METROLOGY for HYDROGEN VEHICLES

Session 5: Impact on Fuel Cells Irreversible impurities (H_2S)

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EMPIR EURAMET FCH

Outline

- Overview test bench and connection to analytical devices
- Description of test procedure with H_2S contamination and CO reference measurement
- First H_2S measurements with test stack
- Break in procedure with HYDRAITE stack
- Challenges and next steps

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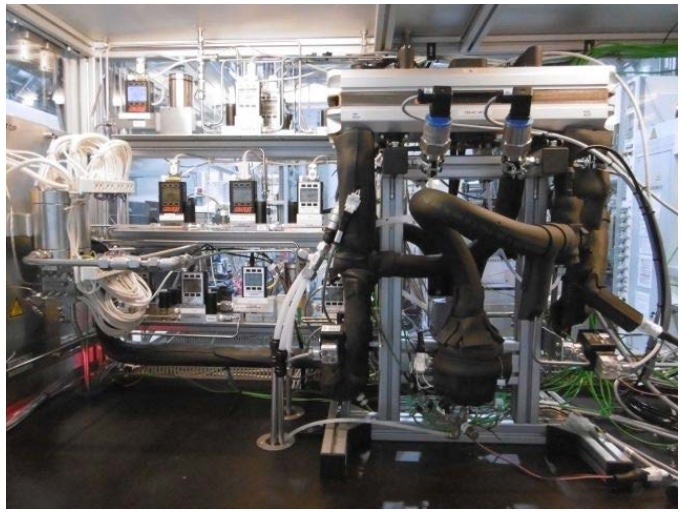
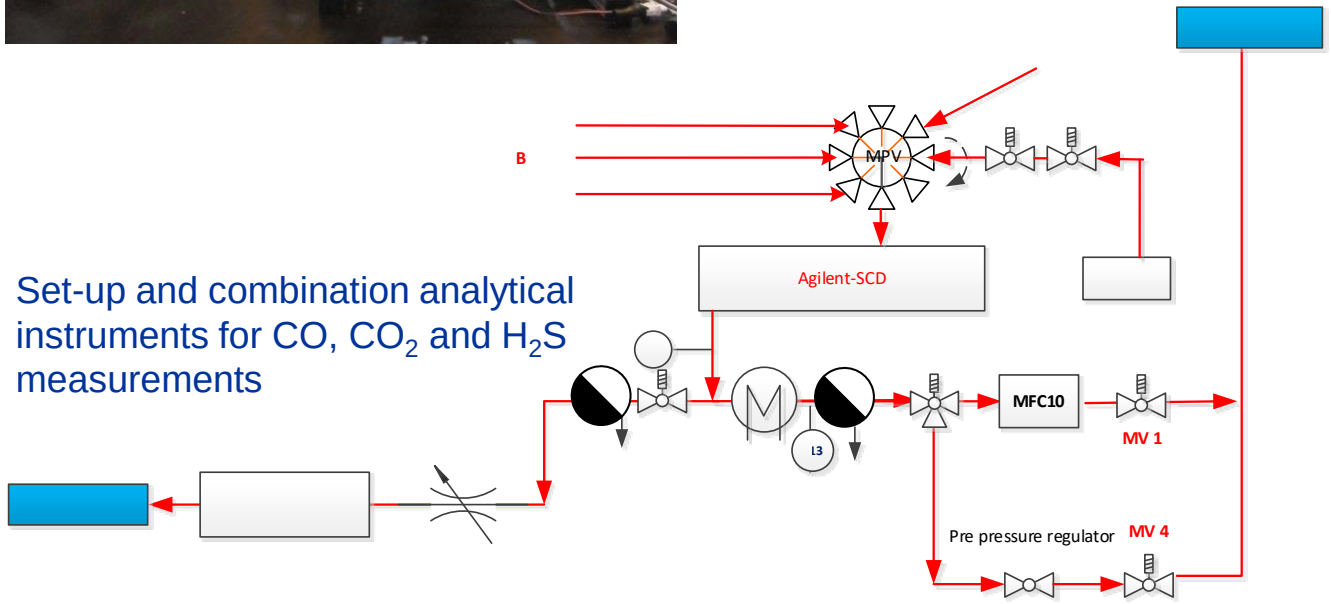
Overview test bench and connection to analytic

- New test bench with compact recirculation loop



Pictures of heating wires before isolation at stack inlet and water trap in recirculation loop

Set-up and combination analytical instruments for CO, CO_2 and H_2S measurements



4 gas sampling points

a. Dry anode supply
b. Upstream of stack inlet within recirculation loop
c. Downstream of recirculation pump
d. Downstream of purge valve

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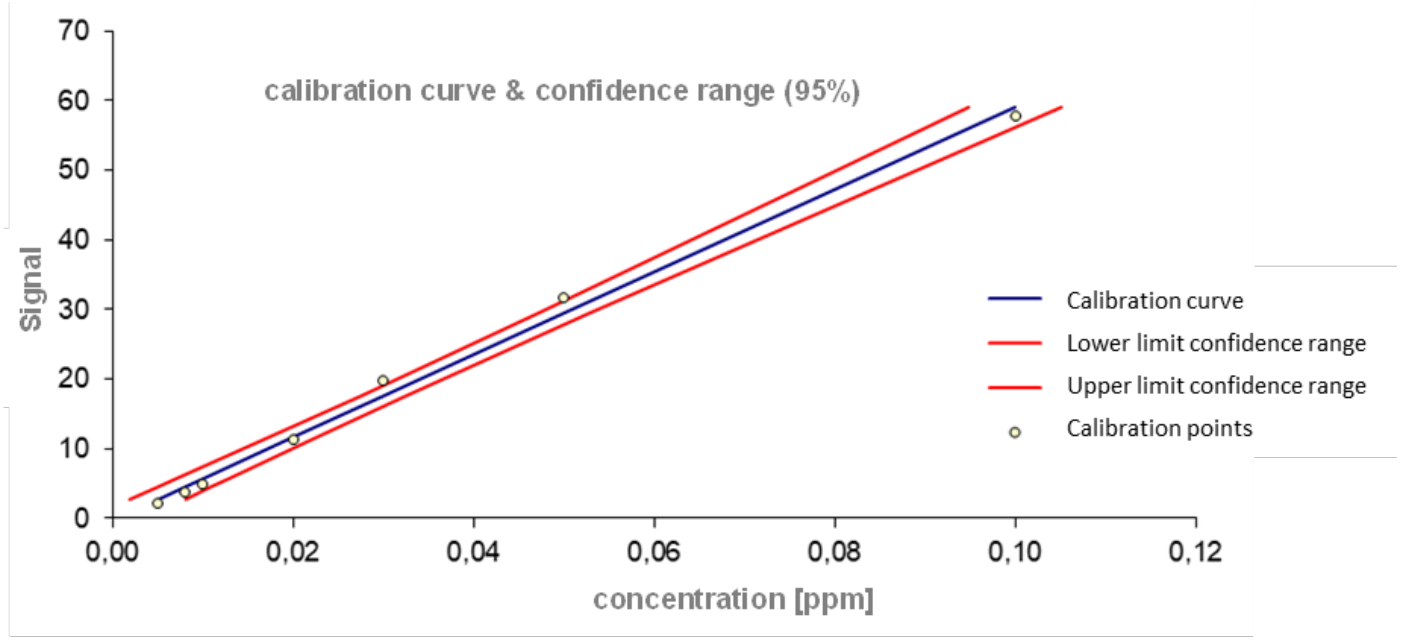
H_2S measurement

- Example of H_2S measurement (dry calibration gas)



GC - SCD

- H_2S measurement in low ppb range possible

Motivation for sulphur tests in HYDRAITE

- Sulphur can be introduced by single events due to delivery and distribution
- If sulphur stays in the Pt anode surface then **the CO tolerance is seriously lowered**
- Tests are not focused on sulphur tolerance of the system

  ➡ Reduction in CO tolerance due to sulphur is to be evaluated

- Contamination with 1 ppm H_2S in H_2 until $U_{avg.}$ drop of 30 mV
- CO reference with 5 ppm CO in H_2 until $U_{avg.}$ drop of 50 mV

Operating conditions and test setup

- Due to the expected degradation caused by H_2S first tests were carried out with test stack from the HyCoRA project
- Test procedures for HYDRAITE stack have already been implemented
  ➡ Slightly larger active area of HyCoRA compared to HYDRAITE results in lower current densities at same current level
- Cell temperature and current density during H_2S contamination and CO reference measurements: 80°C at 0.294 A cm^{-2} (0.3 A cm^{-2} with HYDRAITE stack)
- First tests with stoichiometric operation without purge
  ➡ Fuel utilization 96 – 97 %
- All tests with recirculation and without external humidification at anode

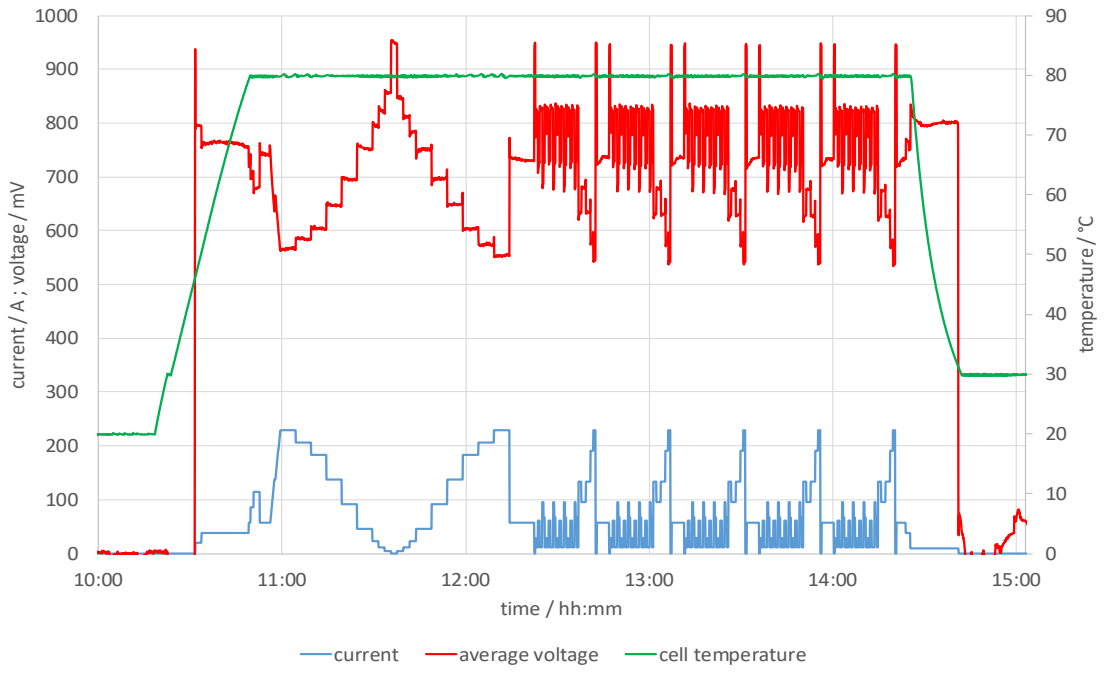
Test procedure

The first measurement campaign involves the following steps and procedures:

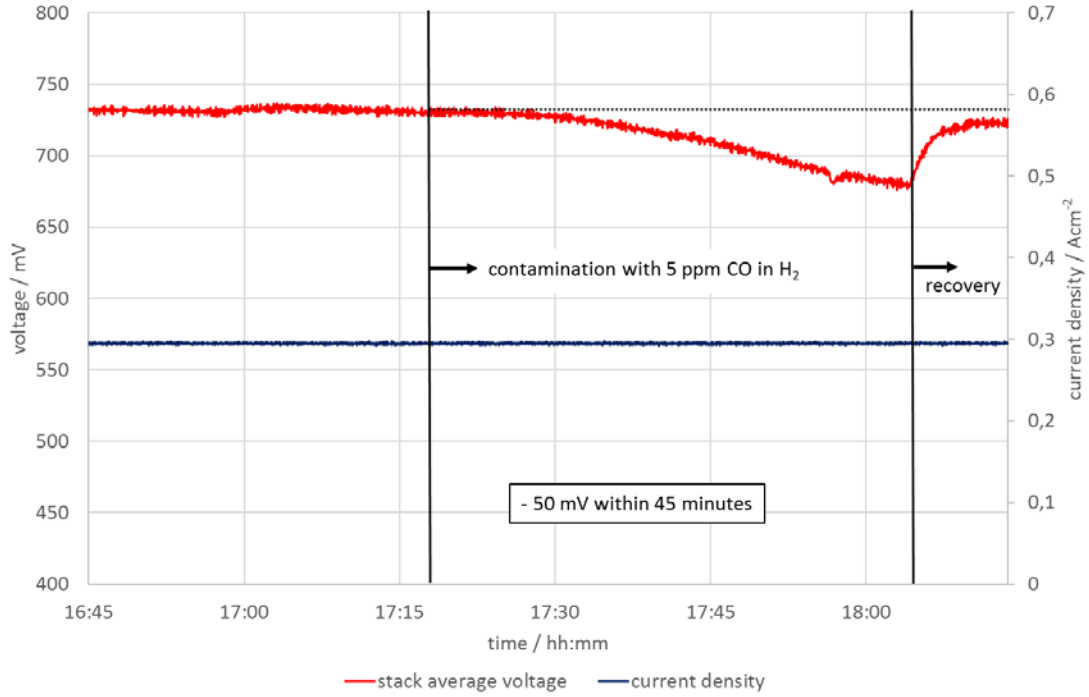
1. Start up, Polarization curve and reference poisoning (5 ppm CO)
2. Stop procedure with air bleed to oxidize CO
3. Start up stack
4. Poisoning with 1 ppm H_2S in H_2 until 30 mV voltage drop is reached
5. Polarization curve and reference poisoning (5 ppm CO)
6. Stop procedure with air bleed to oxidize CO (and H_2S)
7. Start up stack
8. Run defined load cycles
9. Reference poisoning – measure possible change in CO tolerance
10. Further repetitions of points 6 – 9 depending on results

Implementation of load cycles and CO reference

- Example of load cycle and CO reference measurement



Load cycles



CO reference measurement

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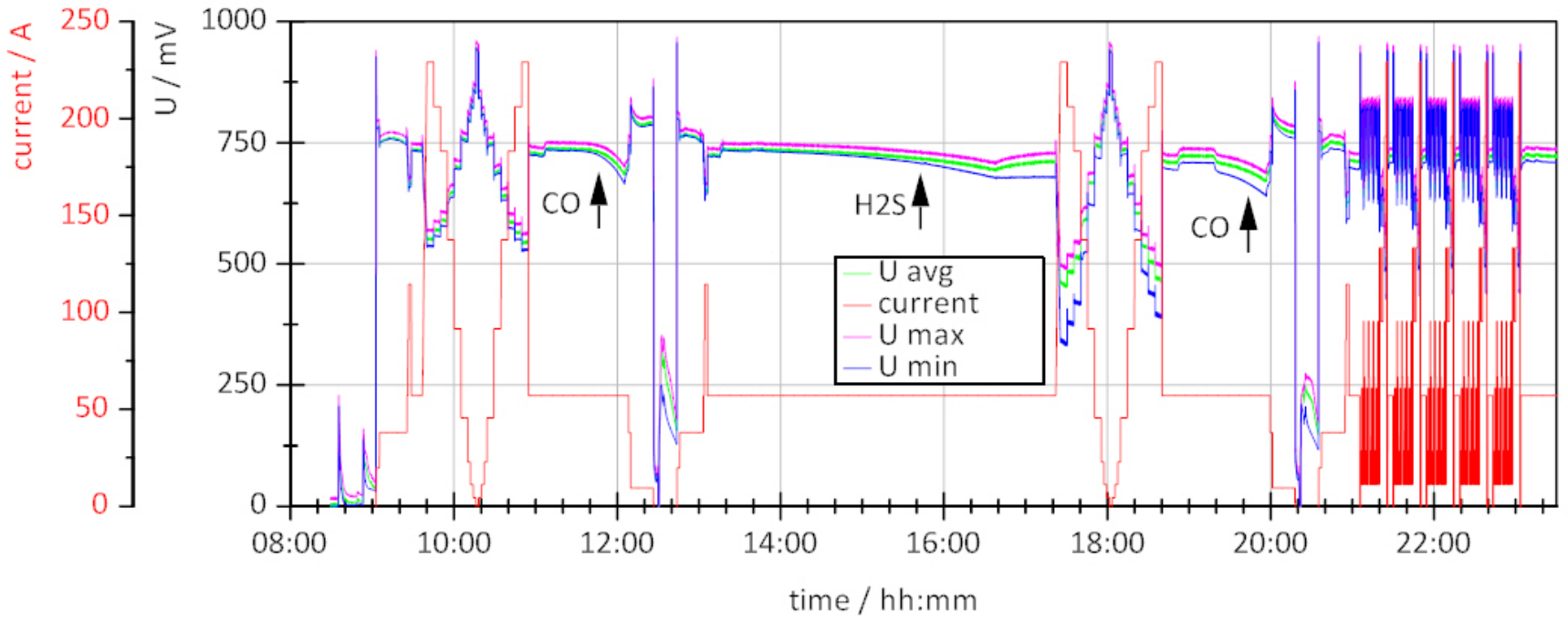
Overview H_2S contamination test procedure



- Successful implementation of CO, H_2S contamination, stop procedure with air bleed
- Strong negative influence of H_2S at higher load levels

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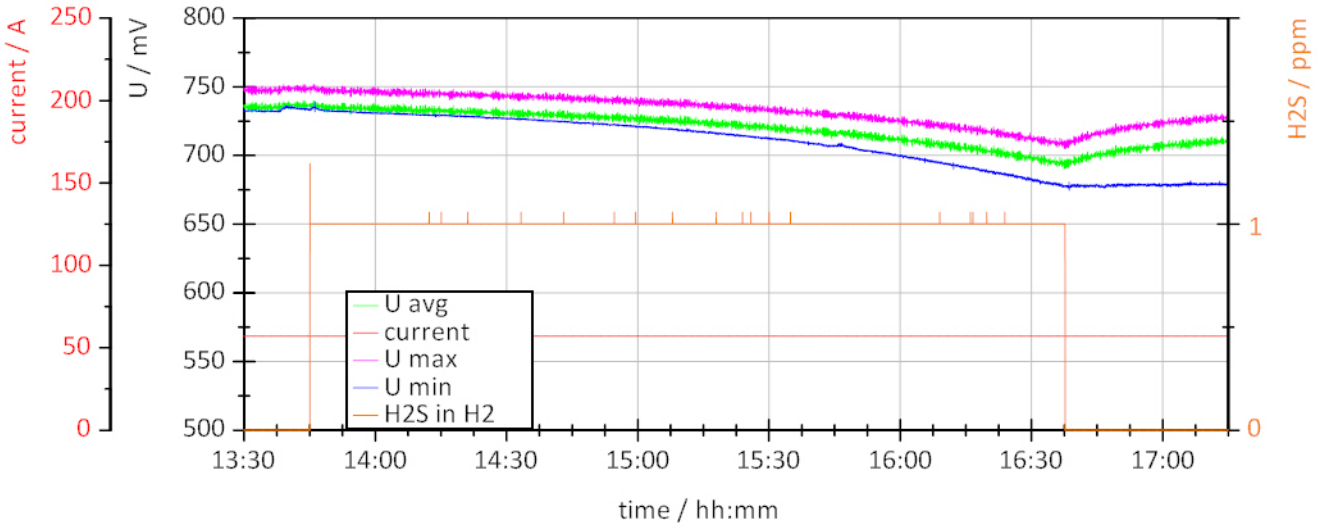
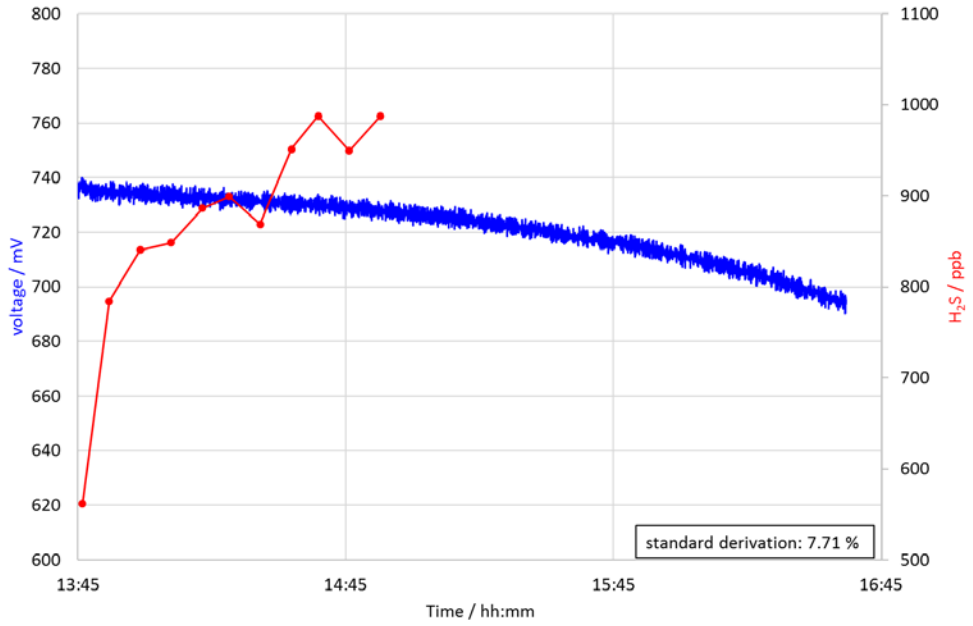
H_2S contamination

- 30 mV voltage loss due to 1 ppm H_2S within 175 minutes
- 2 cells with higher voltage losses compared to U_{avg}
  ➡ no recovery after stop of contamination





- Comparison voltage decay vs. H_2S values at dry inlet measuring point
- Max. H_2S concentration could be measured at dry inlet sampling point after 50 minutes contamination

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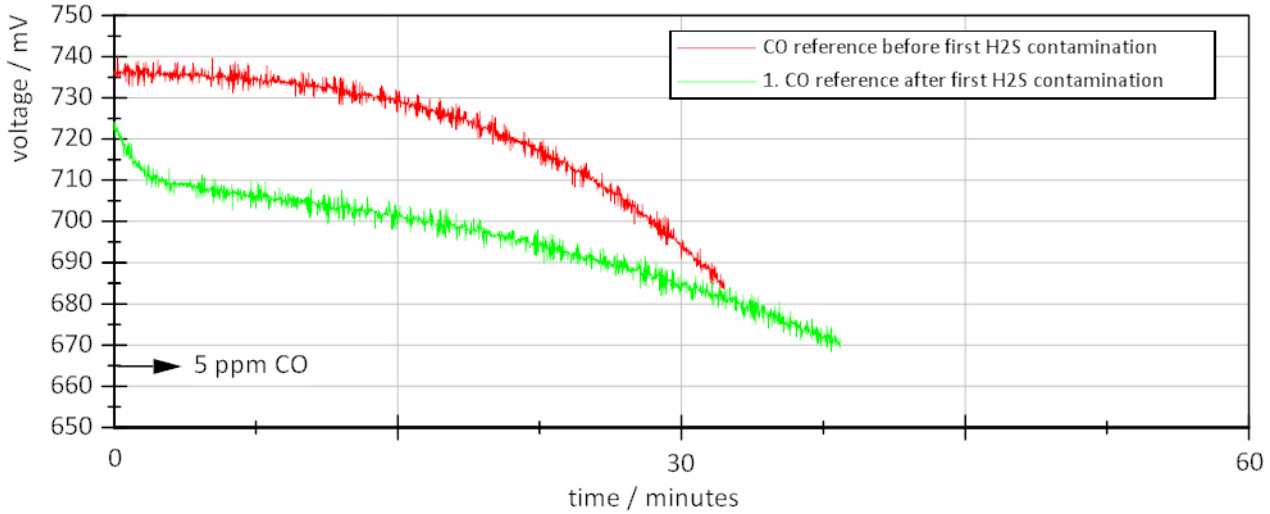
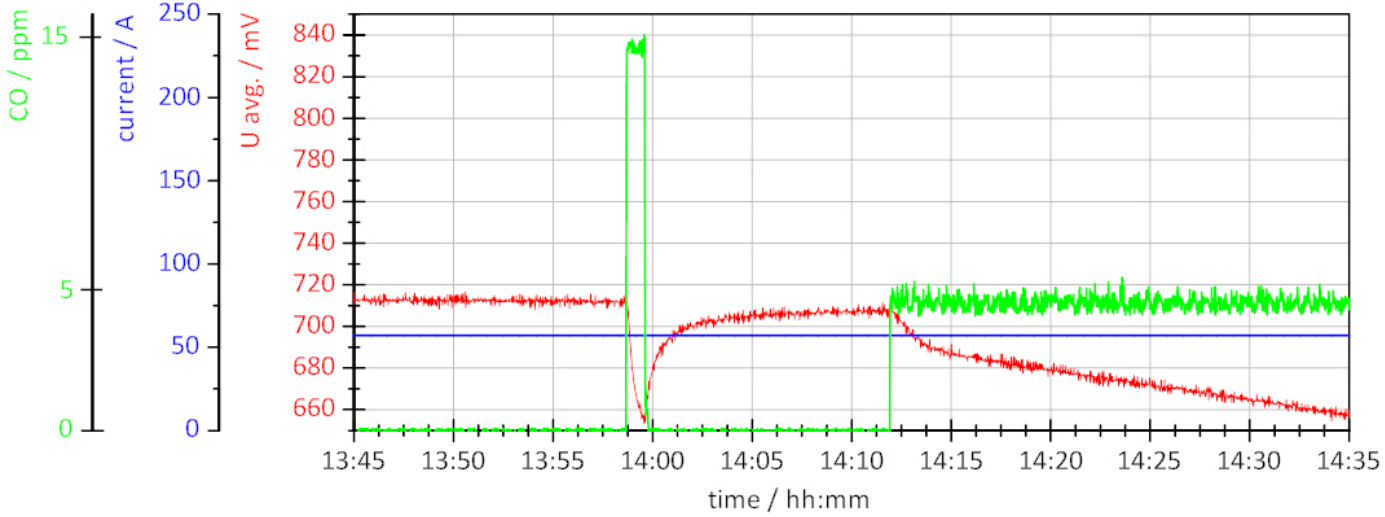
CO tolerance

- 1. CO reference after contamination indicates no lower CO tolerance
- This result was observed up to 16 hours after contamination
  ➡ test with 15 ppm CO in H_2





- Voltage loss of 50 mV within one minute (15 ppm CO)
  ➡ After short recovery again reference with 5 ppm CO

Result: A lower CO tolerance could be detected

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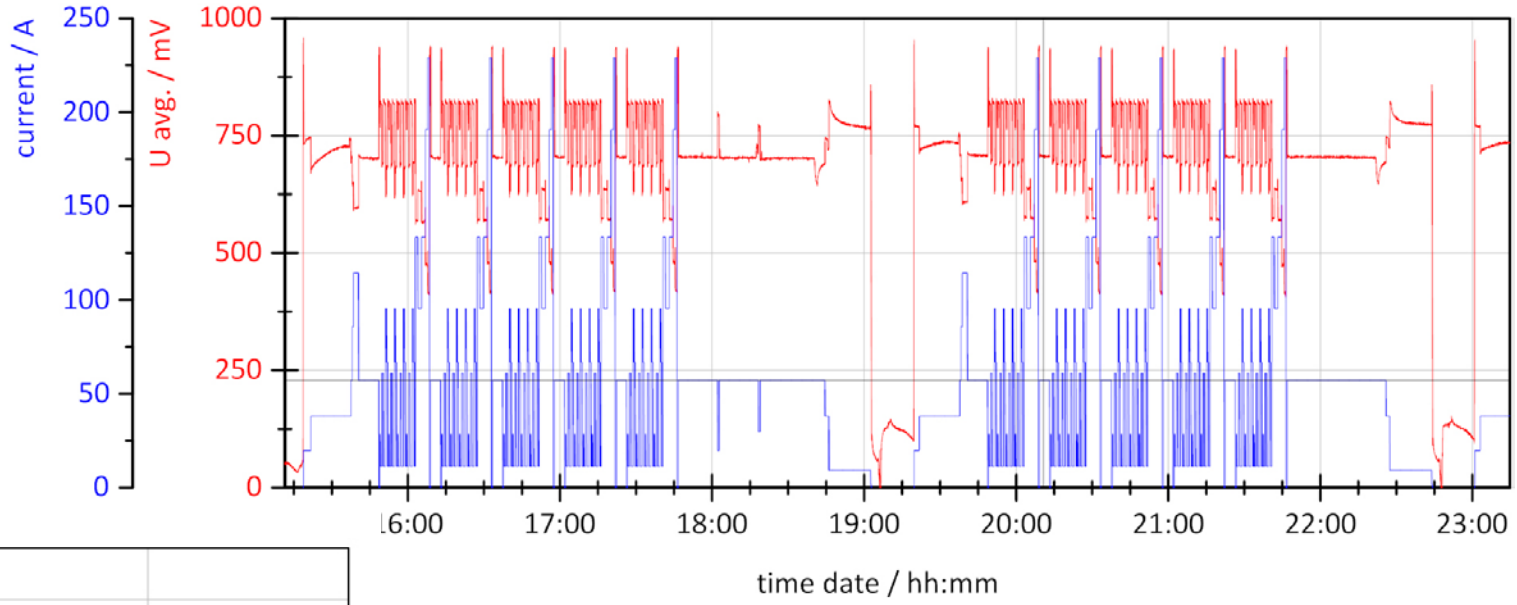
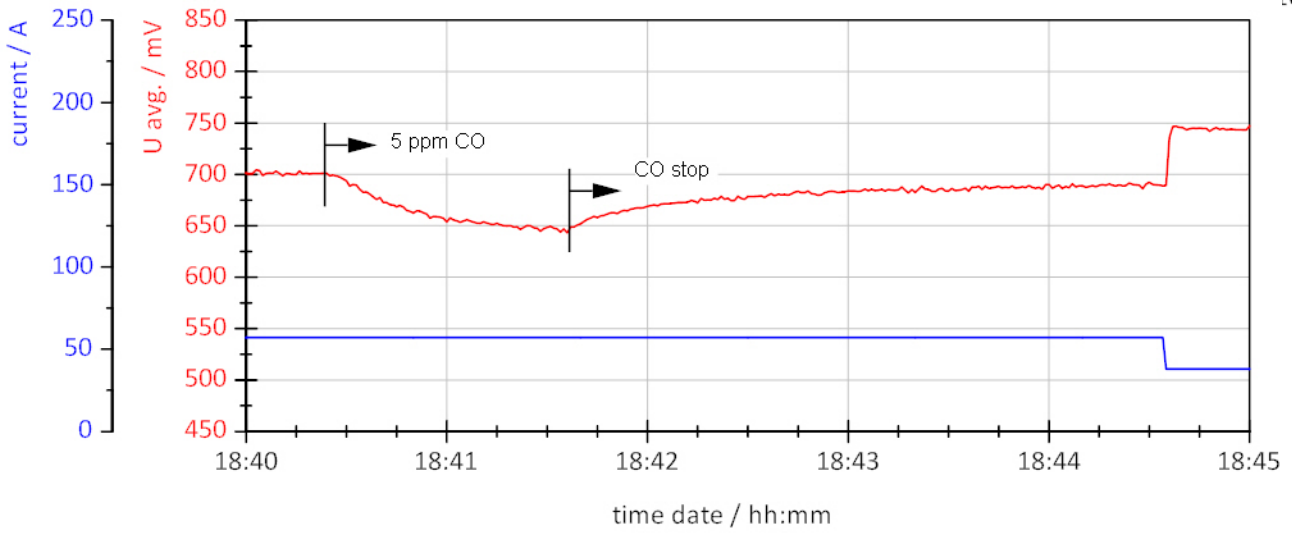
Continuation of procedure with load cycles and CO reference

- After 20 minutes shut down procedure with load cycles and CO reference were performed again





- Seriously lowered CO tolerance
- 50 mV voltage loss due to 5 ppm CO within 2 minutes

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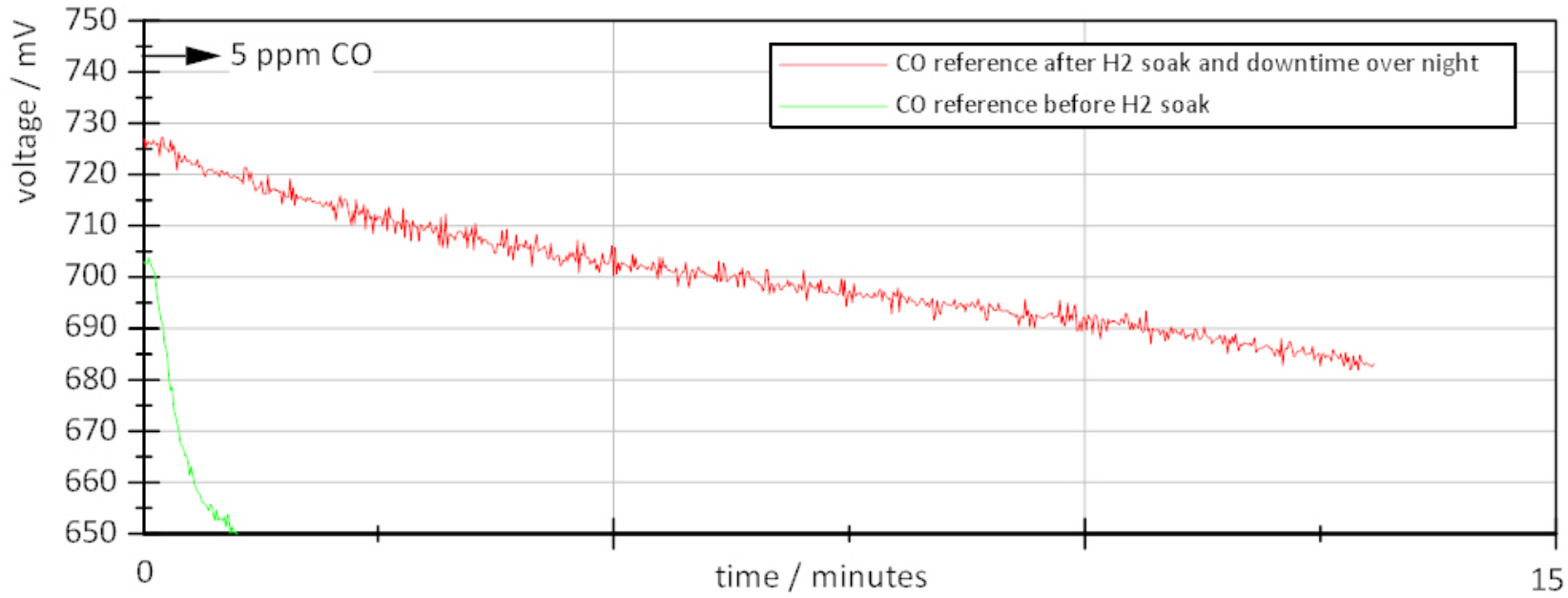
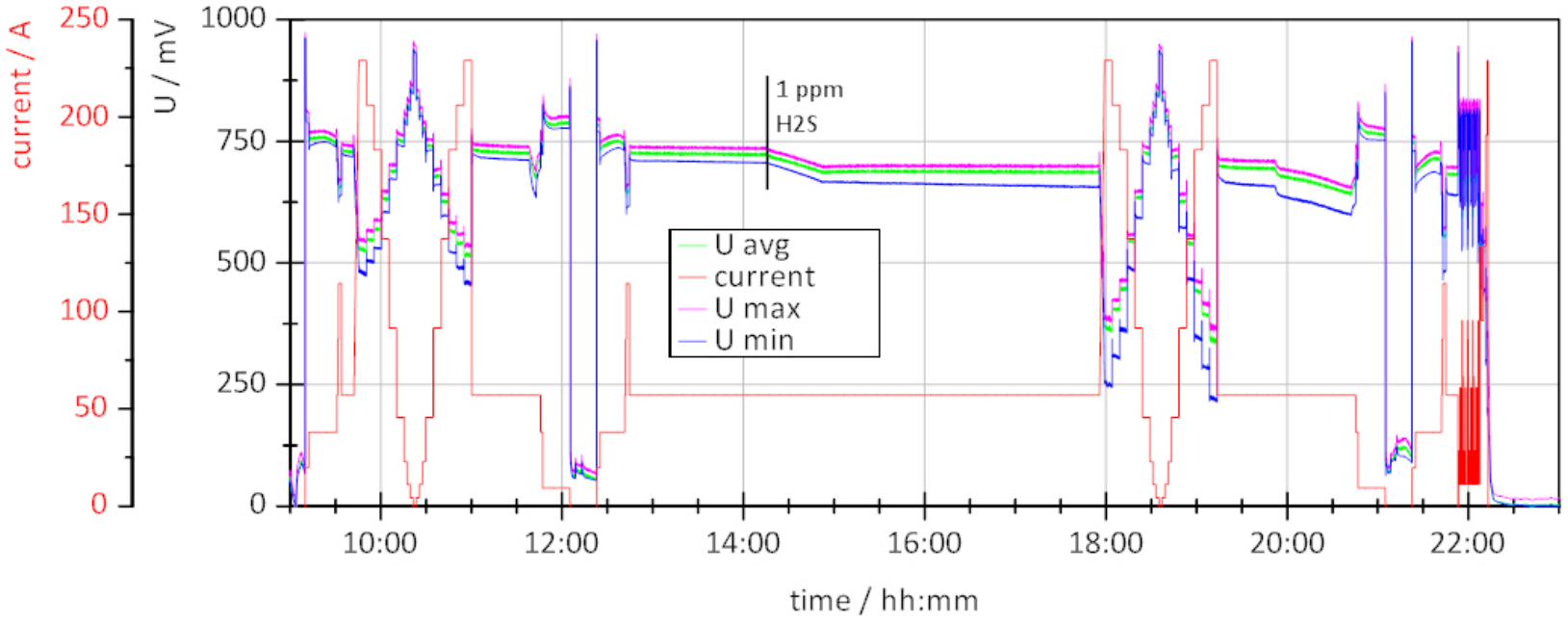
Stop procedure with H_2 soak over night



- Partly recovery due to H_2 soak and downtime over night
  - ➡ Higher CO tolerance → but only a temporary effect
  - ➡ Voltage increase at lower load points
- Second test run with H_2S contamination

Overview H_2S contamination test procedure (second test run)



- Strong negative influence of H_2S at higher load levels (polarization curve)
- No further load cycles realizable due to strong voltage losses

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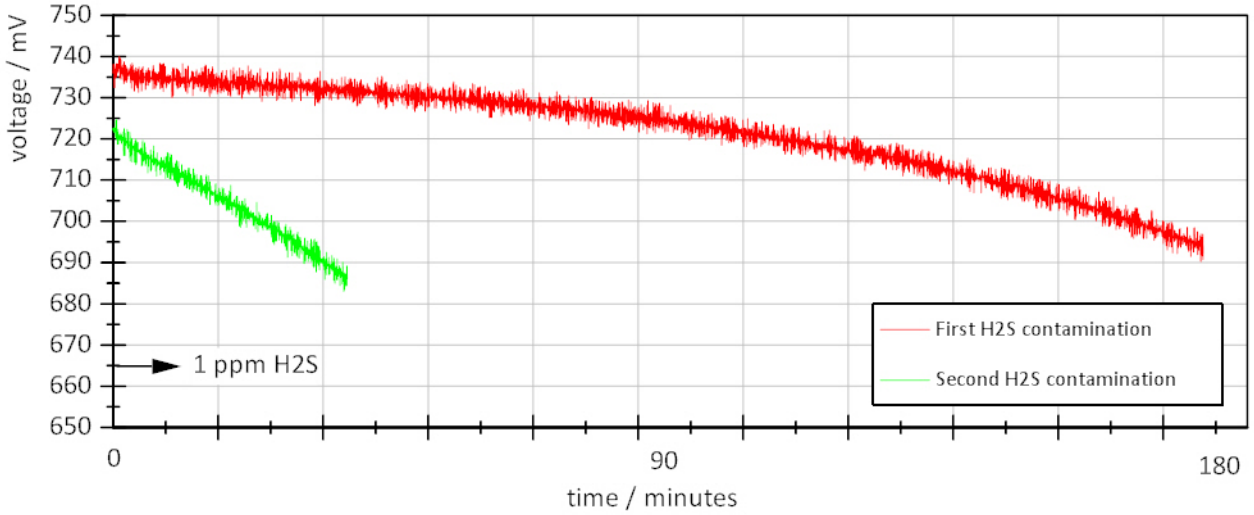
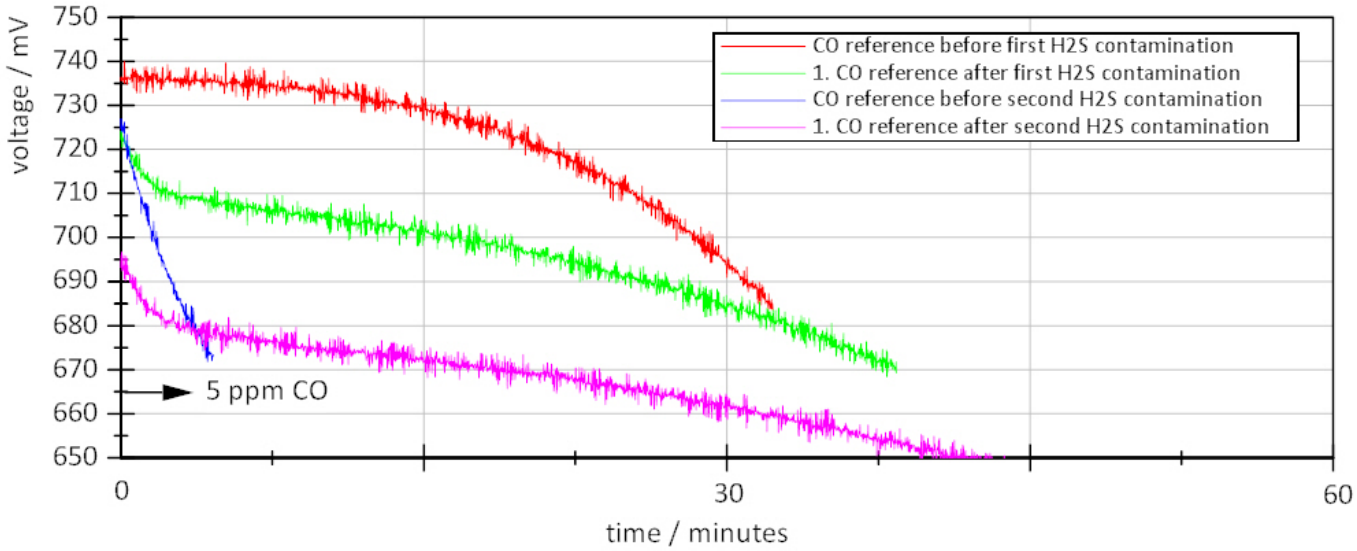
H_2S contamination and CO tolerance (second test run)

- Strong negative influence due to first H_2S contamination
- Second contamination with 1 ppm H_2S faster compared to first contamination





- Fast voltage loss before second H_2S contamination
- Reproducible voltage course at first CO reference after H_2S contamination
- Again higher CO tolerance

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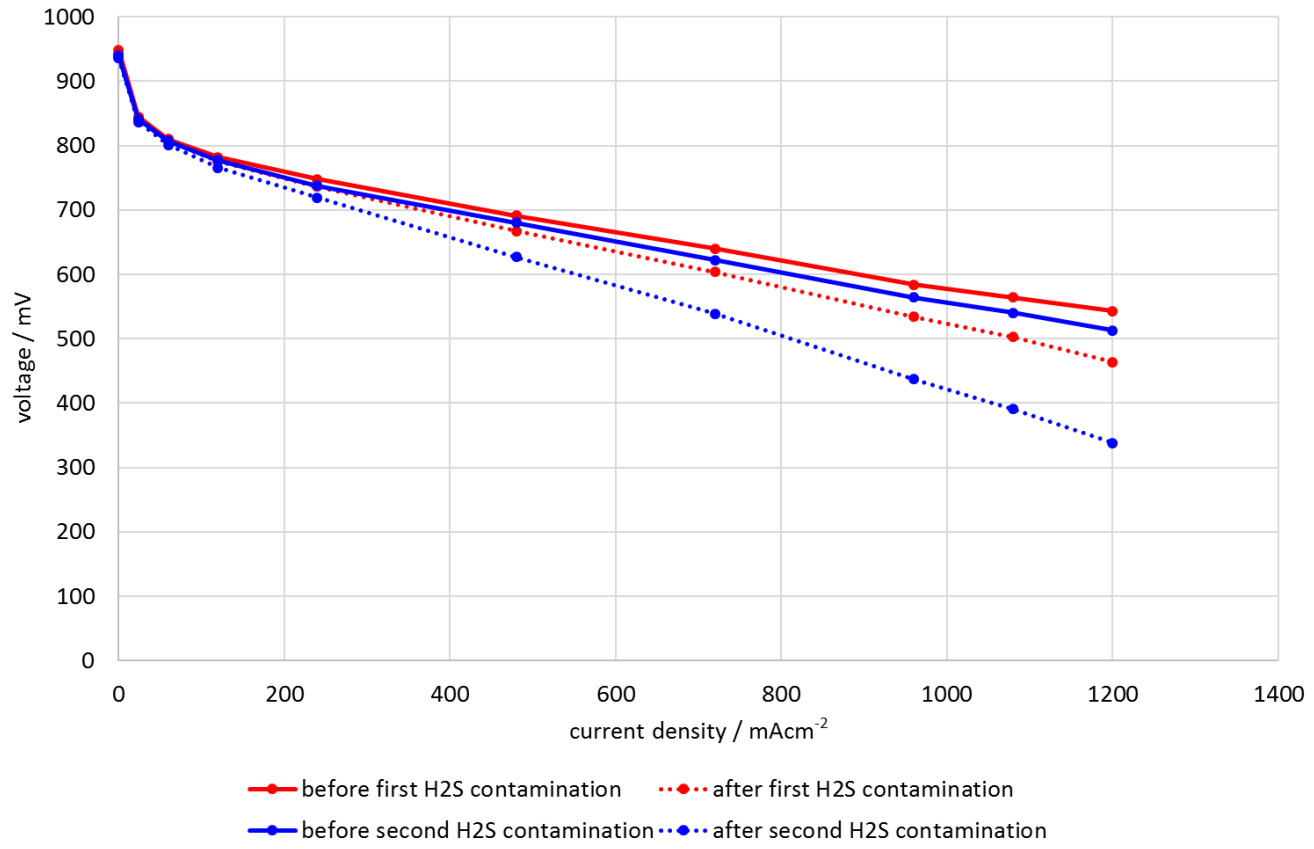
Comparison of polarization curves



- Pt surface on the anode is seriously contaminated before the second H_2S poisoning
- Previously contaminated stack is now more sensitive to H_2S

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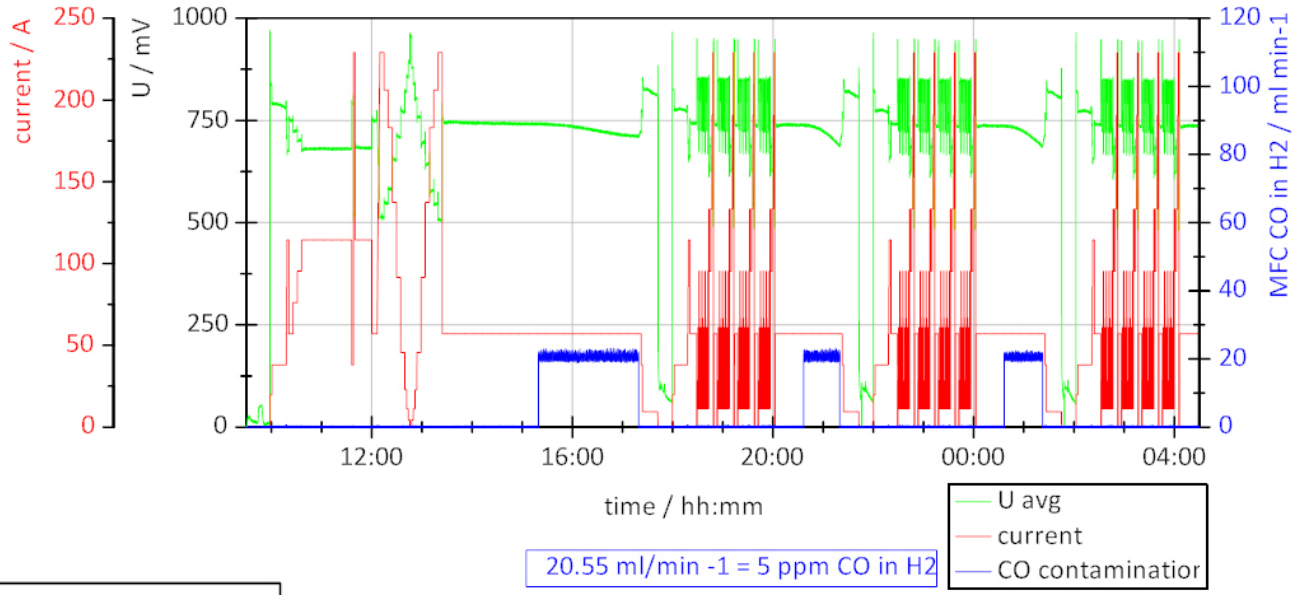
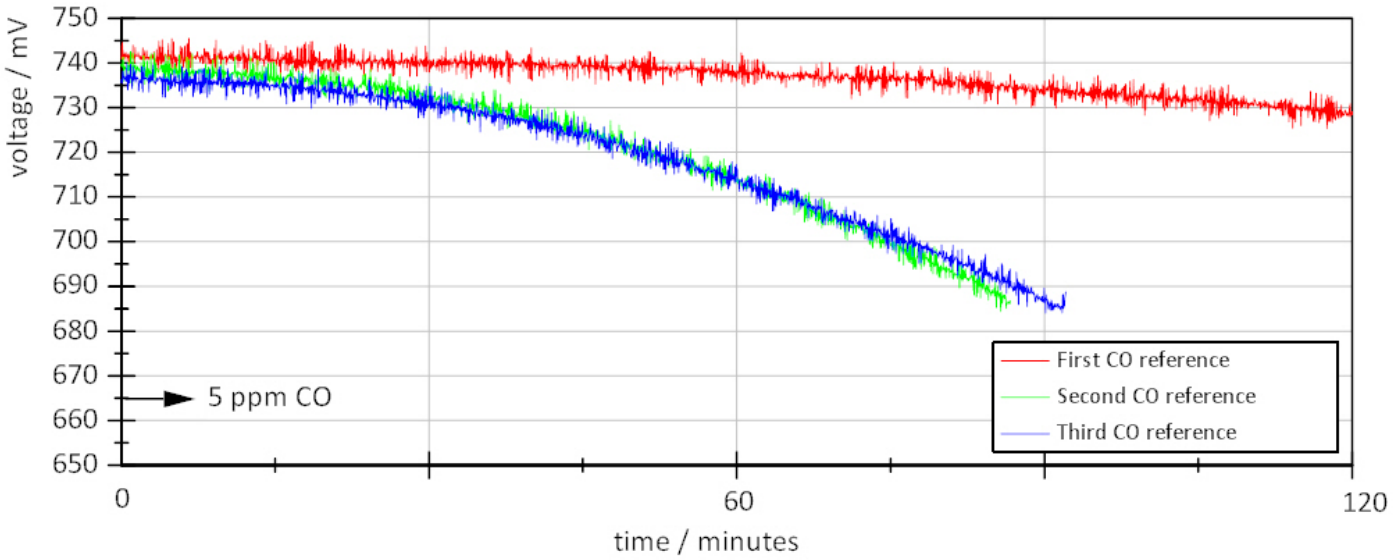
Break in and CO reference with new HYDRAITE stack

- Comparison of 3 CO reference measurements and load cycles (without analytics)
- No reproducible CO reference measurements





Measurements will be repeated with CO analysis to control the CO concentration at dry anode inlet

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Challenges and next steps

- H_2S and CO analytic in recirculation loop (wet gas)
- Perform reproducible CO reference measurements (before contamination with H_2S)
  - ➡ Leckage tests to prevent influence of air flow during CO reference
  - ➡ Measurement of CO inlet concentration and O_2 concentration
- Based on the first results with H_2S
  - ➡ Open discussion and adjustment of the test protocol before starting H_2S procedure with new HYDRAITE stack

Summary

- The effect of H_2S on CO tolerance takes some time
- One possibility: Formation of COS or some other molecule?
- As it seems that the contamination process (after H_2S dosing is stopped) takes some time it must be completed before CO tolerance recovery can be monitored

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THANK YOU

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