HYDRAITE WP2, fetch input from participants

- work plan, questions and challenges

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Jari Ihonen

Work package 2 - objectives

The main objective of this WP is to improve understanding of contaminant effects, and thus present an important base for appropriate future hydrogen standards. This understanding will also support the discussion of "hydrogen quality requirements vs affordable hydrogen costs".

The three sub-objectives are related to existing contaminants in current ISO standards, contaminants not yet included in the ISO standard and developing an EU-harmonised test protocol for hydrogen contaminant measurements:

• Provide recommendations for revision of ISO standards (both 14687-2:2012 and 14687-3:2014), under consideration of dynamic operating conditions, continuous full power operation (2,5 A cm-2) and future MEA configurations with anode PGM loadings of 0.02 mg cm-2 or less.

• Provide recommendations for revision of ISO standards for contaminants introduced by HRS components and operation and operation/maintenance practices. This work includes both existing contaminants in ISO standard as well as new contaminants.

• Develop recommendations for conducting fuel cell contaminant measurements at stack level in automotive type operation. After these recommendations are created, further revisions of ISO 14687 standards become more straightforward. A collaboration mechanism will be developed with the JRC for drafting these recommendations and extending them to EU harmonised protocols.

List of recommendations / harmonization
JRC involvement important

Work package 2 - overview

WP2 - Fuel cell impurity measurements [Months: 1-36]

VTT, SINTEF, CEA, PC, NPL, ZSW, ZBT

In this work package, the effect of contaminants originating from the hydrogen supply chain, as specified in current standards ISO 14687-2:2012 and ISO 14687-3:2014, on fuel cell performance and durability is studied. The work is performed under dynamic load cycle conditions using MEA configurations representative of state-of-the-art transport applications. The susceptibility to contaminants will be characterised at PEMFC system level, using realistic automotive conditions and drive cycles, including frequent voltage and start-stop cycling. The work will be done using automotive type short stacks (models S2 and S3) from Powercell Sweden. When applicable, recommendations from the FCH2 JU Stack-Test project (Grant Agreement No. 303445) will be followed. EU harmonised test protocols will be used for reference measurements using harmonised fuel cell dynamic load cycle (FC-DLC).

Accumulation of relevant contaminants and reaction products in the anode recirculation loop (or at the anode gas outlet) are measured in all experiments. Contaminants are measured in purged anode water, when water-soluble contaminants are studied. The effect of oxygen permeating from the cathode is taken into account by measuring oxygen in the anode recirculation loop (or at the anode gas outlet) for the measurements with CO and CO2, at least.

Mitigating effect not seen in open anode measurements

Work package 2 - overview

E.g. removal of S through the membrane

Cross-over of contaminants to the cathode through the membrane, and vice versa, will be considered for those contaminants that are expected to permeate through the membrane. If conversion of contaminants in the anode recirculation loop (e.g. decomposition of halogenated hydrocarbons) is expected, the levels of these contaminants are analysed.

The minimum amount of total short stack measurement days will be 560. Stack measurement days are distributed to work within tasks according to the test plan. Work plan has been created for Task 2.1 and Task 2.2 and planned preliminary for Task 2.5. For Task 2.3 and Task 2.4 the plan can be created, when contaminants from hydrogen supply chain are identified. More details of the test matrix and methodology are given in Chapter 1.3.

Work package 2 – reversible impurities

Especially important when hydrogen soak in SU/SD

Task 2.1 Study of reversible impurities (VTT, SINTEF, CEA, ZSW, NPL) (M1-M24)
In this task, the effect of reversible impurities (CO, CO2) will be studied. The focus of the work is to study the effect of CO at low ppm levels (50-500 ppb) and study the effect of internal air bleed using 13CO in different operating conditions (T, RH, cathode pressure). The planned minimum amount of total stack measurement days for this task is 150 days.

Task 2.5 Study of impurities using MEA configurations appropriate for future automotive applications (CEA,VTT, SINTEF, ZSW, ZBT) (M16-M35)
In this task, the effect of reversible impurities (CO, CO2) will be studied extending the experimental research matrix from Task 2.1 to ultra-low PGM anodes (down to 0.02 mgcm-2) and very high current density operation (2,5 Acm-2). In addition, the thinnest available membranes will be used for studying further the effect of internal air bleed. The initial test matrix is modified if strong recommendations from the OEM advisory board are received.

The planned minimum amount of total stack measurement days for this task is 150 days.

OEM opinions needed

Task 2.2 Study of known irreversible impurities (ZBT, CEA, NPL) (M1-M30)

In this task, the work will focus only on sulphur, if other strong recommendations are not received from OEM Advisory board. As discussed in Chapter 1.3, there is a large uncertainty concerning the reversibility of the sulphur contamination. Therefore, the focus in this task is on recovery from sulphur poisoning. FC stack is poisoned using sulphur and recovery of the stack performance and CO tolerance are monitored. In the work, dynamic operation is used as well as two different start-stop cycling methods. The planned minimum amount of total stack measurement days for this task is 90 days.

1. H2 soak
2. Air at anode

Task 2.3 Study of new impurities originating from HRS and hydrogen supply chain (NPL, SINTEF, CEA, ZSW,) (M10-M36)

New impurities originating from HRS and from hydrogen supply chain are identified, WP3-5, and their impact on FC performance and durability is studied. This task will start by defining relevant impurities and planning the test matrix (M10-M12).

Currently, the most important sources of supply-chain-based contaminants ate ionic liquids (including additives, solvents and decomposition products), cleansers, lubricants (aromatics, alkenes), siloxanes, solvents, and particulates from different sources.

The planned minimum amount of total stack measurement days for this task is 100 days.

Task 2.4 Study of contaminant mixtures, including new impurities originating from HRS and supply chain (SINTEF, CEA, ZSW, NPL) (M10-M35)

The impact of relevant mixtures of contaminants is evaluated in this task. The selected mixtures are based on risk analysis of hydrogen supply chain. The focus will be on contaminant mixtures that have real possibility to exist, for example frequently detected supply-chain-based contaminant together with CO.

Since impurities from the hydrogen supply chain are not yet identified, also the relevant mixtures can be determined only after contaminants from HRS and supply chain have been identified. The planned minimum amount of total stack measurement days for this task is 70 days.

Work package 2 - deliverables

D2.1: A detailed research plan for Tasks 2.3 and 2.4, Task 2.4 based on the identified new contaminants from hydrogen supply chain, M12, SINTEF

D2.2: A summary report of FC measurements for the first half of the project, M18, VTT

D2.3: First recommendation for short stack test methods for studying hydrogen contaminants in automotive PEMFC systems, M18, ZSW

D2.4: The effect of CO on the automotive fuel cell stacks with ultra-low PGM loading anodes and high current density operation, M35, CEA

D2.5: A proposal for EU harmonised test protocols for short stack test methods for studying hydrogen contaminants in automotive PEMFC systems, M36, ZSW

The motivation behind the approach (stacks and anode recirculation)

- Realistic accumulation of impurities due to high fuel utilization (>99%) is possible
- Best control for oxygen level in hydrogen
  - Oxygen from fuel, from recirculation present
  - Oxygen from the humidifier water avoided
- Realistic amount of CO2 in hydrogen
  - CO2 comes from the cathode
  - CO2 from the humidifier water avoided
- Sufficient amount of gas flow for gas sampling even when high fuel utlisation is targeted

Start-up and shut-down methods – air at the anode during SU/SD

- During a stoppage air is let to fill anode
- “Long-Stop” in Stack-Test Test Module D-03: Start/Stop Durability
  - *No nitrogen is used on system side; tests on fuel cell test benches may include nitrogen due to safety reasons*
  - *The stack is cooled down and in an off-state during Long-Stop.*
  - *Anode compartment is air-flooded before restart and Start-up.*
- Must be done in a way so that no reverse current decay (RCD) will not damage the stack
- Removes all CO by oxidation – clean surface
  - Important for reproducible CO/CO2 measurements

Start-up and shut-down methods – H_2 at the cathode during SU / SD

- "Short stop" in Stack-Test Test Module D-03: Start / Stop Durability
- May be difficult to do with FC test stations (safety)
- During a stoppage hydrogen is the cathode via membrane and cathode compartment is closed
- Probably little removal of CO by oxidation
  - Accumulation from several refillings?
  - Formation/consumption of CO by WGS/RWGS reaction during the shut-down?

Oxygen issue in CO contamination measurements

- Oxygen limit in ISO 14687-2:2012 is 5 ppm
  - In H2 samples several ppm found frequently
  - This is enough to mitigate about 50 ppb CO poisoning
  - The level of O2 in hydrogen should be controlled if lower grade then 5.0 is used in experiments.

- Oxygen can be introduced in the hydrogen from the humidifier water. In the worst case the O2 level can be tens of ppm.
  - This will have a very strong impact on CO poisoning measurements when < 1 ppm CO levels are studied

- Oxygen is introduced in the hydrogen stream, as recirculated hydrogen will contain some ppm or tens of ppm oxygen (by Matsuda et al.)

Oxygen permeation through the membrane

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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]

HIGHLIGHTS

- 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.

O2 detected at the exit of the PEMFC – 10 times more than in ISO 14687

- 30-75 ppm oxygen is detected at the anode exit, depending on CO poisoning level

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

- How in other conditions?
  - Will be measured in HYDRAITE measurements as a part of gas analysis, which are applied in all measurements

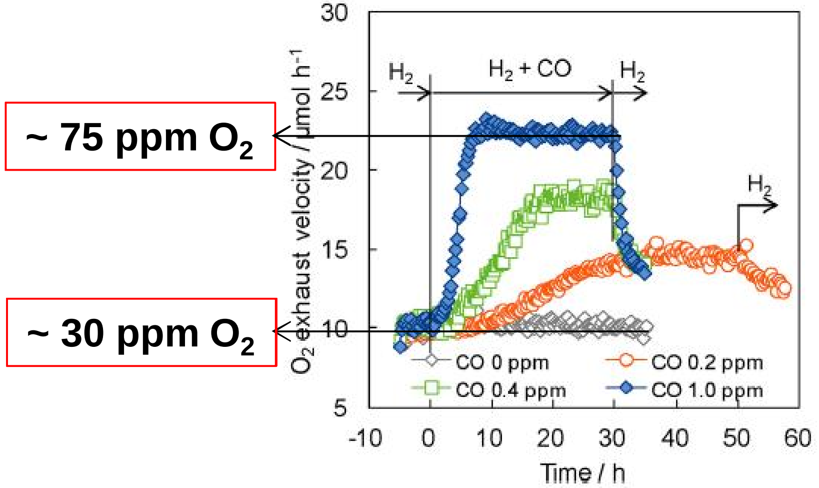
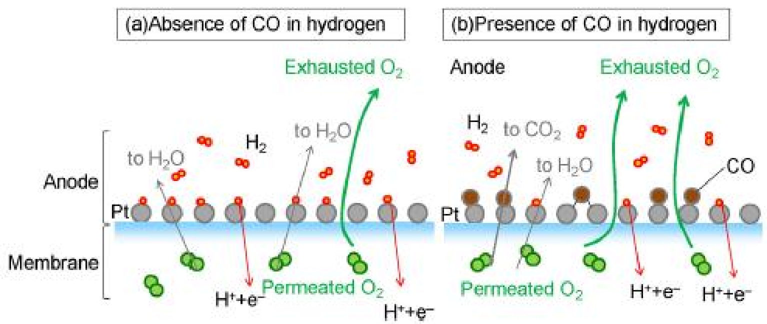
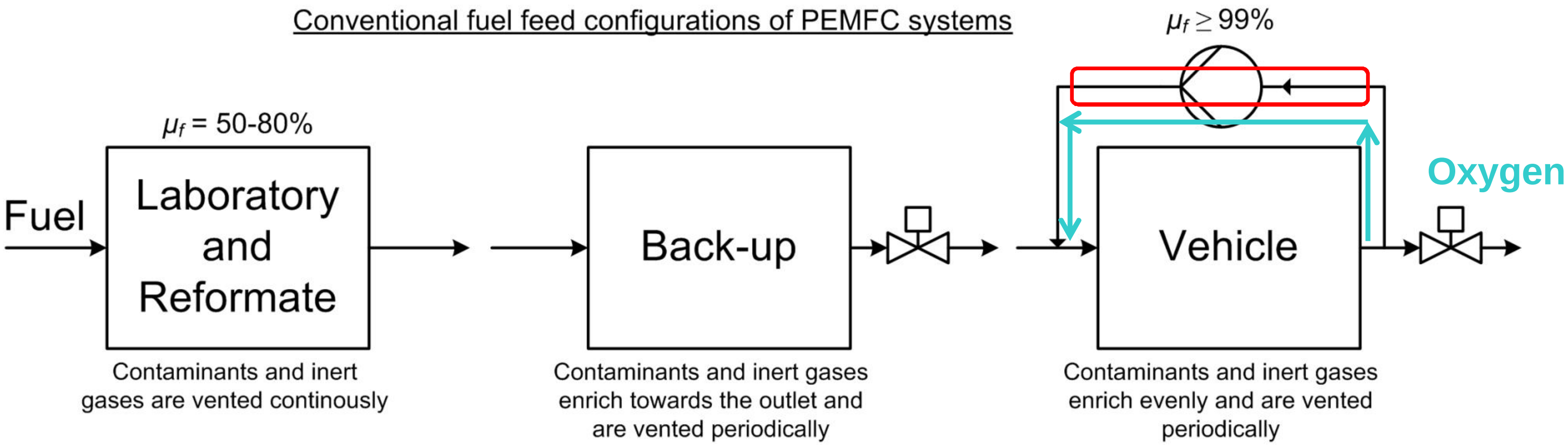


Fig. 7. Oxygen exhaust velocity change at the cell outlet over time during CO exposure. The cell temperature was 60 °C and current density was 1000 mA cm^{-2}.



The effect of recirculation for CO poisoning is unknown

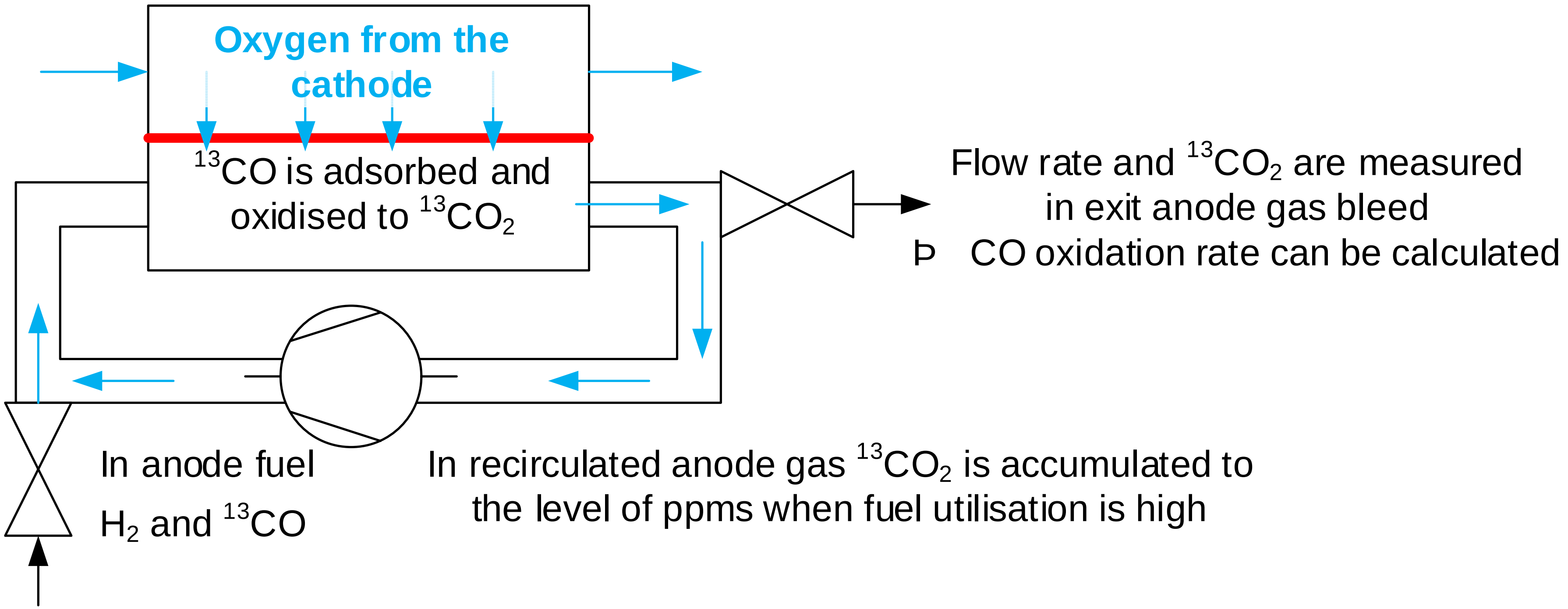


- O2 is recirculated at the level of tens of ppm all the time even at atm conditions, according to single cell measurements
  - With a typical selectivity of 1%, these would mitigate 0.3-0.75 ppm if used as "air bleed" – actual level at the inlet depends on recirculation rate
- Recirculation may have 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.

Experimental challenges for CO and CO_2 tolerance measurements (Task 2.1)

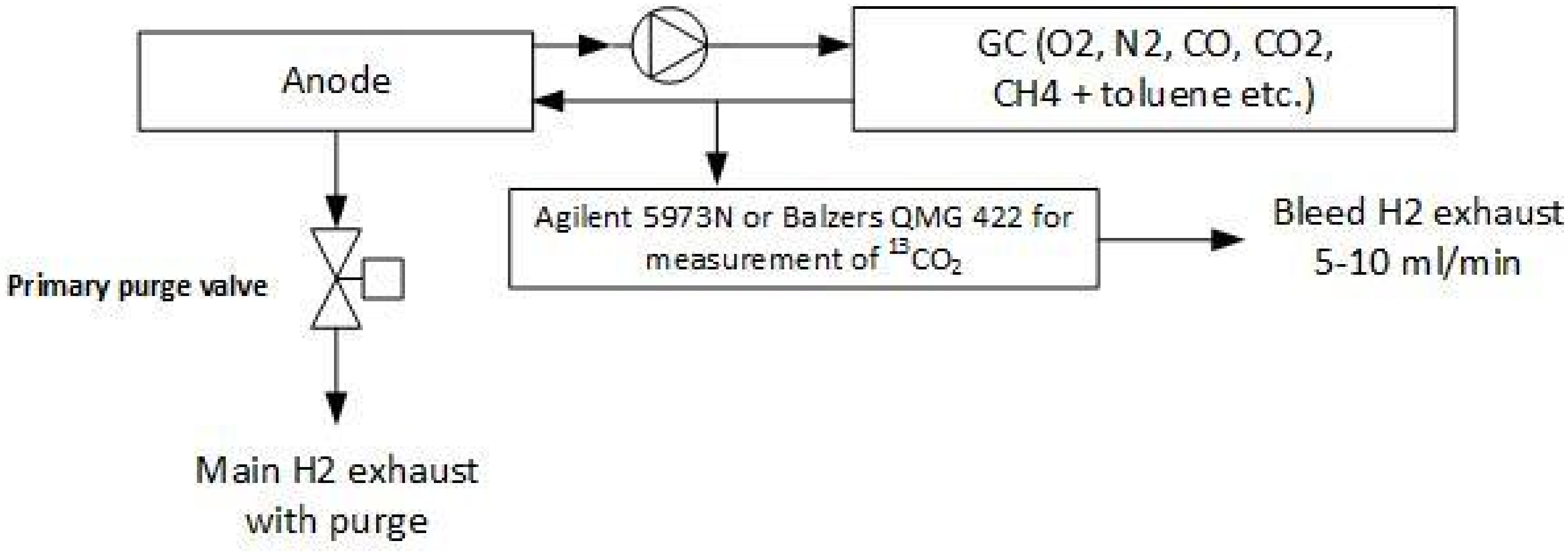
- O_2 level of the hydrogen used should be controlled for all measurements. 5 ppm O_2 will mitigate approximately 50 ppb CO
  - Anode humidifier issue is already avoided by using anode gas recirculation for the humidification
- For CO tolerance measurements the detection level of gas analysis equipment should be at least the same as for contaminant level (50-500 ppb for CO)
- 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 $C^{16,18}O_2$
  - About 1-2 ppm detection limit is needed to measure the effect of internal air bleed, if enrichment factor of 100 can be achieved

Measuring CO oxidation rate measuring from $^{13}CO_2$ production



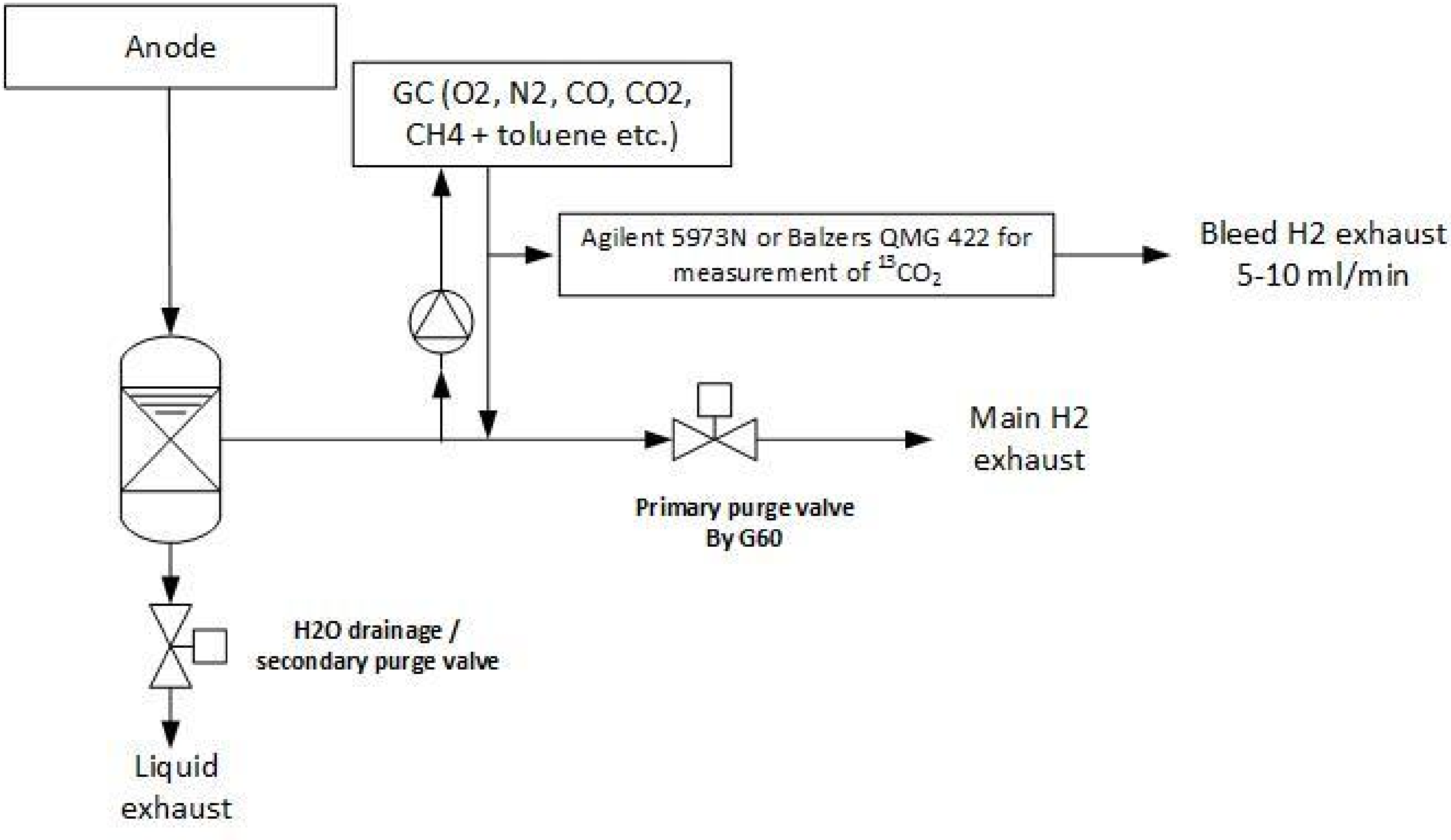
- CO oxidation rate will be dependent on
  - Experimental conditions
    - Permeation rate, selectivity for CO oxidation vs. H2 oxidation
  - Membrane thickness
  - Anode catalyst!!!

$^{13}CO_2$ production measured from recirculation gas – VTT plan for kW unit



- Measurement of contaminants from the recirculate gas
  - No tile lag for GC, but removal of some humidity and some impurities
- Bleed can be down to 1 ml/min but the time lag is then 20-30 minutes for $^{13}CO_2$ measurements as MS/GC-MS is far away

$^{13}CO_2$ production measured from exit gas – VTT plan for G60



- Time lag (minutes) due to exit gas treatment system volume
- Bleed can be down to 1 ml/min but the time lag is then 20-30 minutes for $^{13}CO_2$ measurements as MS/GC-MS is far away

Experimental challenges for S-contamination and desorption

- 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
  - Possibly measurement of cathode gas/exhaust 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

Summary

- The plan for reversible impurities is quite fixed in DoA
- The plan for irreversible impurities is less fixed
- The procedures are not fixed, only general principles
- Feedback from OEM is needed

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Thank you for your attention