Reversible impurities

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Overview

- Experimental procedures, programs and campaigns from HYDRAITE project are presented.
- Results examples for stack level measurements using HYDRAITE procedures and HYDRAITE or HyCoRA stacks
- Preliminary results of gas analyses applied in the FC measurements

Experimental procedures, programs and campaigns in HYDRAITE project

Overall work distribution in WP2

Partner	VTT		SINTEF		CEA		ZSW		ZBT		NPL		Total effort
Task, impurity measurement type	days	period	days	period	days	period	days	period	days	period	days	period	
2.1 CO 0.5 ppm tolerance	10	M1-M24	5	M13-M24	10	M1-M24	10	M1-M24					35
2.1 CO 0.2 ppm tolerance	10	M1-M24	5	M13-M24	10	M1-M24	10	M1-M24			5	M1-M12	40
2.1 CO 0.05 ppm tolerance	10	M1-M24	5	M13-M24	10	M1-M24	5	M1-M24			5	M1-M12	35
2.1 O_2 effect for CO tolerance (internal AB)	15	M1-M24	5	M13-M24							10	M1-M12	30
2.1 Mixed effect of CO + CO_2	5	M1-M12					5	M1-M12					10
Task 2.1 total	**50**		**20**		**30**		**30**				**20**		**150**
2.2 Sulphur contamination recovery					**30**	M16-M30			**30**	M1-M30	**30**	M1-M30	**Task 2.2 90**
2.3 New impurities from HRS - ionic liquids, halogenates, hydrocarbons			**30**	M13-M35	**20**	M13-M35	**30**	M13-M35			**20**	M13-M35	**Task 2.3 100**
2.4 Mixtures (e.g CO, S, CO_2) including new mixtures HRS			**20**	M13-M35	**15**	M13-M35	**15**	M13-M35			**20**	M13-M35	**Task 2.4 70**
2.5 New MEAs CO 0.5 ppm tolerance - S2 stack with new anode Pt alloy (0.02 mgcm-2)	10 + 5(S3)	M16-M35	5	M16-M35	5	M16-M35			5 (S3)	M16-M35			20 (S2) + 10 (S3)
2.5 New MEAs CO 0.2 ppm tolerance - S3 stack and high current	10 + 5 (S2)	M16-M35			10 + 5 (S2)		10	M16-M35	10	M16-M35			40 (S3) + 10 (S2)
2.5 New MEAs CO 0.05 ppm tolerance - S3 stack and high current)	5	M16-M35			10	M16-M35	10	M16-M35	15	M16-M35			40 all S3
2.5 New MEAs O_2 effect for CO tolerance (internal AB). Ultra-thin MEAs or/and new anode Pt alloy	5	M16-M35	5	M16-M35									10 all S2
2.5 Mixed effect of CO + CO_2 with new anode Pt alloys	10	M16-M35	5	M16-M35	5	M16-M35							20 all S2
Task 2.5 total	**50**		**15**		**35**		**20**		**30**				**150**

METROLOGY for HYDROGEN VEHICLES

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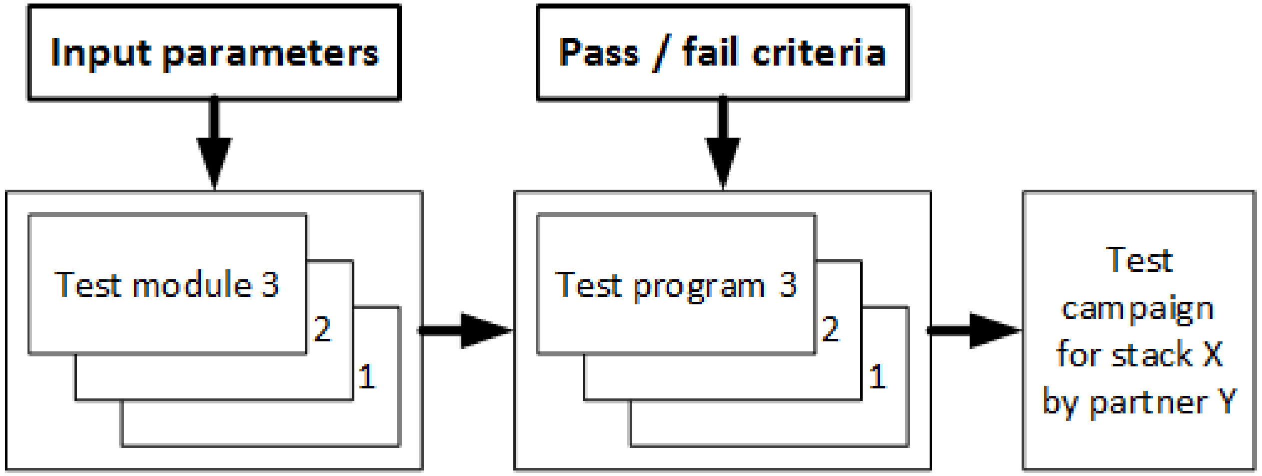
Test modules, test programs and test campaigns for stacks illustrated for Task 2.1

- The experimental work is planned using Stack-test project recommendations.
- Test programs (typically for one day, 6-12 hours) has been built from test modules.
- Ten such programs form a test campaign for one stack by one partner.



Test campaigns - 15 campaigns for Task 2.1

1-1 VTT	1-2 NPL	1-3 ZSW
2-1 ZSW	2-2 CEA	2-3 VTT
3-1 NPL	3-2 VTT	3-3 CEA
4-1 CEA	4-2 SINTEF	4-3 VTT
5-1 SINTEF	5-2 VTT	5-3 ZSW

- Each stack is measured by three partners.
- Each measurements is repeated 2 or 4 times by 2 partners.
- Used stack are sent to Sulphur poisoning testing (Test 2.2)

BoL	Campaign 1	Campaign 2	Campaign 3	EoL before S-poisoning in Task 2.2
Stacks 1-3 for months 1-12				
Powercell Break-in, FAT and Reference CO-poisoning	VTT Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO (2 reps) • 0.2 ppm CO (2 reps) • Internal AB (13-CO)	NPL Reference characterization & Reference CO-poisoning x 2 • 0.2 ppm CO • Internal AB (13-CO)	ZSW Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO • 0.2 ppm CO	Powercell Reference CO-poisoning and FAT
Powercell Break-in, FAT and Reference CO-poisoning	ZSW Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO (2 reps) • 0.2 ppm CO (2 reps) • CO (0.2 ppm) & CO2 (0/2/20 ppm)	CEA Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO • 0.2 ppm CO	VTT Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO (2 reps) • 0.2 ppm CO (2 reps) • CO (0.2 ppm) & CO2 (0/2/20 ppm)	Powercell Reference CO-poisoning and FAT
Powercell Break-in, FAT and Reference CO-poisoning	NPL Reference characterization & Reference CO-poisoning x 2 • 0.05 ppm CO (2 reps) • 0.2 ppm CO (2 reps) • Internal AB (13-CO)	VTT Reference characterization & Reference CO-poisoning x 2 • Internal AB (13-CO) • 0.5 ppm CO (2 reps) • 0.2 ppm CO (2 reps)	CEA Reference characterization & Reference CO-poisoning x 2 • 0.05 ppm CO • 0.2 ppm CO	Powercell Reference CO-poisoning and FAT
Stacks 4-5 for months 13-24				
Powercell Break-in, FAT and Reference CO-poisoning	CEA Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO • 0.05 ppm CO	SINTEF Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO • 0.2 ppm CO	VTT Reference characterization & Reference CO-poisoning x 2 • 0.5 ppm CO • 0.05 ppm CO	Powercell CO reference poisoning
Powercell Break-in, FAT and Reference CO-poisoning	SINTEF Reference characterization & Reference CO-poisoning x 2 • 0.05 ppm CO (2 reps) → 0.35 ppm or 0.8 ppm • 0.2 ppm CO (2 reps) • Internal AB (13-CO)	VTT Reference characterization & Reference CO-poisoning x 2 • Internal AB (13-CO) • 0.2 ppm CO	ZSW Reference characterization & Reference CO-poisoning x 2 • 0.05 ppm CO → 0.35 ppm or 0.8 ppm • 0.2 ppm CO (2 reps) • 0.5 ppm CO (2 reps)	Powercell CO reference poisoning

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Example of test campaign details (VTT 1-1)

Day 1 / Begin and end characterisation • A start-up - modified stack-test • Break-in • Preconditioning • Polarisation curve • Reference CO-poisoning • Shut-down – safe air purge	Day 6 / ^{13}CO – conditions A • A start-up - modified stack-test • Preconditioning • Internal AB – measurement 1 A • Shut-down – safe air purge
Day 2 / 0.5 ppm FC-DLC • A start-up - modified stack-test • Preconditioning • 0.5 ppm CO with FC-DLC (max 6 hours) • Shut-down – safe air purge	Day 7 / ^{13}CO – conditions A • A start-up - modified stack-test • Preconditioning • Internal AB – measurement 1 B • Shut-down – safe air purge
Day 3 / 0.5 ppm FC-DLC • A start-up - modified stack-test • Preconditioning • 0.5 ppm CO with FC-DLC (max 6 hours) • Shut-down – safe air purge	Day 8 / ^{13}CO – conditions B • A start-up - modified stack-test • Preconditioning • Internal AB – measurement 2 A • Shut-down – safe air purge
Day 4 / 0.2 ppm FC-DLC • A start-up - modified stack-test • Preconditioning • 0.2 ppm CO with FC-DLC (max 6 hours) • Shut-down – safe air purge	Day 9 / ^{13}CO – conditions B • A start-up - modified stack-test • Preconditioning • Internal AB – measurement 2 B • Shut-down – safe air purge
Day 5 / 0.2 ppm FC-DLC • A start-up - modified stack-test • Preconditioning • 0.2 ppm CO with FC-DLC (max 6 hours) • Shut-down – safe air purge	Day 10 / Begin and end characterisation • A start-up - modified stack-test • Break-in • Preconditioning • Polarisation curve • Reference CO-poisoning • Shut-down – safe air purge

- One campaing (e.g. 1-1) contains ten days.
- In each day one program is used.
- One program consists in several test modules

Test modules for Task 2.1 (and other Tasks)

Test module	Title	Comment
Test module TM 1	Shut-down without air	Not used normally
Test module TM 2	Shut-down with air	The default
Test module TM 3	Shut-down with hydrogen soak	Only for S-measurements
Test module TM 4	A start-up	
Test module TM 5	A start-up after hydrogen soak	Only for S-measurements
Test module TM 6	Break-in procedure	
Test module TM 7	Preconditioning	
Test module TM 8	Polarisation curve	
Test module TM 9	Reference CO-poisoning	5 ppm CO
Test module TM 10	IAB effect measurement	Internal air bleed using ^{13}CO
Test module TM 11	CO and CO+CO_2 with FC-DLC	CO: 0.05, 0.2 and 0.5 ppm CO2: 0 ppm, 2 ppm, 20 ppm
Test module TM 12	CO and CO+CO_2 with steady-state	CO: 0.05, 0.2 and 0.5 ppm CO2: 0 ppm, 2 ppm, 20 ppm

Test programs for Task 2.1 (Study of reversible impurities)

- The CO levels 0.35 ppm or 0.8 ppm may be added if 0.05 ppm level is not usable.
- The details for the program for ^{13}CO oxidation rate (IAB effect) are still developed
- New results for CO_2 importance may change $CO+CO_2$ programs

Test program	Title	Comment
Test program P-01	Reference characterization	Break-in, Pol curve and ref CO. Day 1 and day 10.
Test program P-02	IAB effect measurement 1	Selected parameters 1 (cathode or cathode/anode pressure as in NPL first measurements in campaign 3-1)
Test program P-03	IAB effect measurement 2	Selected parameters 2 (anode recirculation rate as in NPL in campaign 3-1)
Test program P-04	FC-DLC measurement with CO level 0.05 ppm CO	
Test program P-05	FC-DLC measurement with CO level 0.2 ppm CO	
Test program P-06	FC-DLC measurement with CO level 0.5 ppm CO	
Test program P-07	FC-DLC measurement with CO level 0.2 ppm + 2 ppm CO_2	
Test program P-08	FC-DLC measurement with CO level 0.2 ppm + 20 ppm CO_2	
Test program P-09	Steady-state measurement with CO level 0.2 ppm CO	Optional. For comparing FC-DLC and steady-state.
Test program P-10	Steady-state measurement with CO level 0.5 ppm CO	Optional. For comparing FC-DLC and steady-state.
Test program P-11	FC-DLC measurement with CO level 0.5 ppm CO and H2 soak.	Optional. For comparing SU/SD procedures.

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Test conditions for S2 – mild automotive conditions (limited by pressure ratings of components)

	Parameters	Symbol	Unit	Values
	Nominal stack operating temperature at stack inlet	T.Si,CL	°C	80
ANODE	Fuel gas inlet temperature	T.Si.A	°C	85
	Fuel gas inlet humidity Will depend on recirculation rate. At low power (less than 0.6 Acm^{-2}) dew point is over 64 °C, since minimum flow rate must be maintained.	RH.Si.A DPT.Si.A	% RH °C	50 @80°C 64 (1.5 single pass fuel stoic)
	Fuel gas outlet pressure (absolute)	p.So.A	kPa_a	130
	Fuel gas composition / purity *p. 5 in DoA: The level of oxygen in the hydrogen fuel is also controlled if hydrogen quality is lower than 5.0.*	Conc.Si.A.H2, Conc.Si.A.GasX		According to H2 5.0 quality with details, when needed (CO/CO2 more than 20% of ISO limits).
	Fuel stoichiometry	Stoic.S.A		1.01 (99% total fuel utilisation)
	Single pass fuel stoichiometry The target is to have 50% RH when i = max. (1.2 Acm^{-2}). This recirculation rate (single point) is used in all measurements, excluding possibly ^{13}CO measurements.	Stoic.sp.A		About 1.5 at 100%, which is 14-16 lpm.[1]

	Parameters	Symbol	Unit	Values
CATHODE	Oxidant (or air) gas inlet humidity	RH.Si.C DPT.Si.C	% RH °C	50 @80°C 64
	Oxidant gas outlet pressure	p.Si.C	kPa_a	120
	Oxidant	Conc.Si.C.O2, Conc.Si.C.GasX		According to ISO 8573-1:2010
	Cathode stoichiometry	Stoic.S.C		2.0
	Minimum current density for stoichiometry operation	I.S.MinGasFlow	A/cm2	0.3
	Minimum air flow rate **value for 10 cell S2 stack**	I.S.MinGasFlow	dm3/min	19.4

The nominal current density is 0.6 Acm^{-2}. 50% of nominal current density is 0.3 A cm^{-2} and all the measurements are started from this current density and returned to this current density.

This is also the minimum current density for stoichiometry operation (stoic 2). The cathode flow rate is kept constant (19.4 dm3/min) if current density is reduced.

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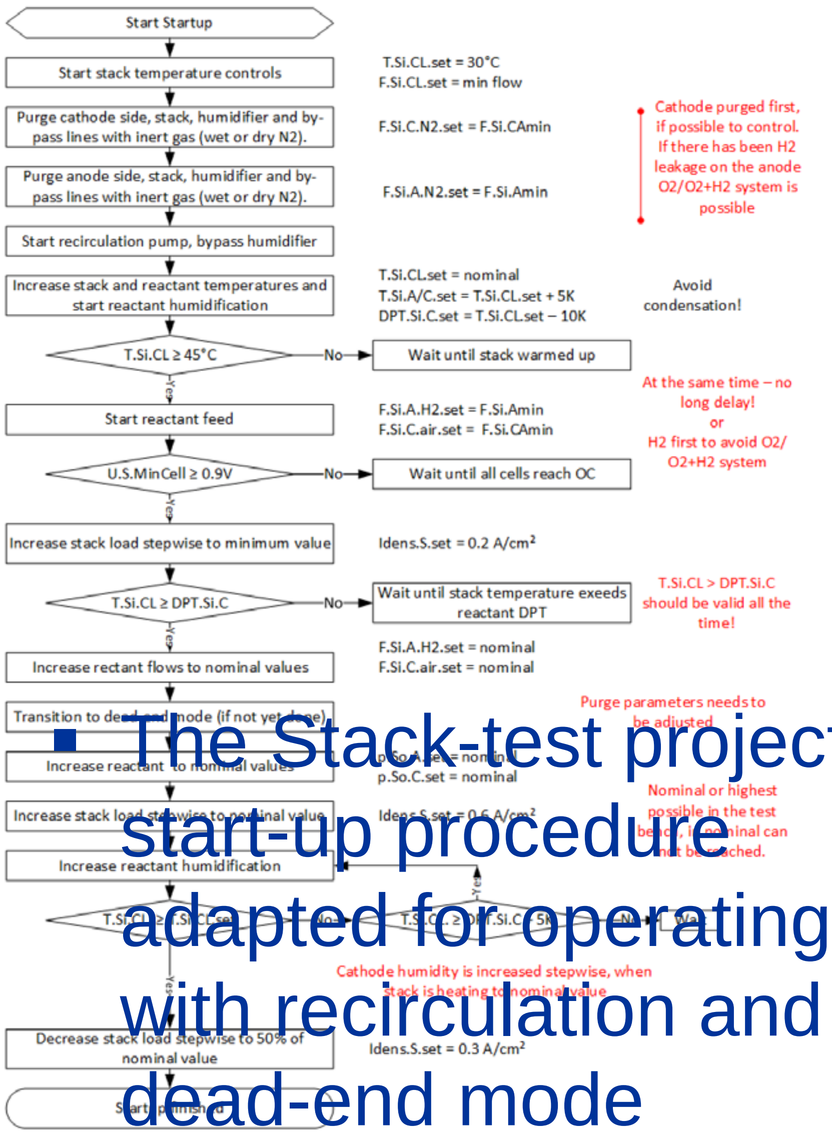
Stacks used in measurements: S2 and S3 from Powercell Sweden

- Anode MEA 0.05 mgPt/cm-2 with or without CRT additives
- In this S2 version MEA has 191 cm2 active area.
- Low pressure drop, easy integration, but only 1.2 Acm-2 max i

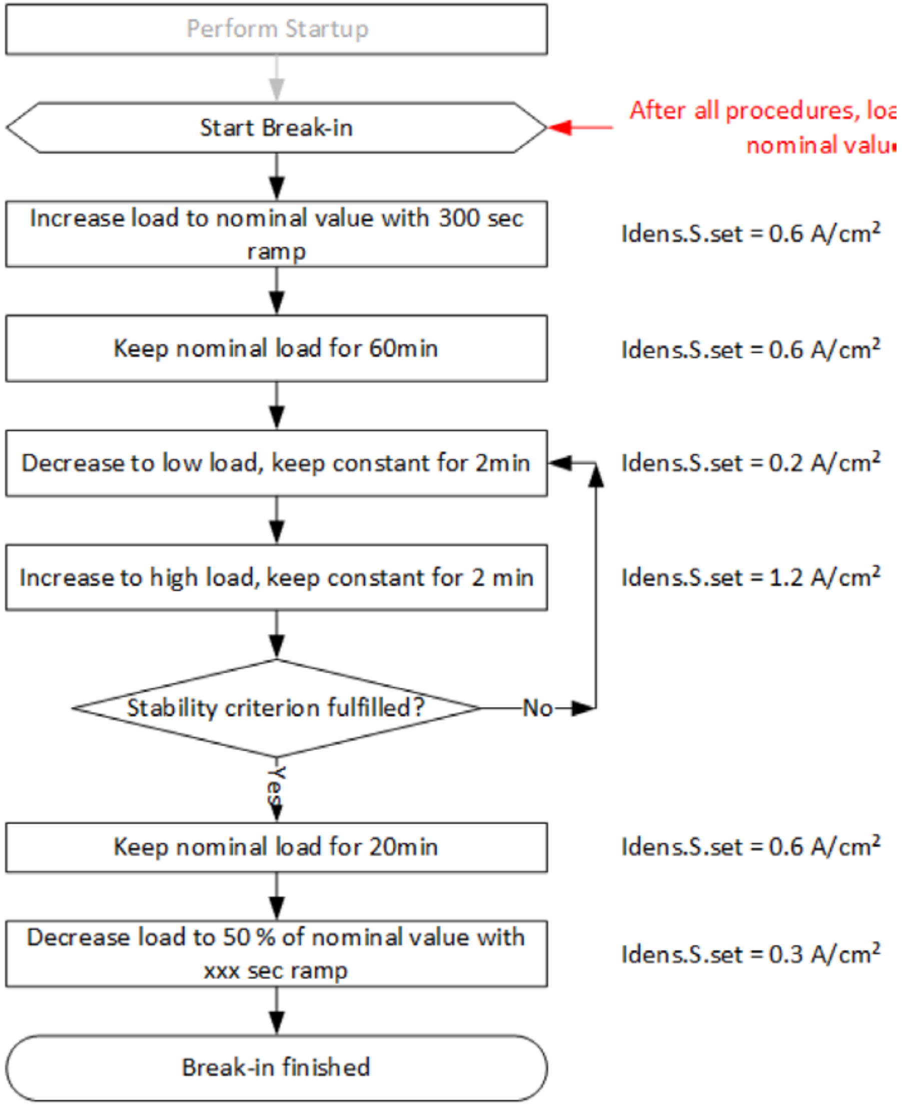
Max continuous temperature	85 °C
Humidity	Non-condensing at inlet
Fuel Pressure	< 1.2 Bar (g)
Coolant pressure	< 1.5 Bar (g)
Ambient temperature	-30 - 70 °C
Fuel composition (dry basis)	40-100 % H_2 (0-60% inert dilutants, i.e. He + N_2 + Ar)

Result examples from different test procedures and programs

Example – start-up and preconditioning procedures

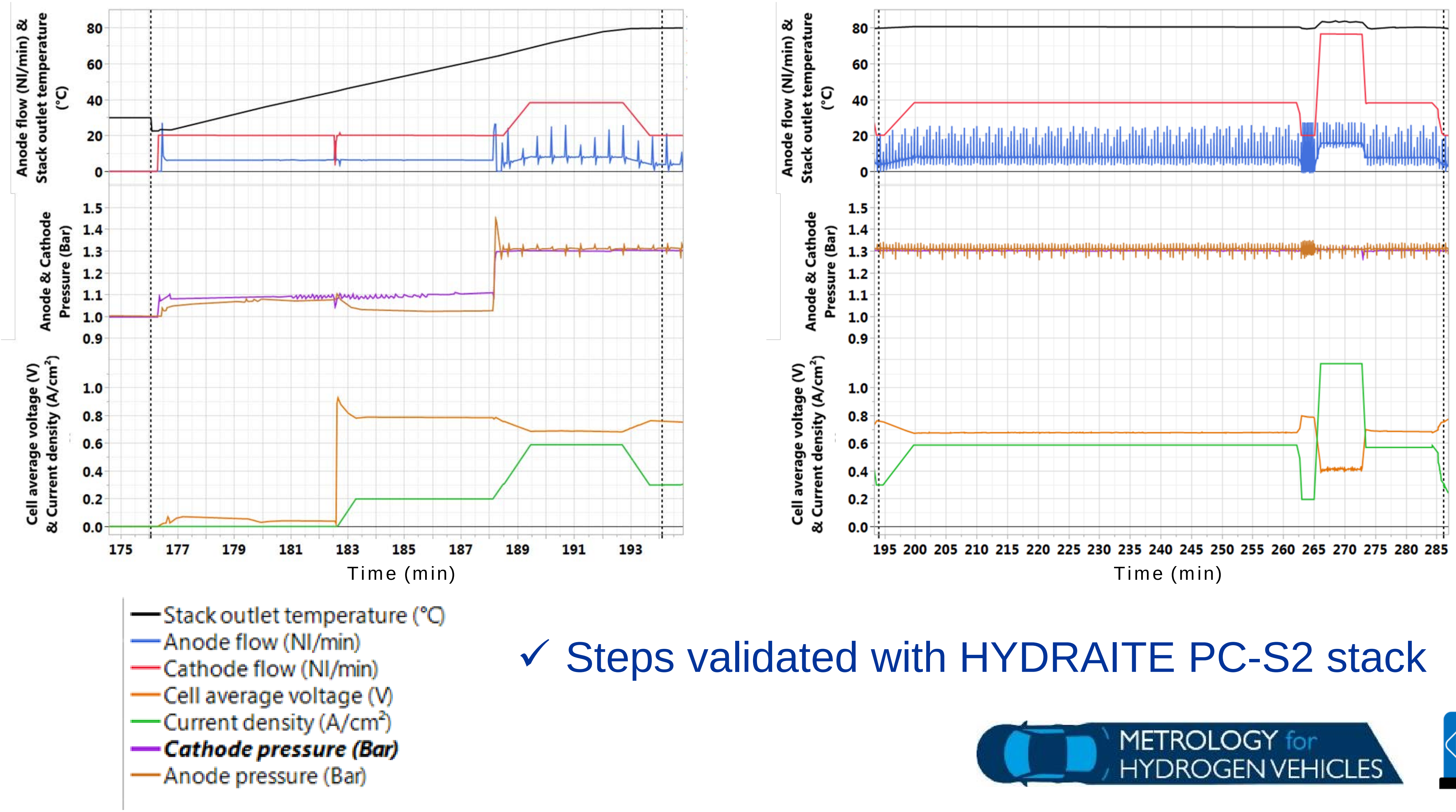


- The Stack-test project start-up procedure adapted for operating with recirculation and dead-end mode



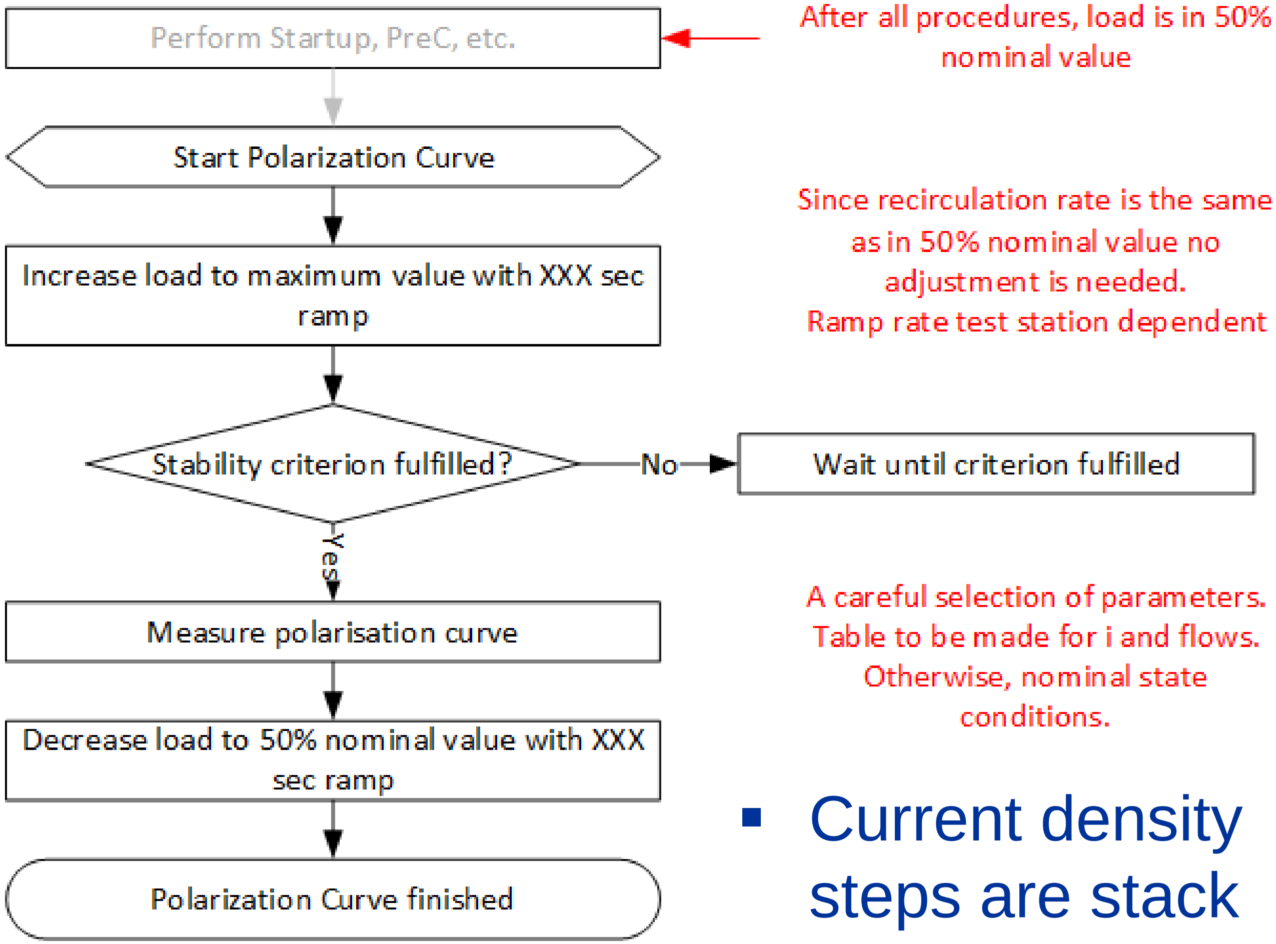
- The purpose of the pre-conditioning is to ensure controlled and similar status of the stack before specific tests

Example – start-up and preconditioning procedures



✓ Steps validated with HYDRAITE PC-S2 stack

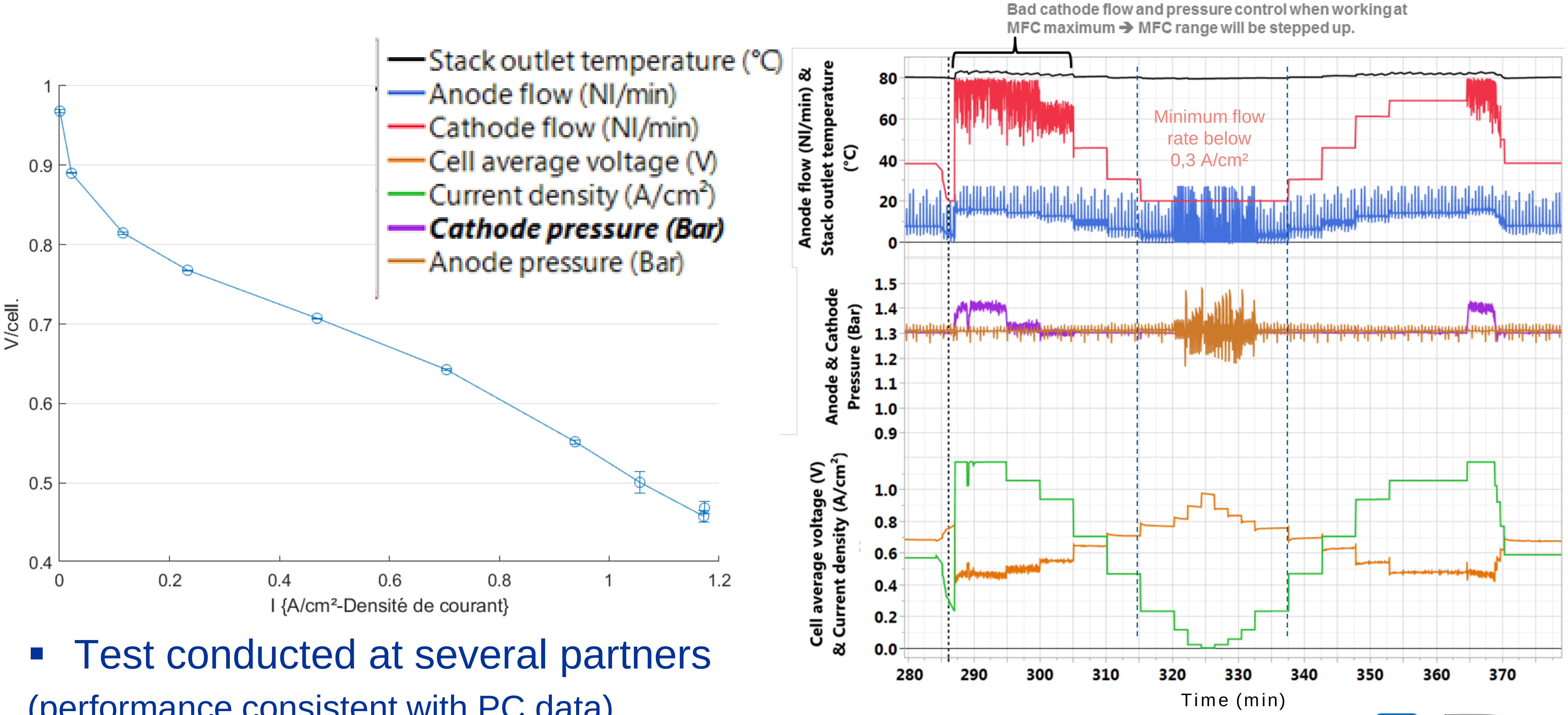
Example – polarisation curve procedure



- Current density steps are stack design related (here for S2)

Step	Load [%]	i / Acm^-2	dwell
1	100	1.2	5
2	90	1.08	5
3	80	0.96	5
4	60	0.72	5
5	40	0.48	5
6	20	0.24	5
7	10	0.12	2
8	5	0.06	2
9	2	0.024	2
10	0	0	2
11	2	0.024	2
12	5	0.06	2
13	10	0.12	2
14	20	0.24	5
15	40	0.48	5
16	60	0.72	5
17	80	0.96	5
18	90	1.08	5
19	100	1.2	5
		Total time	74

Example results – polarisation curve HYDRAITE



- Test conducted at several partners

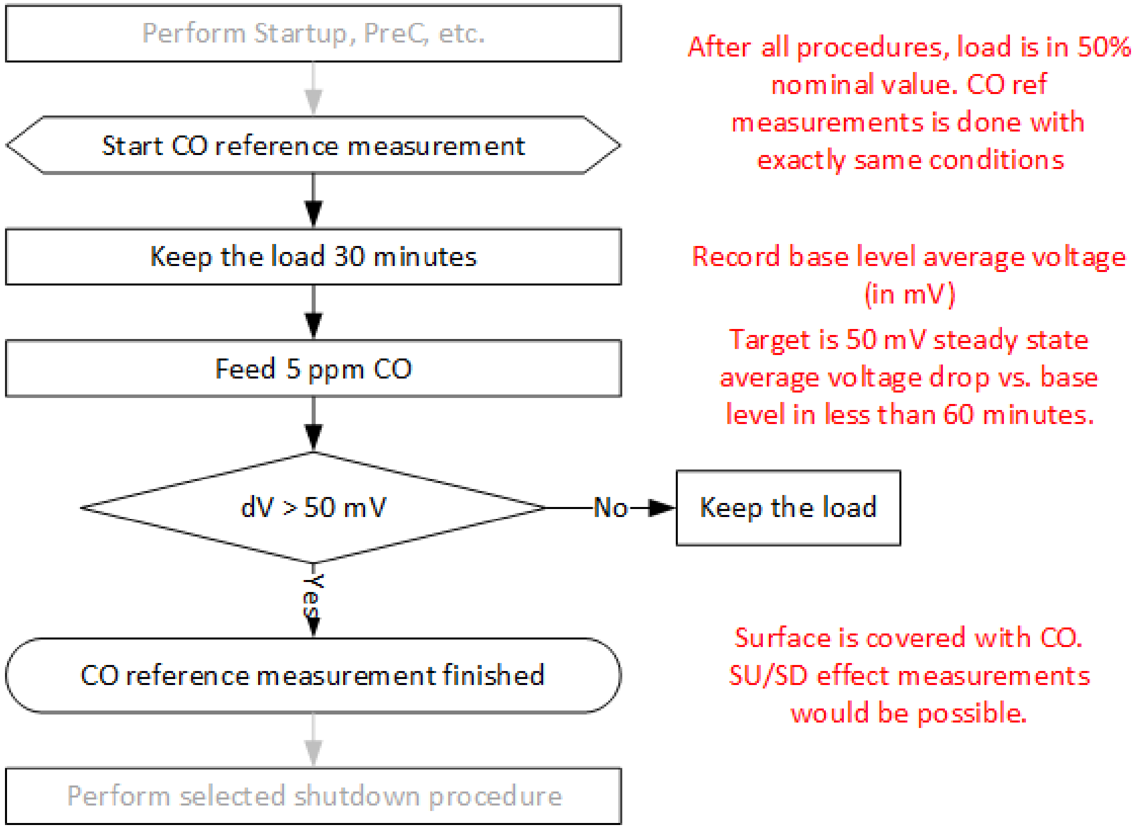
(performance consistent with PC data)

✓ *Procedure ok – Test to be repeated for final validation*

METROLOGY for HYDROGEN VEHICLES

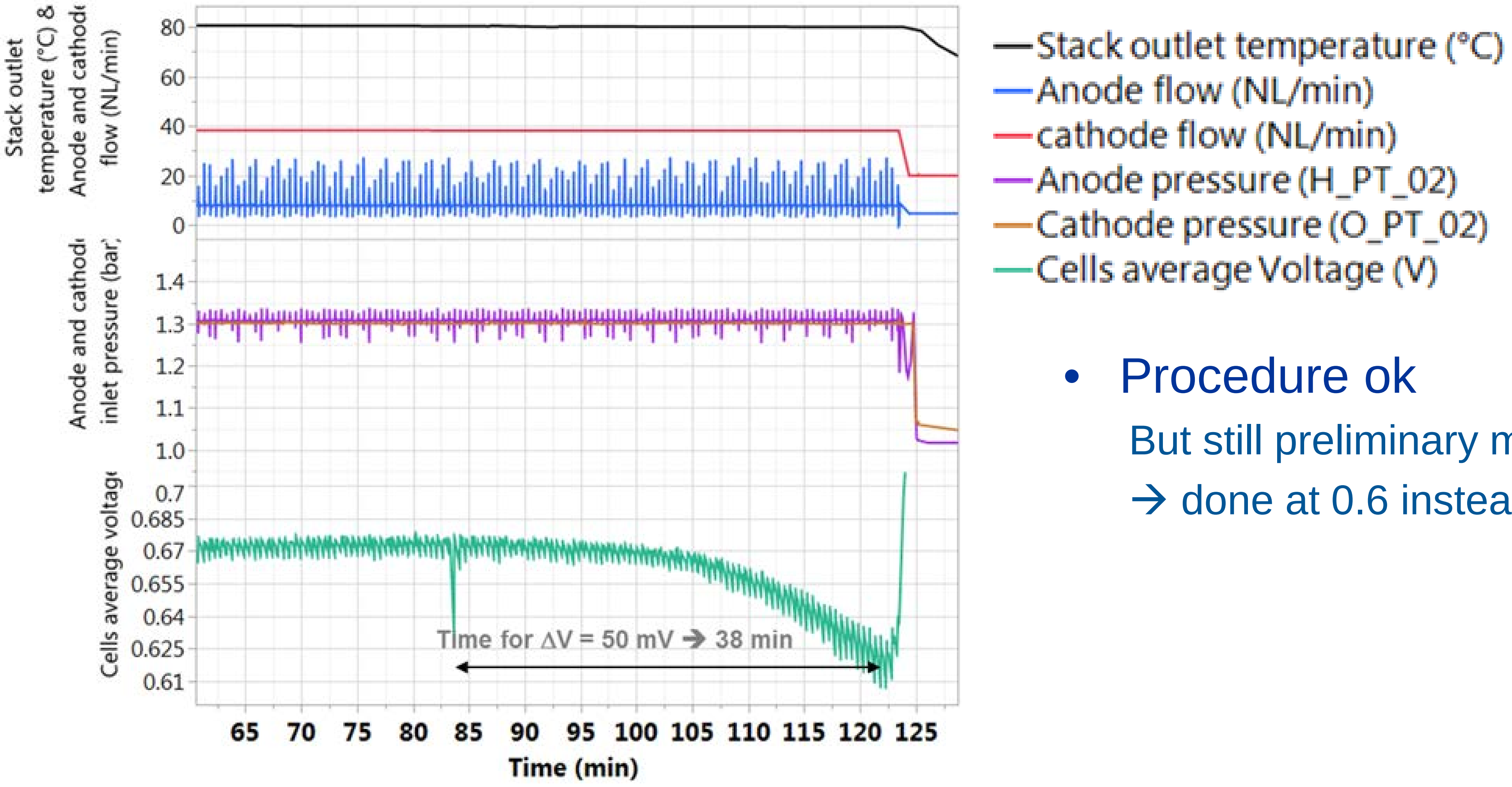
HYDRAITE

Example results – CO reference poisoning



- The purpose with CO reference poisoning is to
  a) Verify that stack has not been aged too much during previous tests
  b) Verify that CO poisoning by different partners can give similar results
- The CO concentration is high to minimize effects of test station

Example results – reference (5 ppm CO) poisoning



- Procedure ok

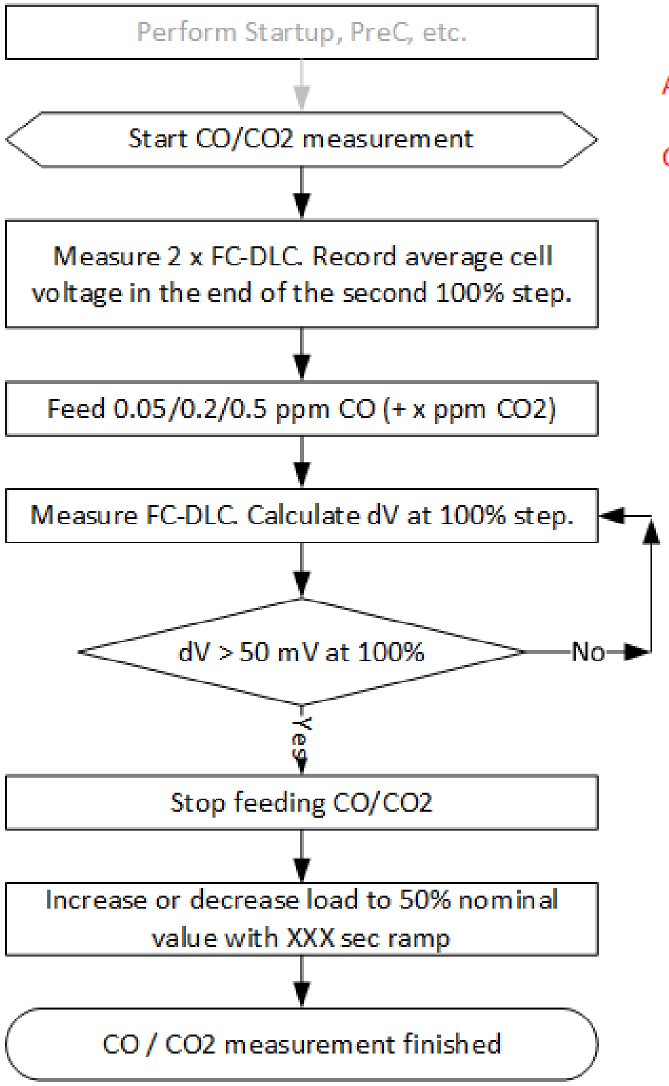
  But still preliminary measurement

  → done at 0.6 instead of 0.3 Acm^{-2}

METROLOGY for HYDROGEN VEHICLES

HYDRAITE

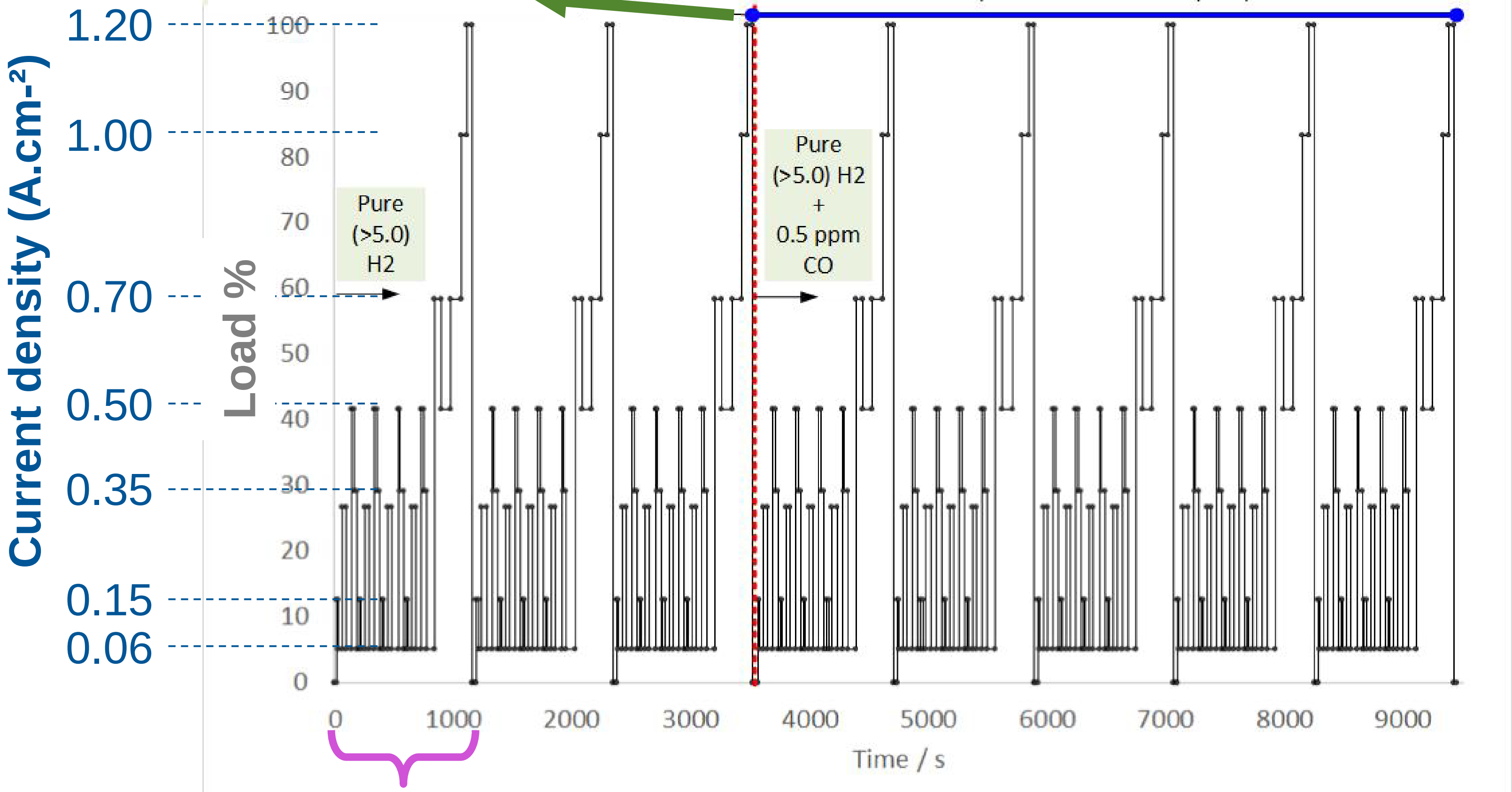
Example results – FC-DLC measurement



After all procedures, load is in 50% nominal value ($i = 0.3\ Acm^{-2}$).
CO ref measurements is done with exactly same conditions

Reference voltage value at 100% load in the end of 3 FC-DLC

3 FC-DLC with pure H2 followed by H2+CO
FC-DLC until 50mV loss at 100%
(or maximum number of cycles about 15-25)



Total time 1181 s
Average I = 64,5 A
Average i = 0.331 A/cm²

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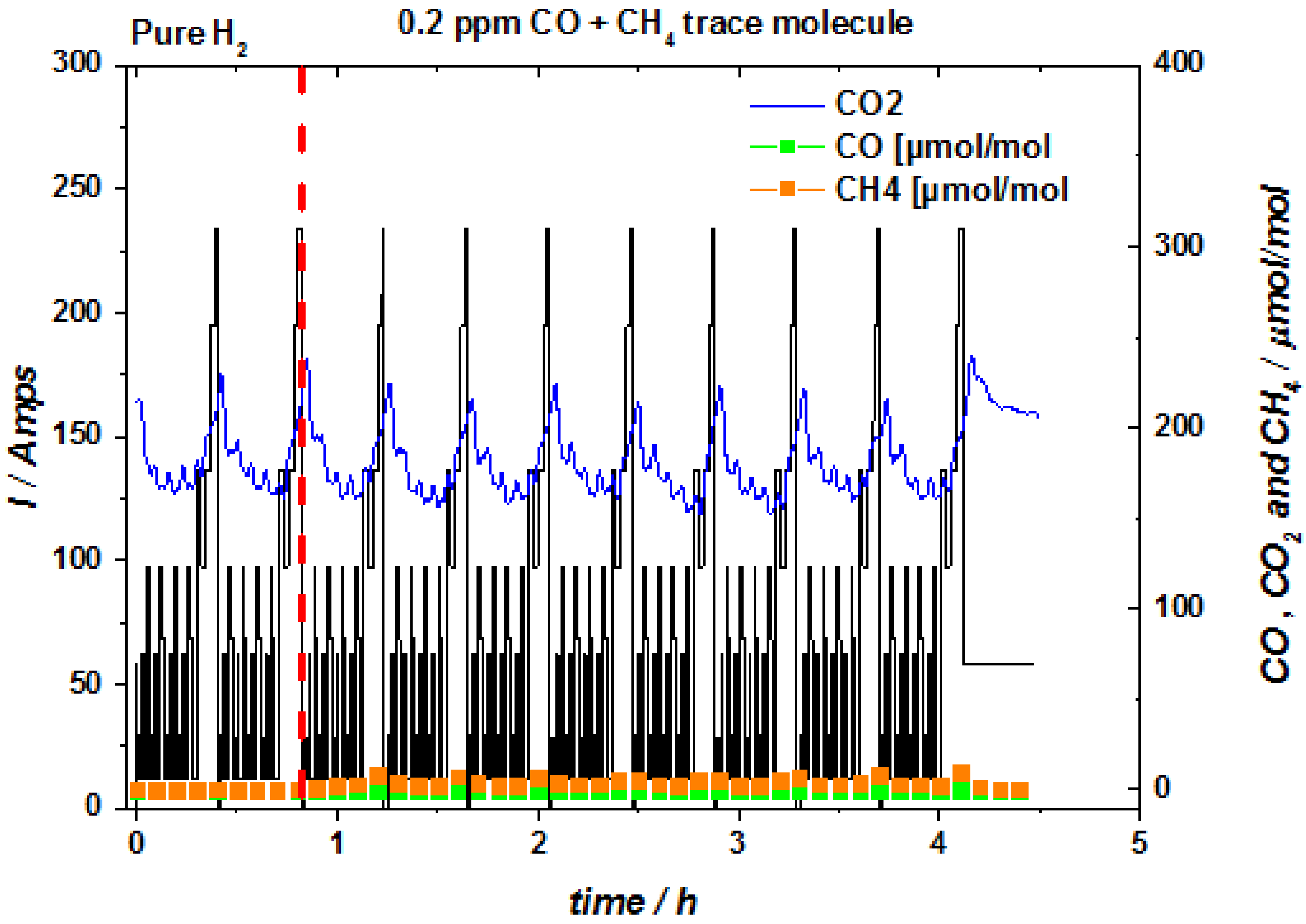
Example results – FC-DLC with 0.2 ppm CO



- Procedure tested on HyCoRA stack at NPL
- Low (95%) fuel utilisation
  - Still 150-200 ppm CO_2
- No CO detected at the exit of the stack

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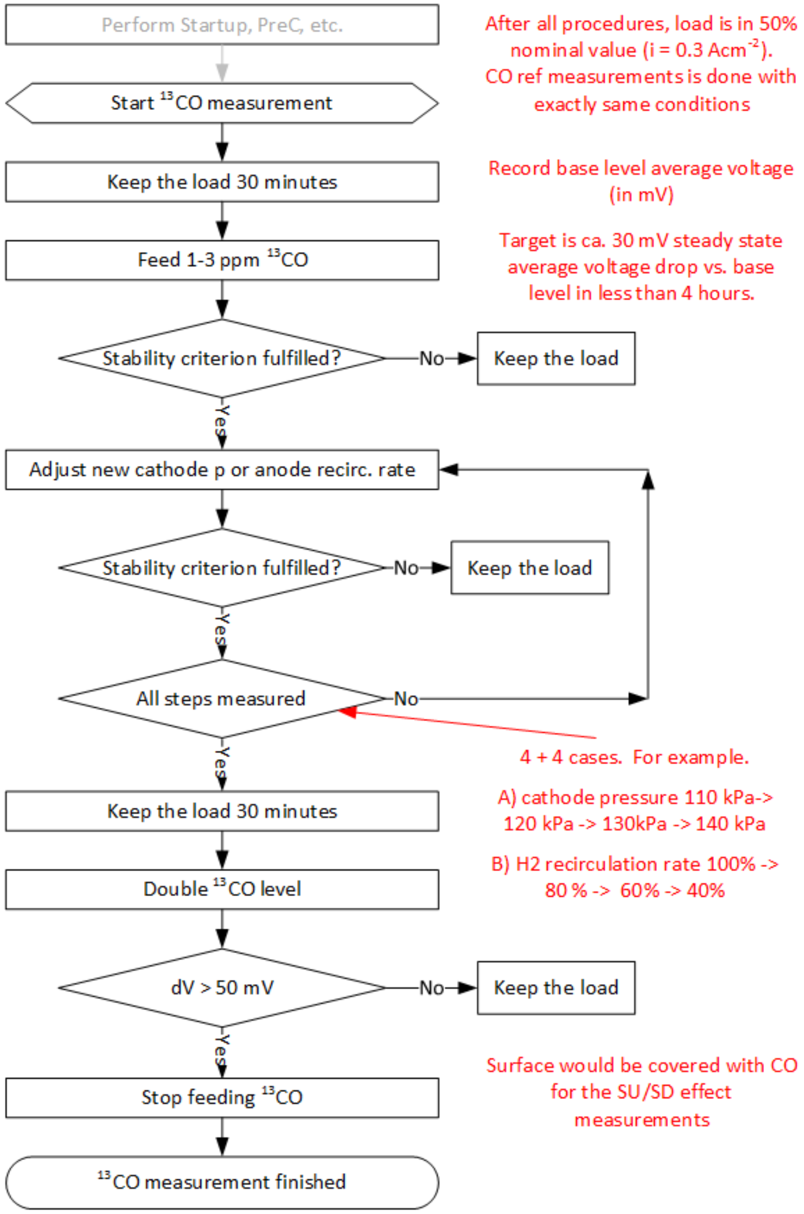
Example results – ^{13}CO measurement (HyCoRA stack)



- A central part of the experimental work in WP2 in HYDRAITE project is to measure CO oxidation rate when CO contamination is proceeding using ^{13}CO.
- In ^{13}CO measurements the rate of CO oxidation is measured as a function of different parameters (pressure, recirculation rate).

→ Low levels of CO oxidation can be measured from the level of $^{13}CO_2$ formed.

→ Give very important information for the contamination risk model.

Example results – ^{13}CO measurement

- Test conducted at NPL with HyCoRA stack
  - 2.5 ppm ^{13}CO used
  - $^{12}CO_2$ and $^{13}CO_2$ measured at the anode recirculation loop.

✓ First time CO oxidation rate measured in operated PEMFC

While significant amount of CO_2 is present.

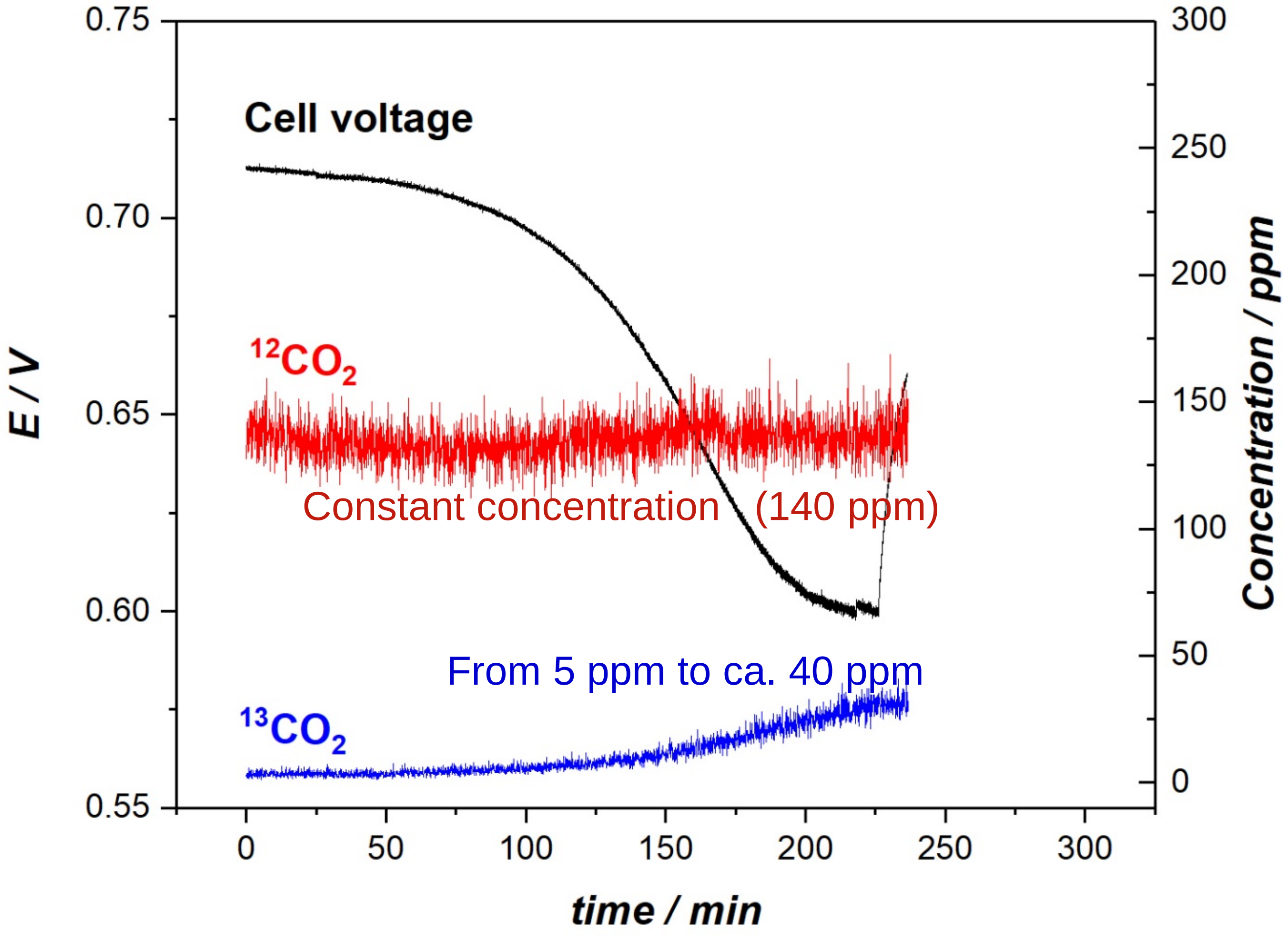
✓ Successful differentiation between

$^{12}CO_2$ from cross-over from the cathode

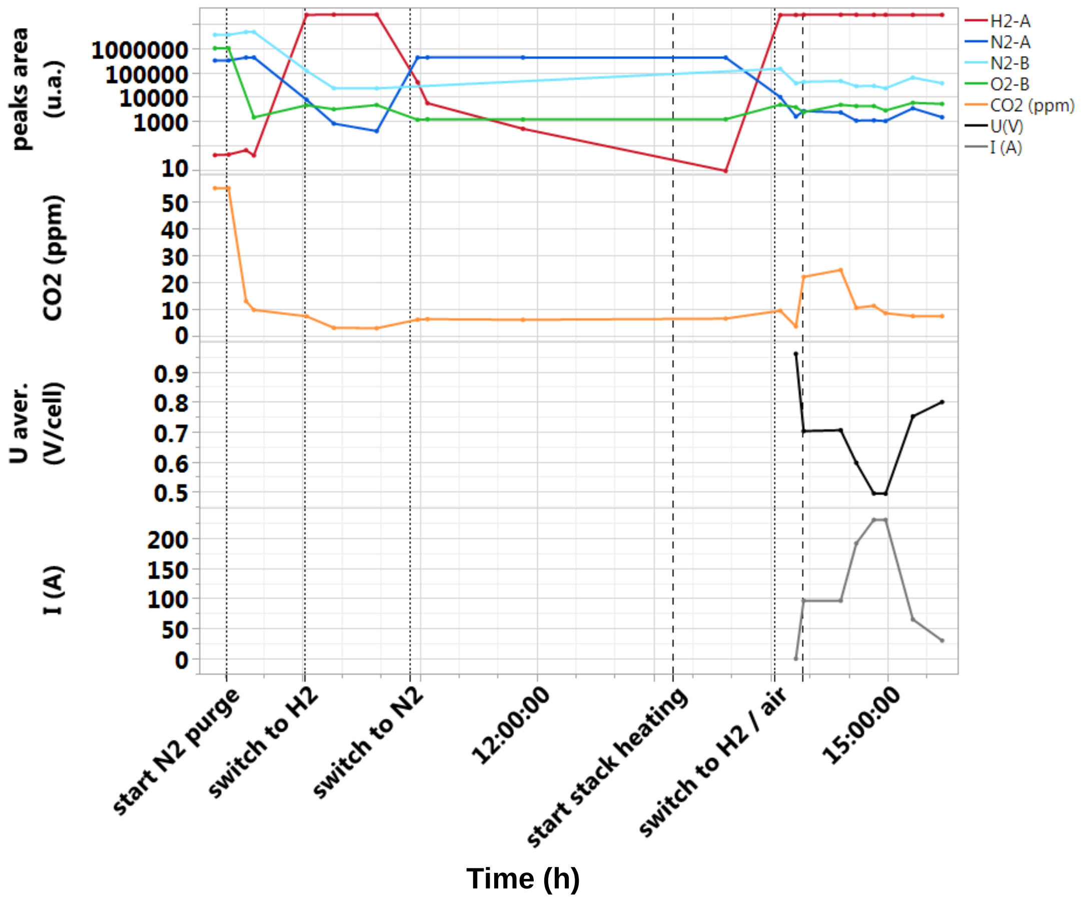
$^{13}CO_2$ produced by ^{13}CO oxidation at the anode.

- *Next step: same but with increased fuel utilization*

bleeding a total of 140 ml min-1 of dry gas out of the loop (low Uf 96.6%) - > 99% possible now.



Example results – on-line gas analysis implementation



Evolution of gas peaks area measured with µGC (top) and CO2 measured with laser IR (middle), cells voltage and current (bottom) during gas switch and stack operation

CO2 peak area with µGC vs measurement with OFCEAS (ppm)

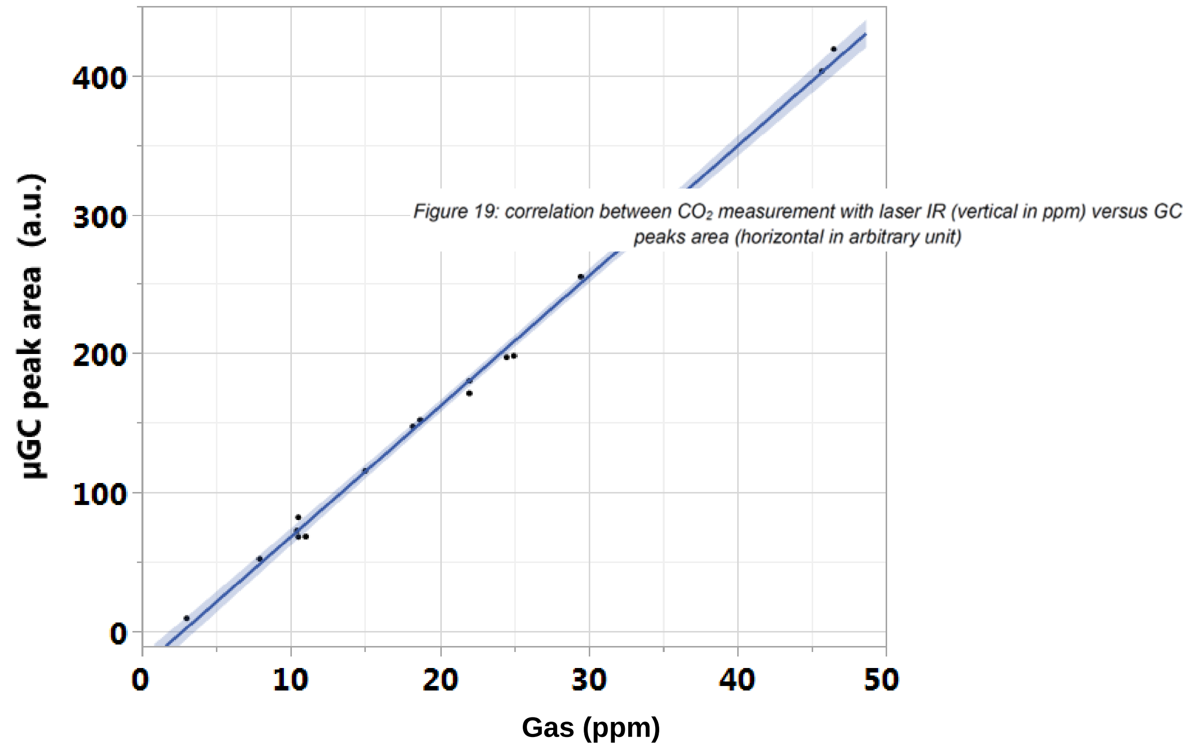
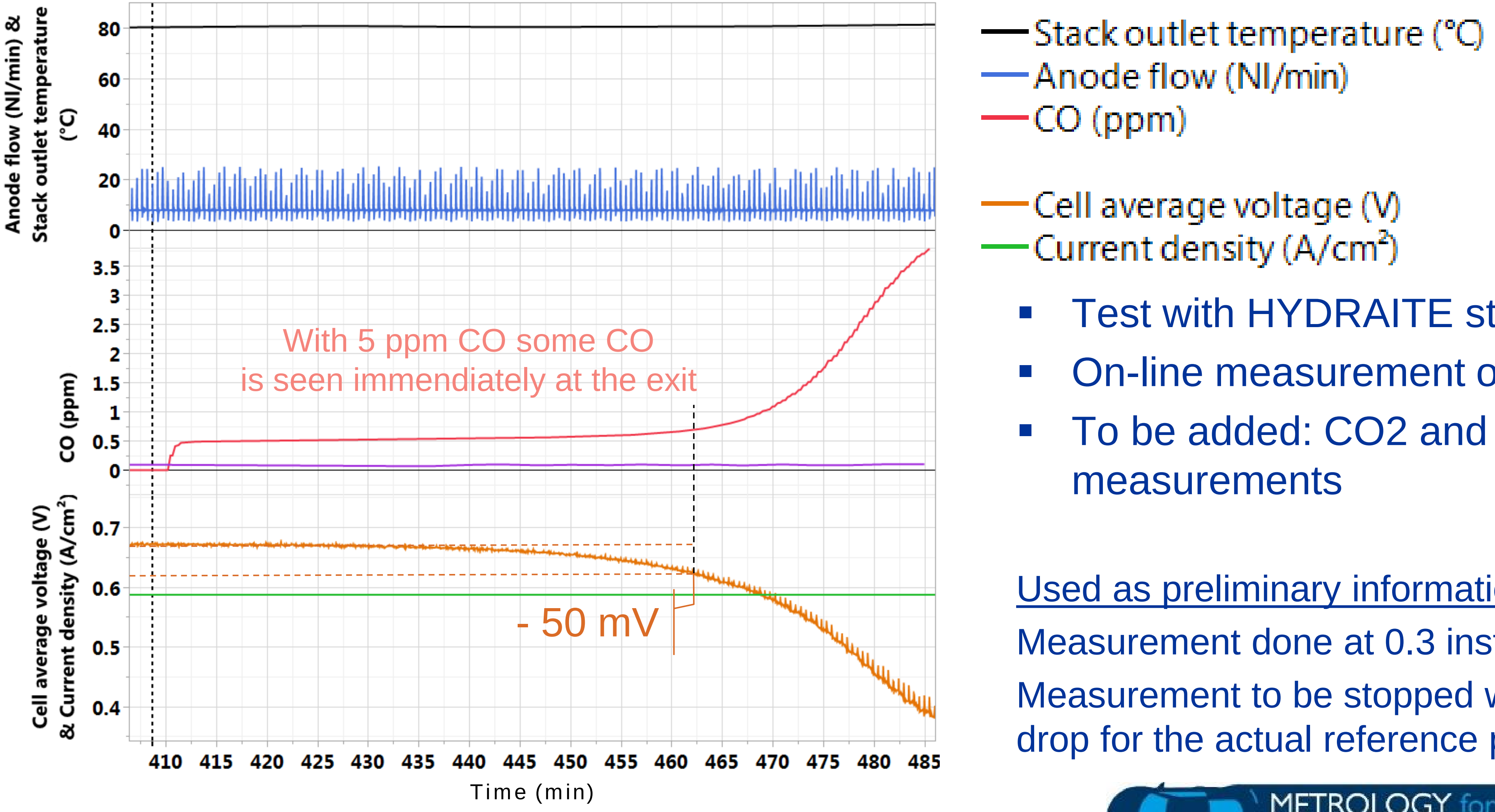


Figure 19: correlation between CO_2 measurement with laser IR (vertical in ppm) versus GC peaks area (horizontal in arbitrary unit)

Example results – on-line gas analysis during preliminary reference (5ppm CO) poisoning test



- Test with HYDRAITE stack at CEA
- On-line measurement of CO ok
- To be added: CO2 and valid O2 measurements

<u>Used as preliminary information</u>

Measurement done at 0.3 instead of 0.6 Acm^{-2}

Measurement to be stopped with 50 mV voltage drop for the actual reference poisoning test

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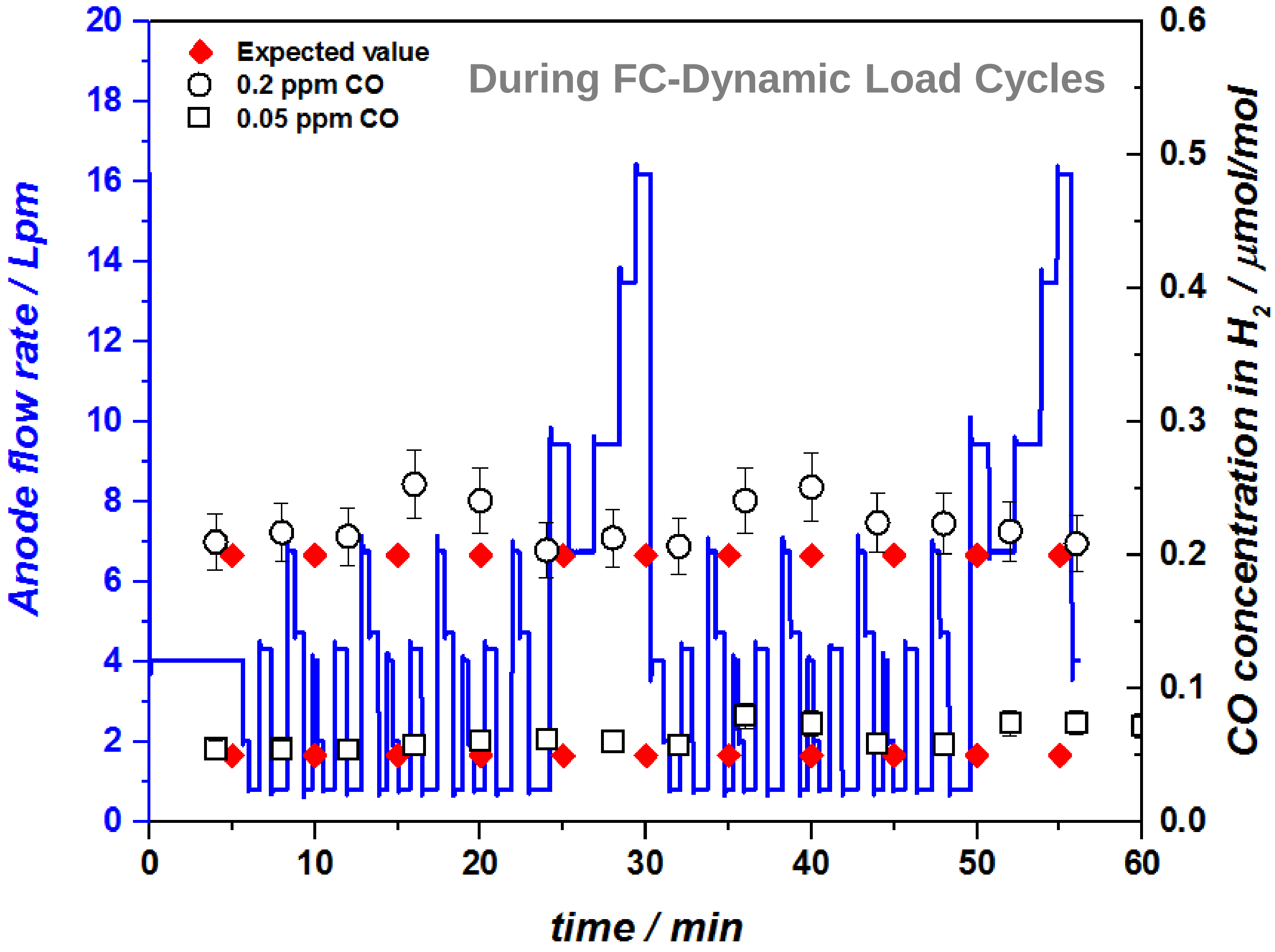
Example results – on-line gas analysis during FC-DLC with 0.2 or 0.05 ppm CO



- **Test conducted with HyCoRA stack**
- **Dilution system by NPL**

✓ FC-DLC with 0.2 ppm CO ok

✓ FC-DLC with 0.05 ppm CO ok

Summary – Reversible impurities testing in HYDRAITE

- Experimental HYDRAITE procedures defined for Fuel Cell stack measurements
  - based on previous project and adapted to specific requirements for the anode side such as fuel recirculation, dead-end mode and fuel contamination

- Procedures implemented and validated at stack level
  - Preliminary measurements using HYDRAITE or HyCoRA stacks completed for each steps
  - First online gas analyses data available during FC measurements (particularly ^{13}CO)

- On-going work and next steps
  - Complete application of the test programs for the different levels of CO concentration (down to 0.05 ppm when possible), $CO+CO_2$ mixtures and sharing of the stacks among partners for comparison.

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THANK YOU

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