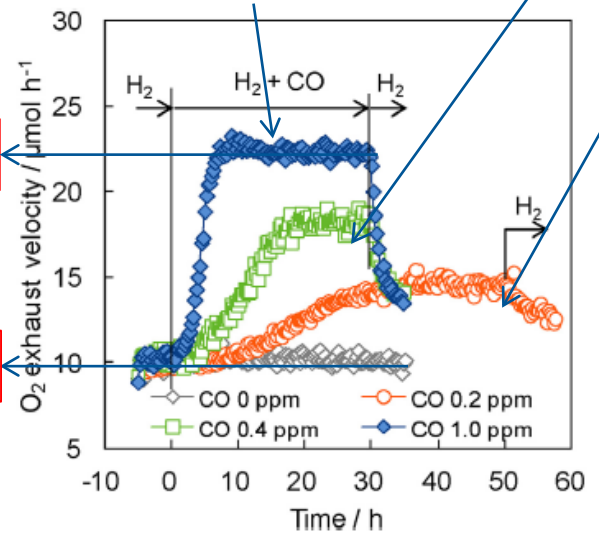
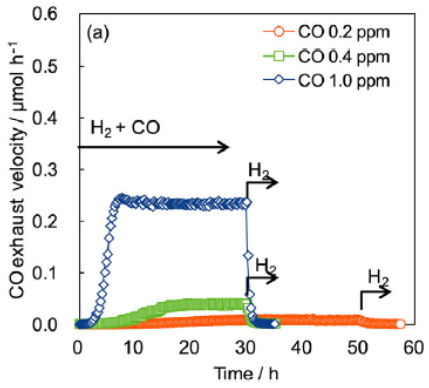
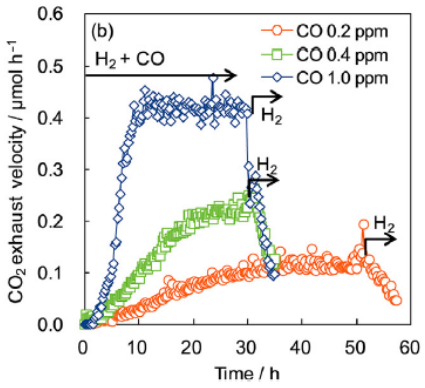
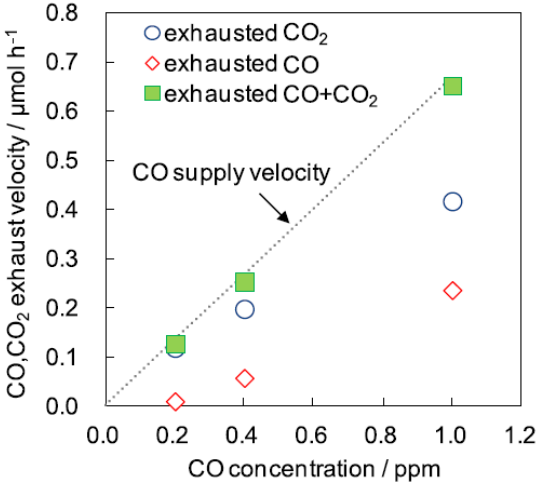
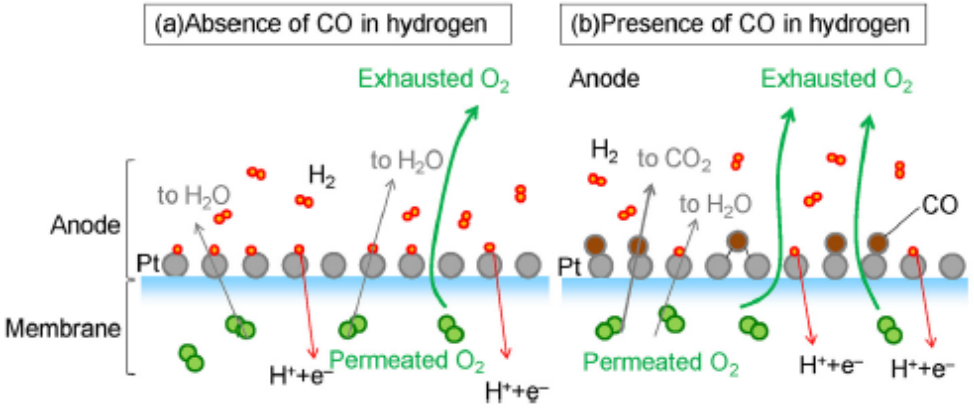


Fig. 7. Oxygen exhaust velocity change at the cell outlet over time during CO exposure. The cell temperature was 60 °C and current density was 1000 mA cm^{-2}.









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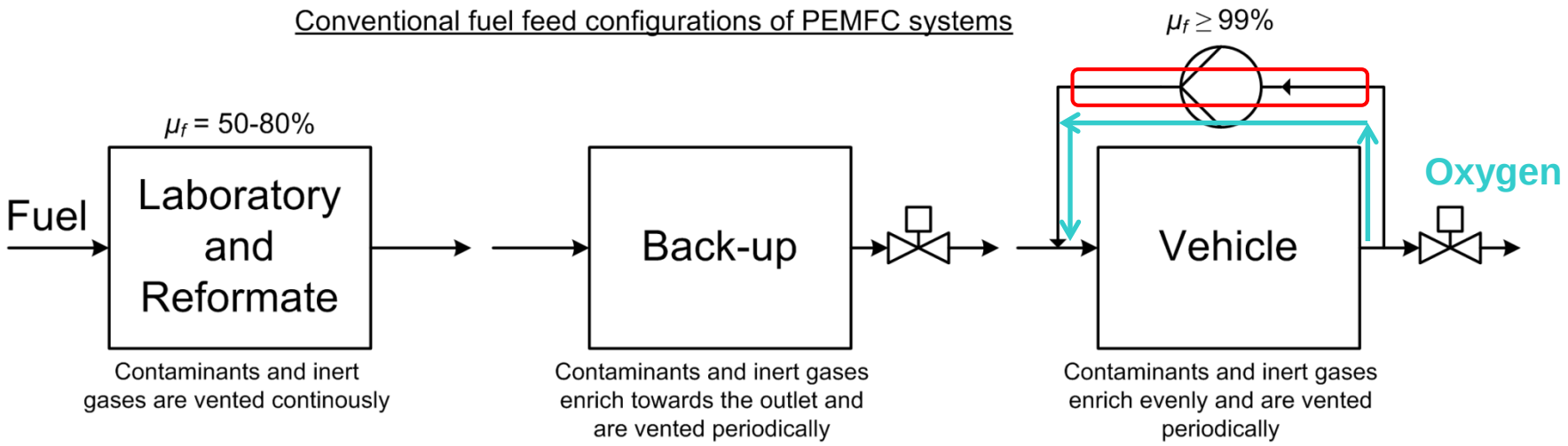
The effect of recirculation for CO poisoning



- O2 is recirculated at the level of tens of ppm all the time even at when cell is not pressurised, according to single cell measurements
  - With a typical selectivity of 1%, these would mitigate 0.3-0.75 ppm if used as ”air bleed” – actual level at the inlet depends on recirculation rate
- Recirculation may actually have a beneficial effect in CO poisoning compared to open anode due to recirculated oxygen.
  - For durability of membrane and catalyst layer (H2O2 formation) the effect might be negative.
- Importance increases with H2 soak SU/SD

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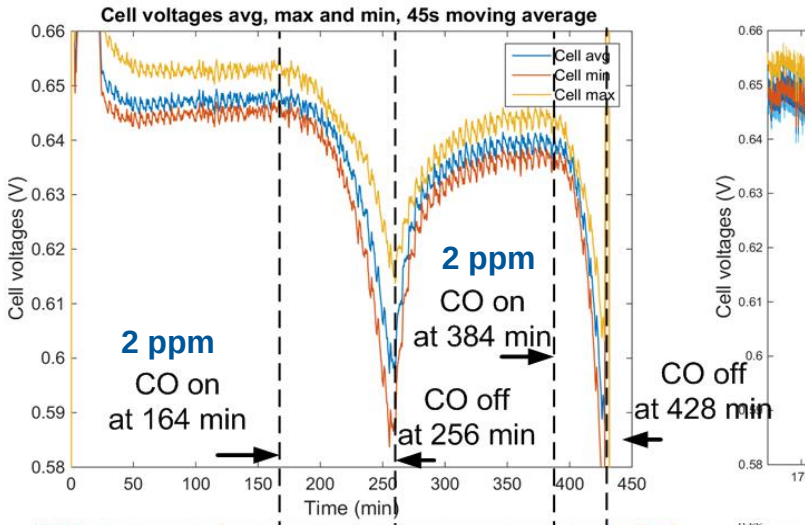
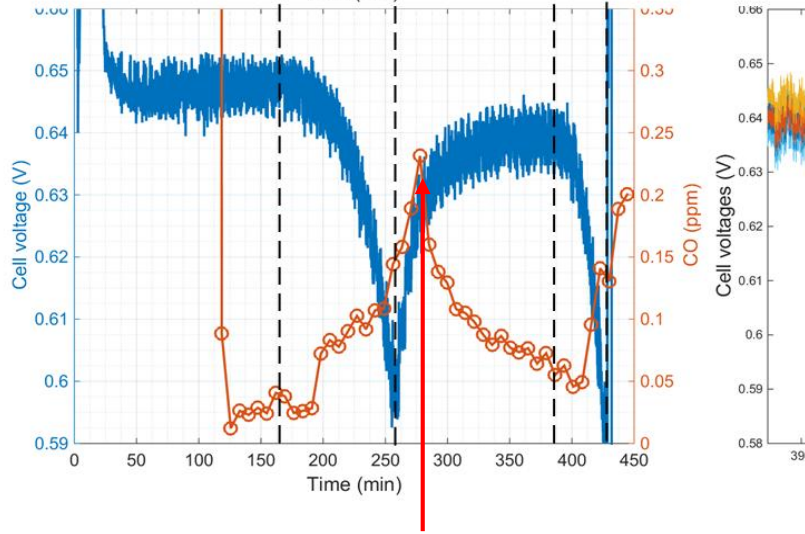
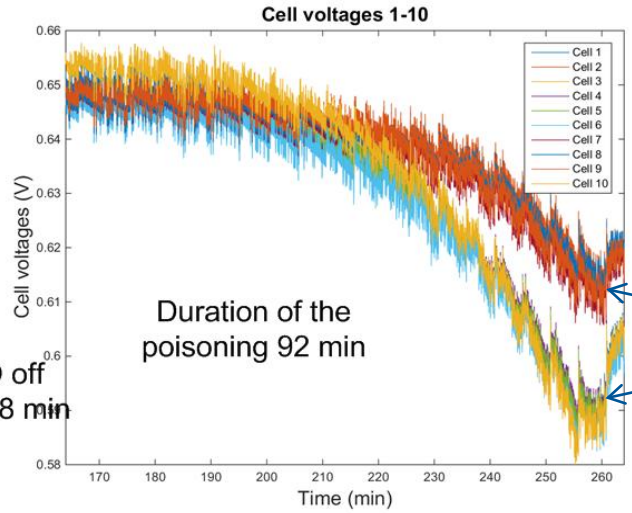
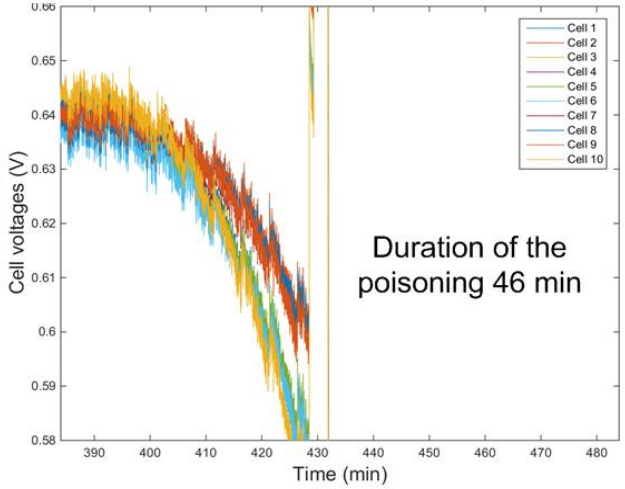
CO adsorption and enrichment in anode loop

- significant level of CO in the loop during the “recovery period”









10 cells in
2 groups:

4 and
6 cells

CO peak concentration 15 min after injection was stopped

Carbon dioxide issue

The contamination effect of CO_2 (+CO) is largely unknown

- The carbon dioxide limit of the ISO 14687-2:2012 is 2 ppm. At maximum fuel utilisation level (about 99.8%) this would lead to the level of 1000 ppm in the anode recirculation gas.
- CO2 from the cathode permeates to the anode. Therefore, there will always be some CO2 on the anode even if the hydrogen fuel is completely CO2 -free.
- It has been shown (e.g. Erbach) that there is a significant formation of CO from CO2. However, some of the measurements have been done in H2-H2 cell with limited relevance. The unavoidable existence of CO2 on the anode side means that there can always be formation of CO.
- In the literature, CO oxidation due to internal air bleed (and via electrochemical oxidation) has been measured using carbon balance calculation. In these measurements, CO2 free air has been used. The removal of CO2 from the cathode air reduce CO2 level at the anode side to the level, which is not representative compared to automotive type operation.
- Measurement CO oxidation rate **with CO2 present in hundreds of ppm** is a huge challenge!

The contamination effect of CO_2 by Erhach et al.

- anode Pt loading of 0.05mgcm-2, 15 μm membrane, but no anode recirculation, no CO+CO2 measurements

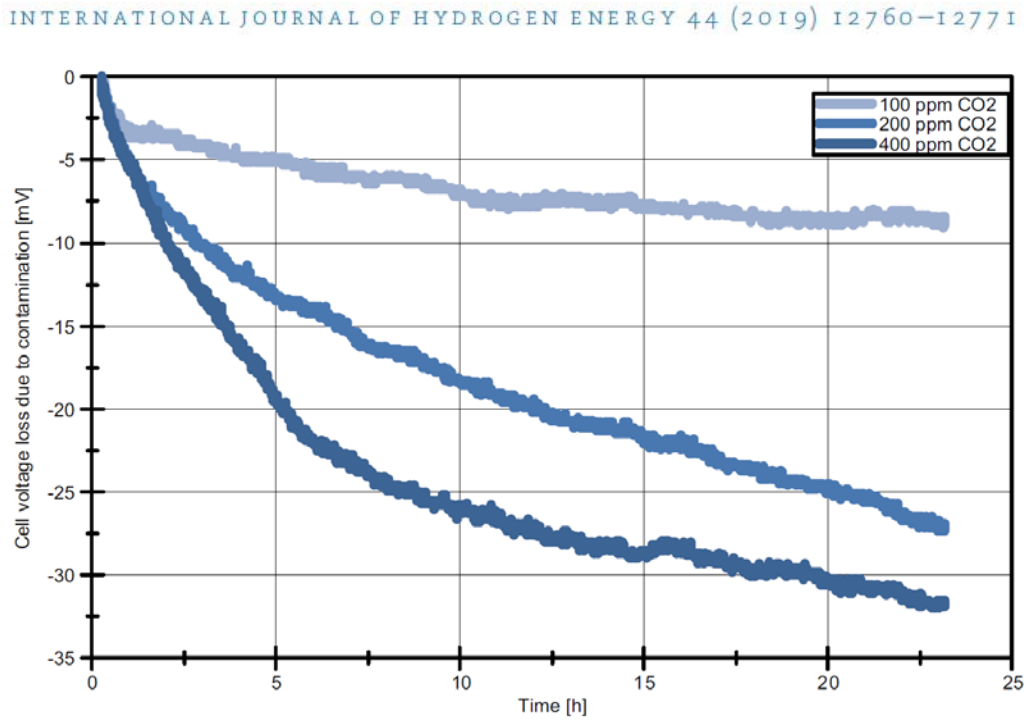


Fig. 4 Cell voltage loss for different levels of CO2 contamination at 1 A cm-2 in single cell.

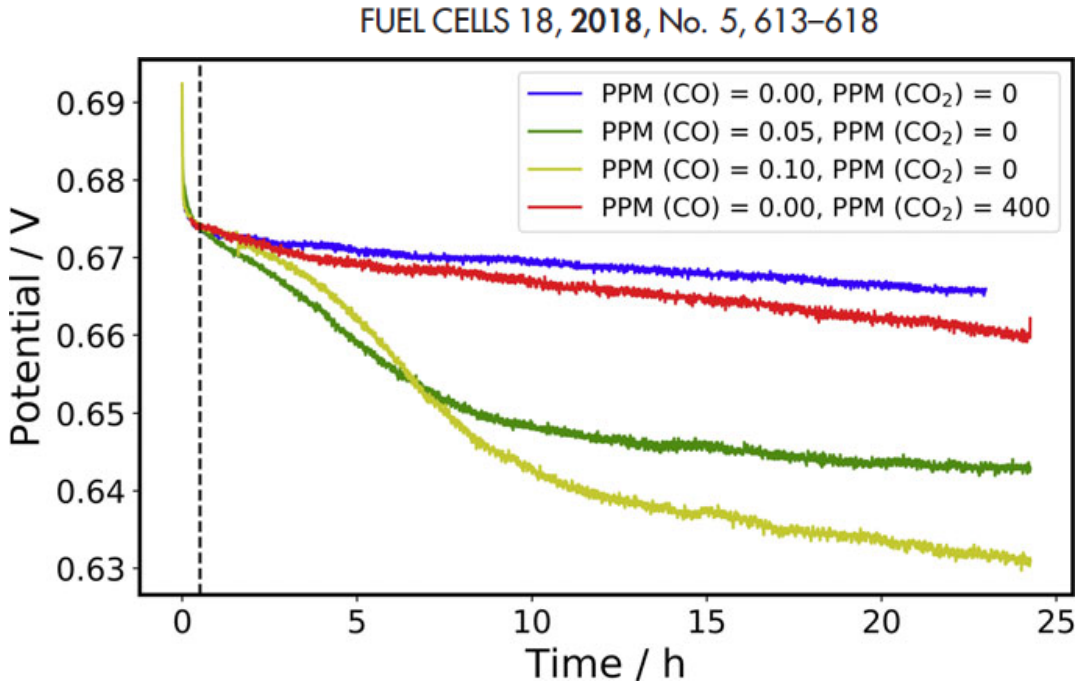
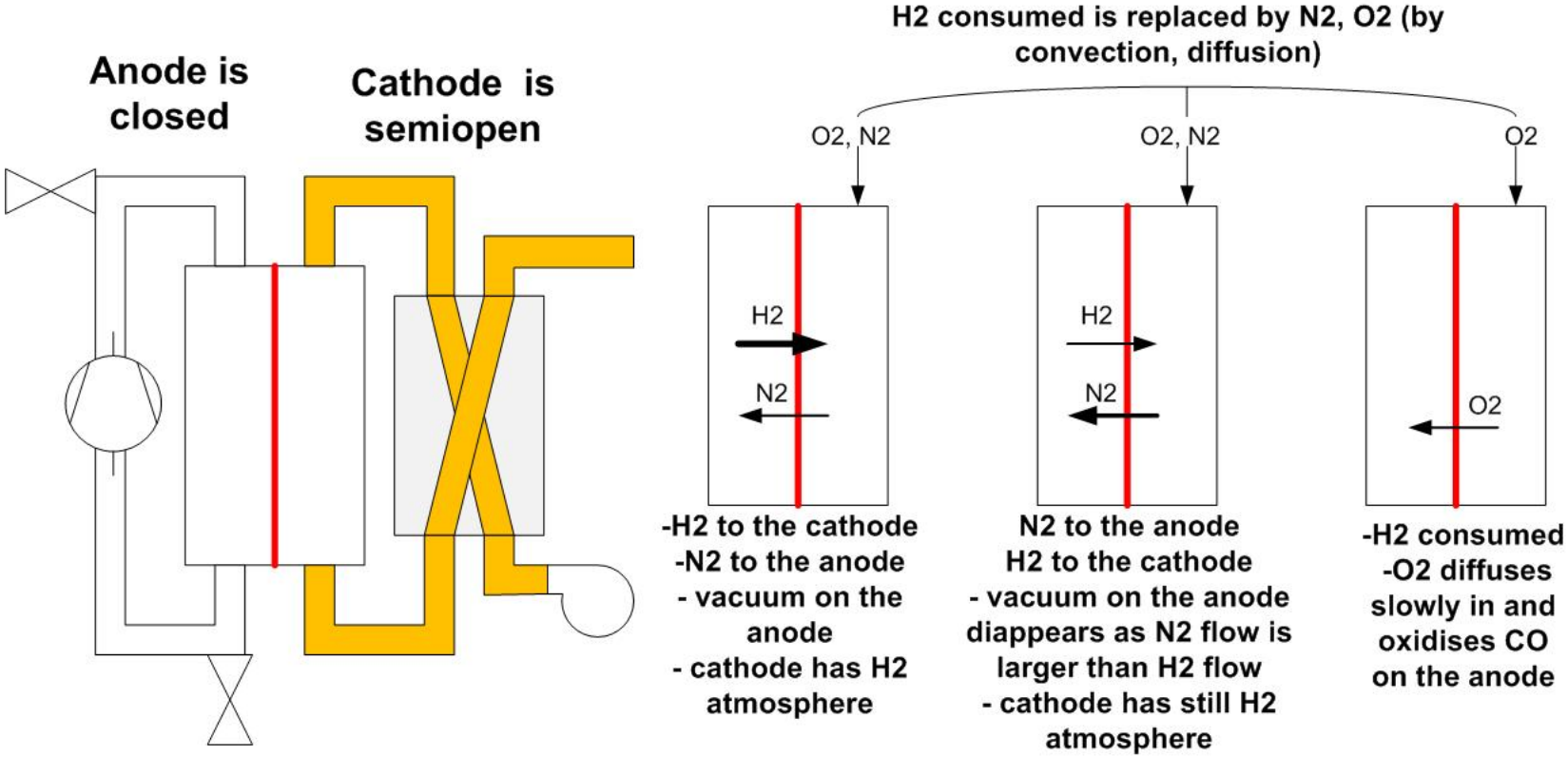


Fig. 4 Influence of different levels of contamination on the performance as function of time at 1Acm–2.

Start-up and shut down issue

Catalyst cleaning during shut-down and start-up

- with one shut-down strategy



The same gas exchange process is behind the problem of the reverse current decay. Modelling and measuring of the time constants for the process is the key for cleaning CO and minimising issues with reverse current decay.

Impact of SU/SD with 10 cell short stack in system

The ratio between the anode side volume (recirculation loop) and membrane area is 0.32 cm^3/cm^2.

In commercial systems the ratio is smaller.

Ratio will affect the cleaning of anode catalyst surface by air.

START		STOP	
Time (s)	***Start-up routine***	*Time (s)*	***Ramp-down routine***
0	Enable gas line heating	0	Load 80 A = 0.41 $A{\cdot}cm^{-2}$
10	Start air blower at 10 $l{\cdot}min^{-1}$		Impurity flow 2.231 $ml{\cdot}min^{-1}$ (2 ppm CO)
15	Check that air flow rate is OK		H2 recirc. pump control to 20%FS
10	Start coolant pump	34	Load 40 A = 0.21 $A{\cdot}cm^{-2}$
16	Check that coolant flow rate is OK		Impurity flow 1.116 $ml{\cdot}min^{-1}$ (2 ppm CO)
	Start H2 recirc. pump at 0% of full scale (%FS)		H2 recirc. pump control to 10%FS
18	Open H2 supply valve	68	Load 20 A = 0.10 A/cm^2
23	Check that anode inlet pressure is OK		Impurity flow 0.558 $ml{\cdot}min^{-1}$ (2 ppm CO)
24	Perform 200 ms purge		
25	Check that anode inlet pressure is still OK		***Shutdown routine***
30	Check that OCVs and CV-deviation are OK	103	Impurity flow to 0
	Load setpoint to 0 A		Set load to 0 A
31	Connect fuel cell main relay		Disable stoichiometric air flow control
32	Connect load to circuit (<0.1 A current drawn)	104	Disable purge duty cycle
33	Check that CVs and CV-deviation are OK		Perform air blower pulse
35	Set purge duty cycle to 200 ms/300s	105	Perform 200 ms purge (OPTIONAL)
			Disconnect load from circuit
	Ramp-up routine	106	Disconnect fuel cell main relay
46	Enable air flow control at 2.5 stoichiometry		Stop air blower
	Minimum flow corresponds to 40 A load demand		Close H2 supply valve
50	Enable coolant control with 80 °C setpoint	136	Stop H2 recirculation pump
59	Load to 20 A = 0.10 $A{\cdot}cm^{-2}$		Stop coolant pump
	Impurity flow 0.558 $ml{\cdot}min^{-1}$ (2 ppm CO)		Disable coolant control
92	Load to 40 A = 0.21 $A{\cdot}cm^{-2}$		Disable gas line heating
	Impurity flow 1.116 $ml{\cdot}min^{-1}$ (2 ppm CO)		
	H2 recirc. pump control to 10%FS		
126	Load to 80 A = 0.41 $A{\cdot}cm^{-2}$		
	Impurity flow 2.231 $ml{\cdot}min^{-1}$ (2 ppm CO)		
	H2 recirc. pump control to 20%FS		
160	Load to 117 A = 0.60 $A{\cdot}cm^{-2}$		
	Impurity flow 3.263 $ml{\cdot}min^{-1}$ (2 ppm CO)		
	H2 recirc. pump control to 30%FS		

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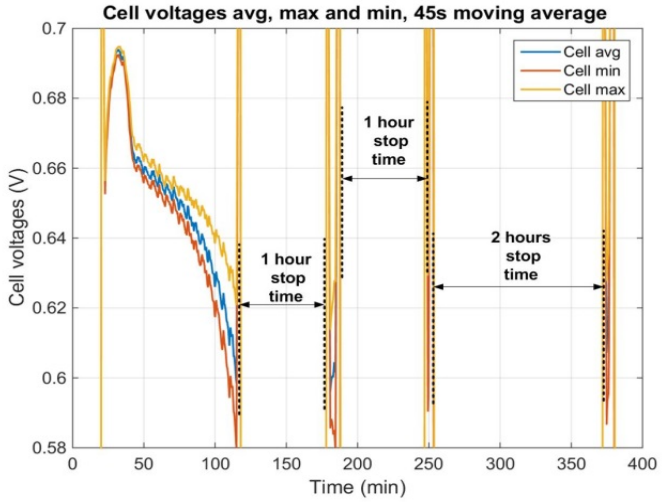
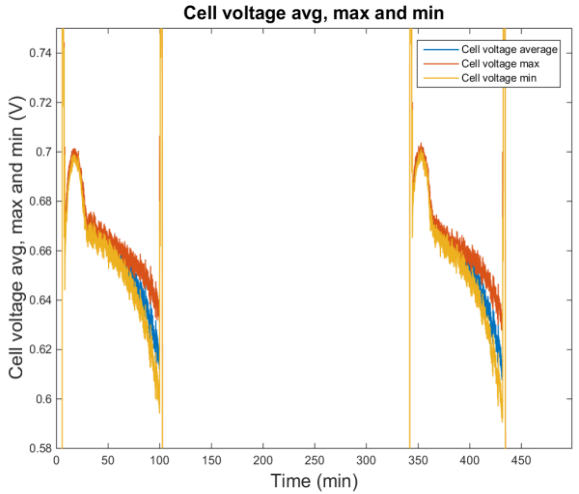
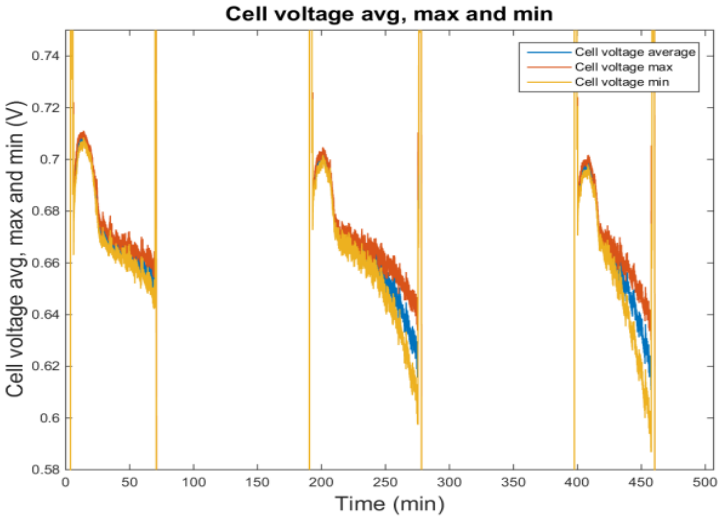
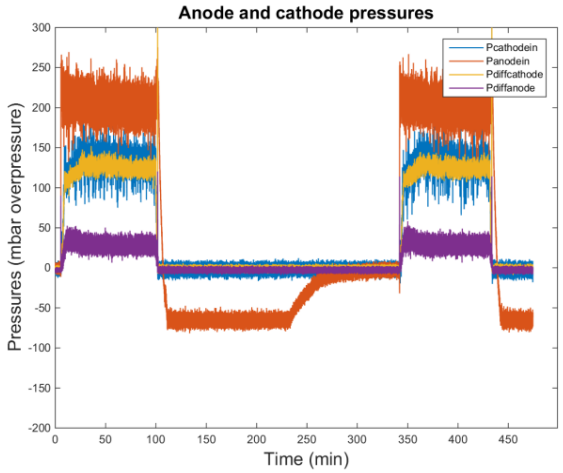
Impact of SU/SD – 2 ppm CO poisoning

- 1 hour has no effect, 2 hours some effect, 4hours almost full effect
- always a complete clean-up when the system was left overnight
- in future FCEV systems hydrogen soak is used and cleaning will be completely different









The main requirements for measurements

- Anode gas recirculation is needed for
  a) achieving very high (98-99.5%) fuel utilisation rate (uf)
  b) to omit anode humidifier and avoid O2/CO2 issues from water
- Gas analysis should be applied for measuring
  a) contaminant enrichment in the anode loop
  b) oxygen coming from the cathode and mixed with pure and dry inlet gas
  c) control of inlet contaminant mixture, including O2 if less than H2 5.0 used
- Stack level measurements are needed for
  a) reaching the same mass transfer and dynamics as in stacks
  b) achieving high uf when gas is consumed for gas analysis

The main requirements for measurements

- Complete removal of CO between measurements from anode needed
  - The anode catalyst surface needs to be clean from the beginning of the measurement
  - The procedure for cleaning the surcae should be verified

- SU/SD procedures should be compared
  - Shut-down with hydrogen filling cathode may be the main SD mode

- CO2 importance should be studied
  - For measurements to study internal air bleed effect MS or GC-MS needed for measuring $^{13}CO_2$ or $^{13}C^{16,18}O_2$ or $C^{16,18}O_2$

Plan for contamination measurements with sulphur

M5-M12 2 stacks from Task 2.1	**BoL**	**Irreversible contaminant**
	Powercell FAT and Reference CO-poisoning after Task 2.1 work	ZBT, NPL Reference characterization & Reference CO-poisoning S-contamination and recovery • SU/SD procedure keeping H2 on the anode side
M16-M30 Stacks from Task 2.1 and 2.5, or 4 new stacks	**BoL**	**Irreversible contaminant**
	Powercell Break-in, FAT and Reference CO-poisoning	CEA, ZBT Reference characterization & Reference CO-poisoning S-contamination and recovery • SU/SD procedure keeping H2 on the anode side
	Powercell Break-in, FAT and Reference CO-poisoning	CEA, NPL Reference characterization & Reference CO-poisoning S-contamination and recovery • SU/SD procedure including oxygen on the anode side

Experimental challenges for S-contamination and desorption measurements

- S-measurement (preferably H_2S and SO_2 but total S is ok) with detection level of few tens of ppb.
- Condensing and collection of anode exhaust water

  H_2S and SO_2 dissolve in water

- Capability to perform CO tolerance measurements

  Exit gas CO measurement preferred, but not mandatory

  Control of O2 level for the used hydrogen

- Capability to perform at least 2 different SU/SD procedures applied (or planned) by automotive industry

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Examples of experimental equipment and methods used in HYDRAITE project

Solutions for experimental challenges

Exit/recirculation gas measurement

Partner	Exit gas measured and accuracy (LoD, LoQ)	Instrument used and comments (e.g. gas consumption)
VTT	CO, CO_2, CH_4 LoQ estimated ~ 0.1 ppm H_2, N_2, O_2 LoQ estimated ~ 5 ppm ^{13}CO, $^{13}CO_2$ LoQ estimated several ppm	Agilent GC 7890B (FID, TCD + PD HID) - gas consumption very low (valve loop only) OmniStar quadrupole MS several mL/min (10 mL/min), not verified
SINTEF	CO, CO_2, N_2, O_2. LoD and LoQ for different components not yet determined quantitatively ^{13}CO, ^{12}CO and CO_2: FTIR LoD ~ 5 ppm	GC-PDHID run in anode recirculation loop of test station. Gas consumption is only the amount injected onto column < 1 mL/min so negligible. FTIR will be used to differentiate ^{13}CO from ^{12}CO. No gas consumption.
CEA	CO and CO_2 validated (LoD 1 ppb and 2 ppb respectively) CH_4 and H_2S (LoD 10 ppb and 2 ppb respectively expected) N_2, O_2 and H_2O (LoD not yet determined)	ProCeas (laser IR spectrometer) – to be adapted/calibrated for CH_4 and H_2S Addition of O_2 measurement is current priority (with the µGC or new device will be purchased) ProCeas H_2 purity analyser (laser IR spectrometer) gas consumption 3-9 L/h Proceas will be upgraded for CH_4 and H_2S detection too SRA µGC-TCD, injection loop = 1-15 µL
NPL	CO (LoQ 19 ppb – 5 mL loop in the GC) CO_2 (LoQ 5 ppb – 5 mL loop in the GC) CH_4 (LoQ 5 ppb – 5 mL loop in the GC) $^{13}CO_2$ (LoQ estimated 1 ppm) H2S (LoQ estimated few ppb)	GC-methaniser-FID (CO, CO_2, CH_4) SIFT-MS ($^{13}CO_2$, H_2S)
ZSW	CO, LoD: 0.1 ppm, LoQ: 0.2 ppm CO_2, LoD/LoQ: *not quantified yet*	SICK GMS810 (NDIR, TC, paramagnetic O_2 sensor), sampling and feeding back to anode loop is planned
ZBT	Exit (dry): H_2S, H_2S tendencies (wet, recirculation) Water sampling Mankenberg (external analysed) (uncoated, inaccurate, as water must be partly filled before the test in order to seal the device) Recirculation gas	Exit Agilent SCD, MS4-Combisense* * start up and validation phase Mankenberg water trap

Inlet hydrogen measurement

Partner	Limit of detection (LoD) and/or limit of quantification (LoQ)	Instrument used and comments (e.g. gas consumption)
VTT	CO, CO_2, CH_4 LoQ estimated ~ 0.1 ppm H_2, N_2, O_2 LoQ estimated ~ 5 ppm ^{13}CO, $^{13}CO_2$ LoQ estimated several ppm	Agilent GC 7890B (FID, TCD + PD HID) - gas consumption very low (valve loop only) OmniStar quadrupole MS several mL/min (10 mL/min), not verified
SINTEF	CO, CO_2, N_2, O_2, LoD and LoQ for different components not yet determined quantitatively	GC-PDHID run in anode recirculation loop of test station with stack anode bypassed
CEA	CO and CO_2 validated (LoD 1 ppb and 2 ppb respectively) *Normally Hydrogen 4.5 is used at CEA on test stations but for HYDRAITE, Hydrogen type 5.7 will be ordered to ensure highest purity requested at stack inlet*	ProCeas H_2 purity analyzer (laser IR spectrometer) – to be adapted / calibrated for CH_4 and H_2S Addition of O_2 measurement is current priority (with the µGC or new device will be purchased)
NPL	CO (LoQ 19 ppb – 5 mL loop in the GC) CO_2 (LoQ 5 ppb – 5 mL loop in the GC) CH_4 (LoQ 5 ppb – 5 mL loop in the GC) $^{13}CO_2$ (LoQ estimated 1 ppm) H_2S (LoQ estimated several ppb)	GC-methaniser-FID (CO, CO_2, CH_4) SIFT-MS ($^{13}CO_2$, H_2S)
ZSW	Hydrogen purified at the test bench inlet, 7.0 grade or higher CO, LoD: 0.1 ppm, LoQ: 0.2 ppm CO_2, LoD/LoQ: *not quantified yet*	SICK GMS810 (NDIR, TC, paramagnetic O_2 sensor) – for validation procedures. Gas analysis moved to the anode loop after mixing bank performance validation.
ZBT	Purifier 9.0 or analysis of H_2 (5.0) content (H_2S LoD < 5 ppb, O_2 < 5 ppm) Analysis of contamination volume flow (1 ppm H_2S, 5 ppm CO)	Alicat mass flow controller (device error tolerance), purifier 9.0 or analysis of H2 (5.0) content. Agilent SCD, MS4-Combisense* * start up and validation phase

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Solutions for experimental challenges

Method for estimating fuel utilisation (enrichment ratio)

Partner	Method	Estimated accuracy and comments
VTT	Measurement of purge volume with MFM Tracer gas, CO2, N2	Accuracy to be verified
SINTEF	Crossover N2 used as a tracer. Estimate using exhaust flow or volume measurements.	Plan to compare these two techniques. Expect N2 crossover to be more accurate but still with ca. 10% error on purge volumes.
CEA	Calibrated H2 mass flow controller Measurement of H2, N2, H2O at fuel. Calculation of purge gas flow.	Still to be validated
NPL	CH_4 accumulation (CH4 = tracer gas)	U=3.22% (*k*=2)
ZSW	Measuring the fuel losses due to purge control strategy. Total purge gas volume estimated as a function of the volume loss per opening and number of the openings. Anode loop inlet flow is measured continuously by a mass flow meter.	
ZBT	H2 MFC and pre pressure regulator measurement, measurement of prolonged purge	

Method for estimating fuel recirculation rate (amount of O2&H2O recirculated)

Partner	Method	Estimated accuracy and comments
VTT	Humidity balance Calibrated pressure drop through stack against measured flow	
SINTEF	Pump characteristic curve Mass balance	Expect quite low accuracy (worse than 10%) for both methods.
CEA	Humidity balance	Method to be validated in agreement with other partners
NPL	Estimation of gas flow through stack based on stack anode pressure drop measured against calibrated flow	
ZSW	Pump characteristic curve + metering with 100% hydrogen	
ZBT	Humidity balance Calibrated pressure drop through stack against measured flow	

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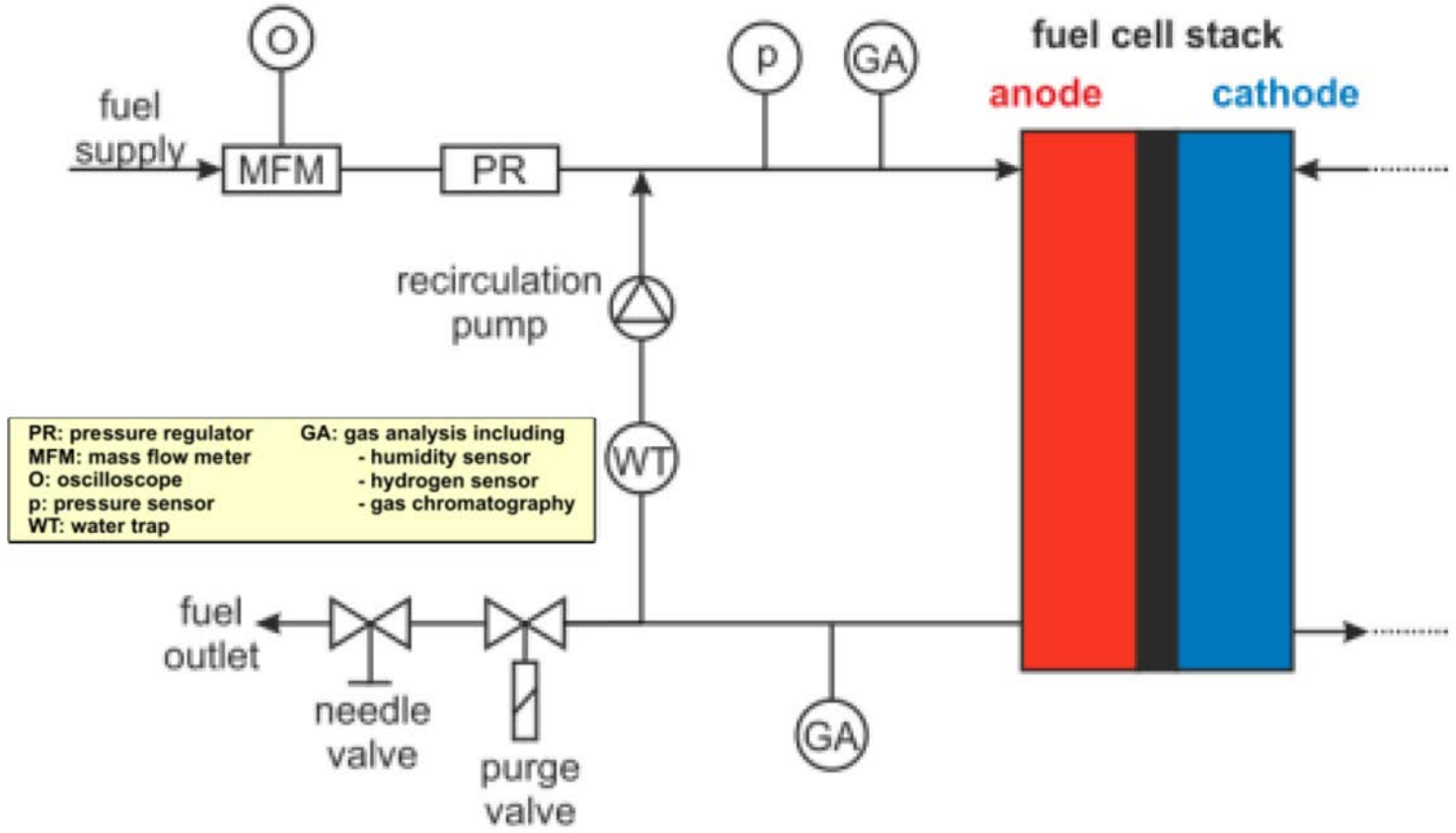
Instructions for building a recirculation set-up: STACK-TEST project



(Figure adapted from STACK-TEST:TM P-11 Dead End Operating Conditions http://stacktest.zsw-bw.de/media-centre/test-modules.html)

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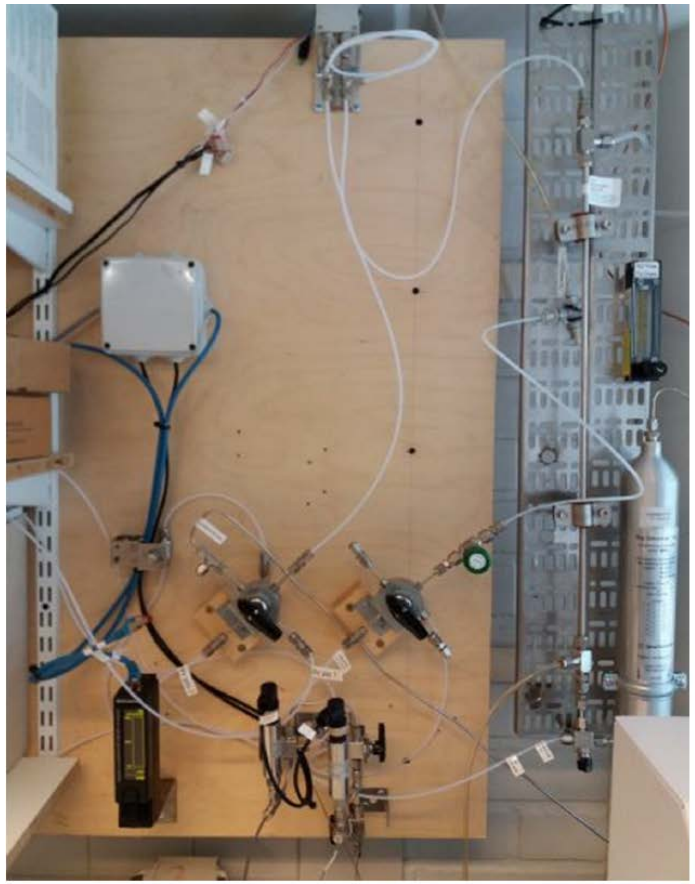
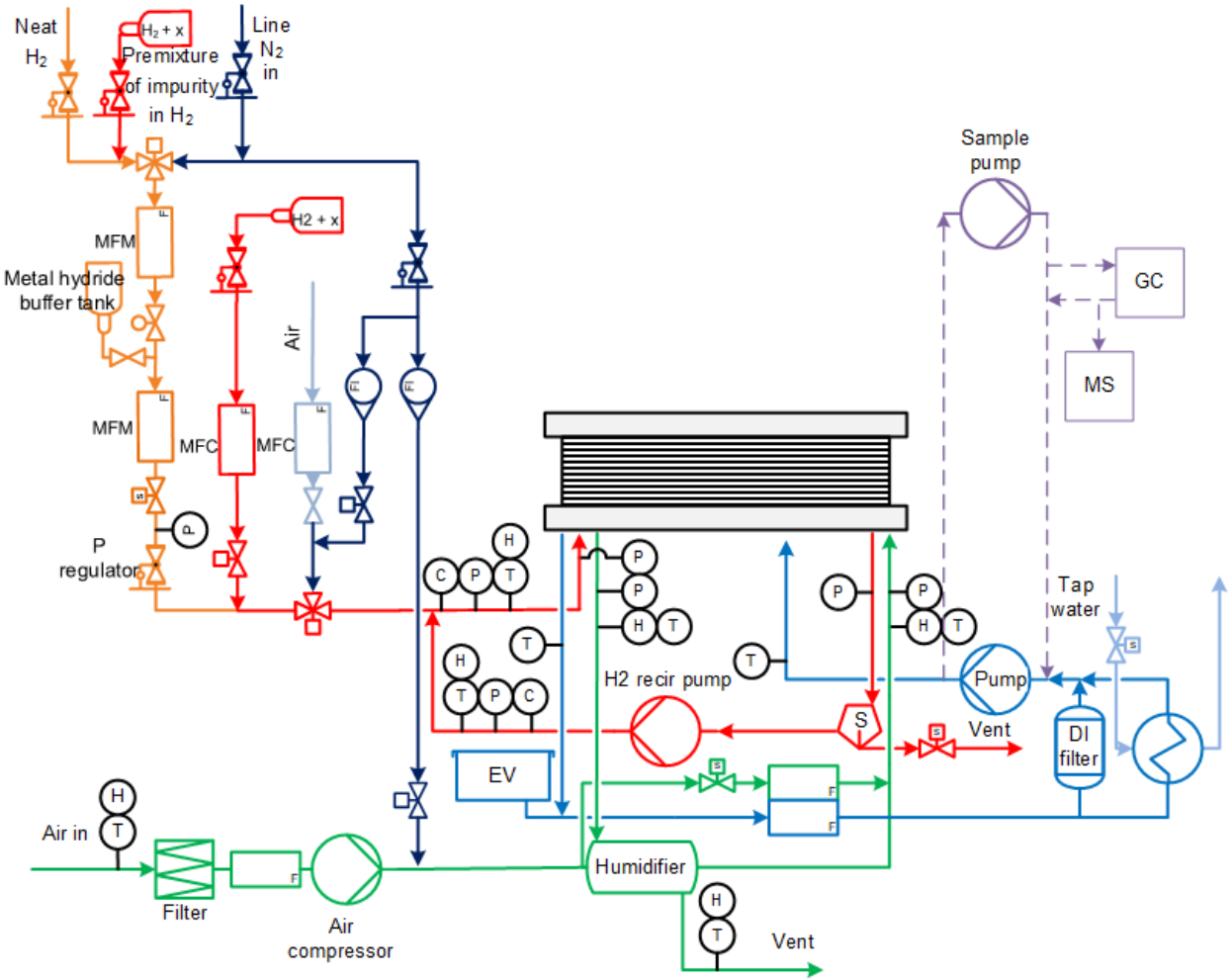
VTT – in-house-built 1 kW FC test system and GC-PDHID&TCD&FID and MS (OmniStar MS) for 13CO



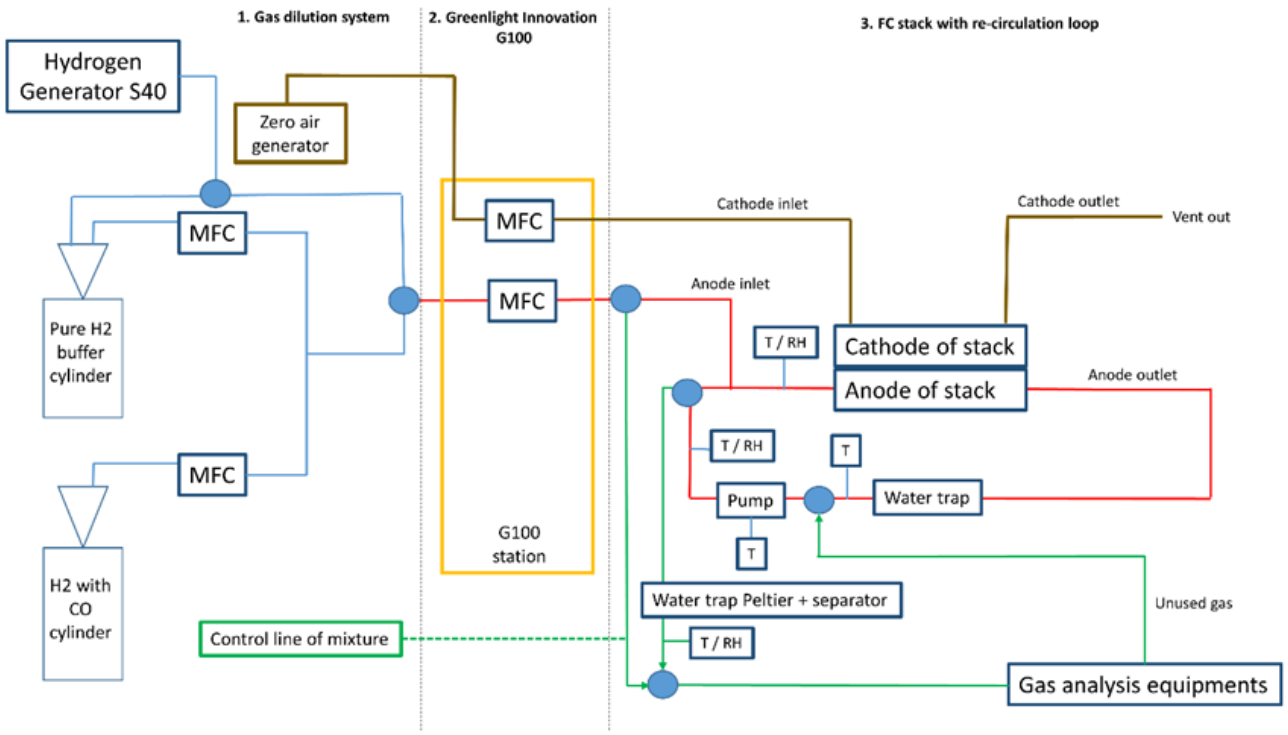


METROLOGY for HYDROGEN VEHICLES

HYDRAITE

NPL Greenlight G100 with anode gas recirculation and GC-FID (with methaniser) and SIFT-MS

1 : anode inlet
2 : recirculation pump
3 : water trap
4 : anode outlet
5 : sampling point to gas analysis
6 : return point for unused analysed gas (future)



Available resources

- HyCoRA reports, : http://hycora.eu/deliverables.htm
  - D1.1 Review on the impact of impurities on PEMFC and analytical methods for hydrogen QA
  - D1.2 Report on reference measurements and test protocols
  - D1.3 Intermediate report the second risk assessment workshop
  - D1.4 Final report for the third risk assessment workshop

- STACK-TEST reports: http://stacktest.zsw-bw.de/

- Articles:
- Matsuda, Y., Shimizu, T., Mitsushima, S. (2016) Journal of Power Sources, 318, pp. 1-8.
- Tuominen, R., et al (2018) International Journal of Hydrogen Energy, 43 (9), pp. 4143-4159.
- Viitakangas, J., et al. (2018) Journal of the Electrochemical Society, 165 (9), pp. F718-F727.

This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 779475. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme and Hydrogen Europe and Hydrogen Europe Research.

THANK YOU

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