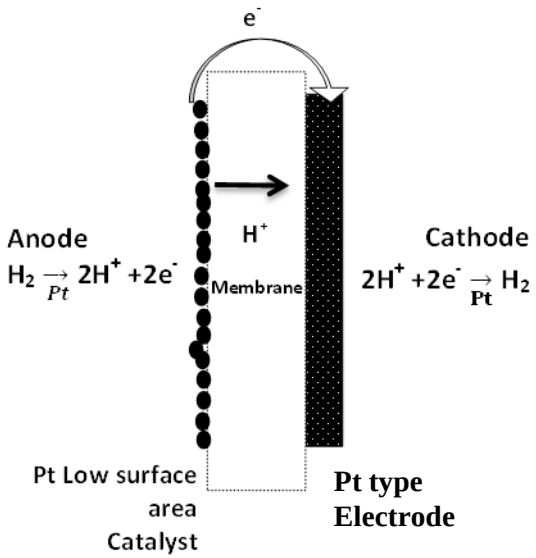
Hydrogen Safety Codes and Standards Activities at LANL

HYDRAITE Workshop
Ulm, Germany



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Team:

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Part I: Fuel Impurity Testing

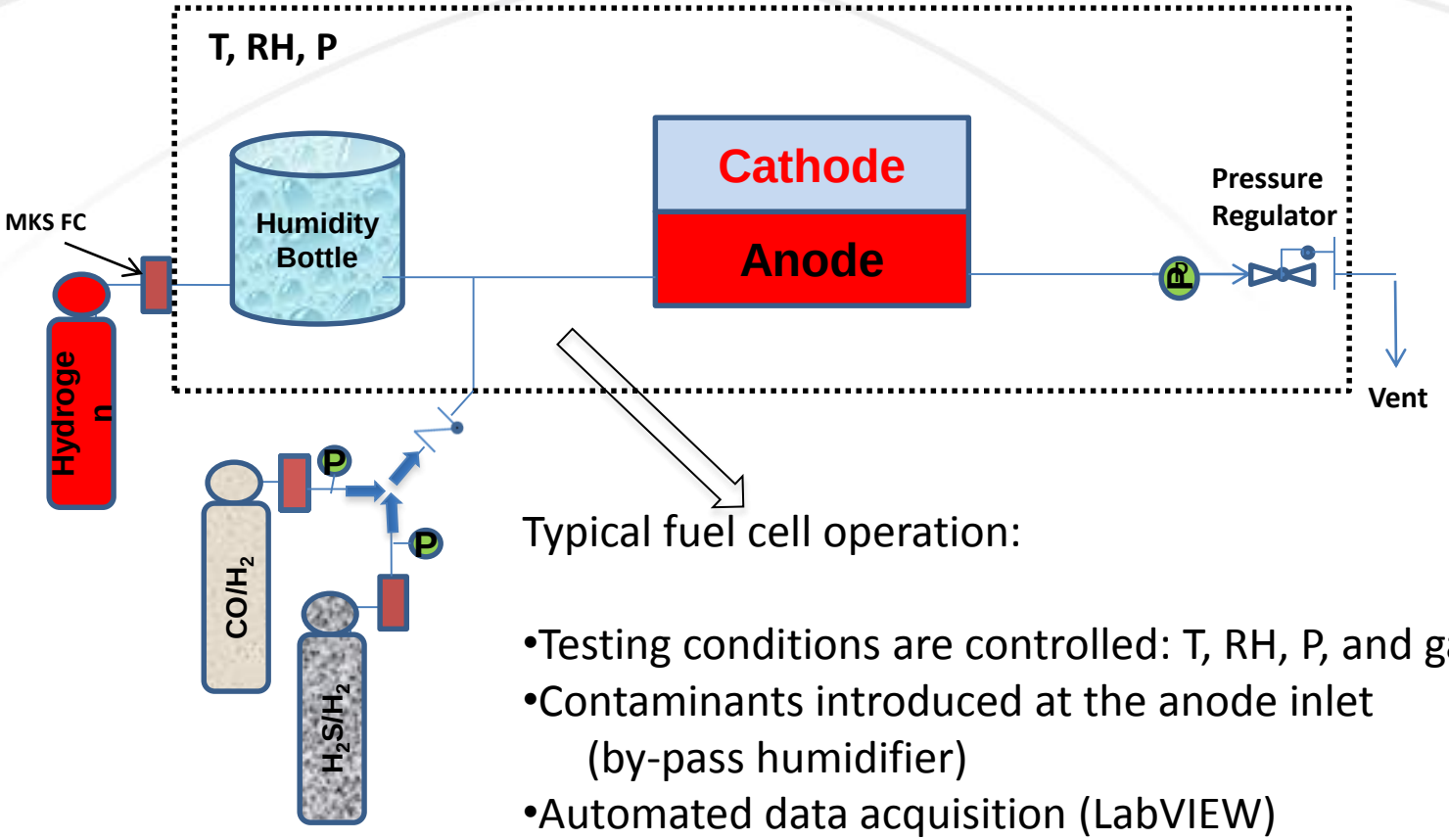
- **Background**
- **Experimental Set-Up**
- **Results with CO and H_2S**
  - **Fuel: Single-pass mode vs. Re-circulation mode**
  - **Pre-Dosing**

Background

- Current fuel specifications: ISO 14687-2 and SAE J2719 allow 200ppb CO and 4ppb H_2S plus others
- Previous FC studies were instrumental in their development; but higher loaded Pt electrodes (≥ 0.4 mg_{Pt}/cm^2) were used, and tests were conducted in single-pass mode at constant current densities
- U.S. DOE 2020 target loading calls for 0.125 mg_{Pt}/cm^2 which results in an anode loading approaching 0.025 mg_{Pt}/cm^2
- Focus: Low loaded electrodes tested in both single pass mode and fuel re-circulation mode at impurity levels in the fuel specification

Question: Do the standards need revision?

Fuel Re-Circulation System: Single-Pass Mode



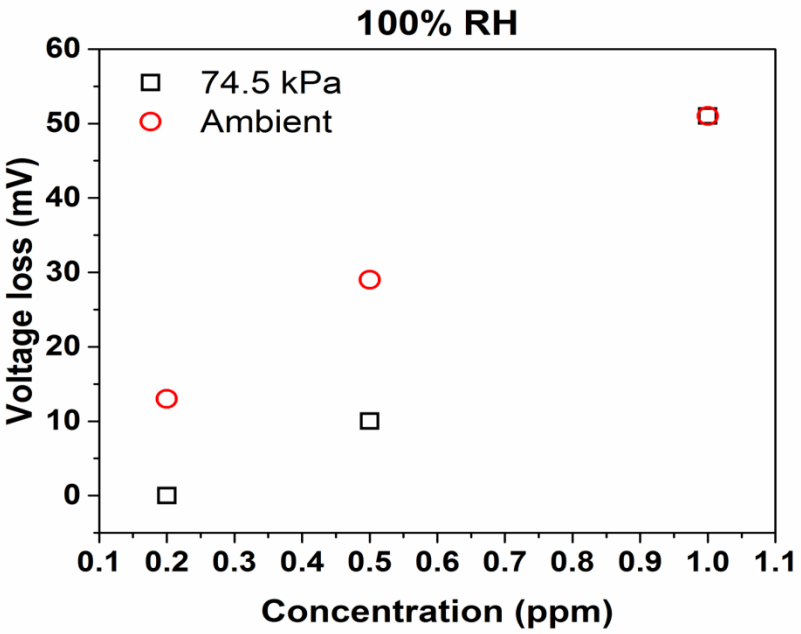
Typical fuel cell operation:

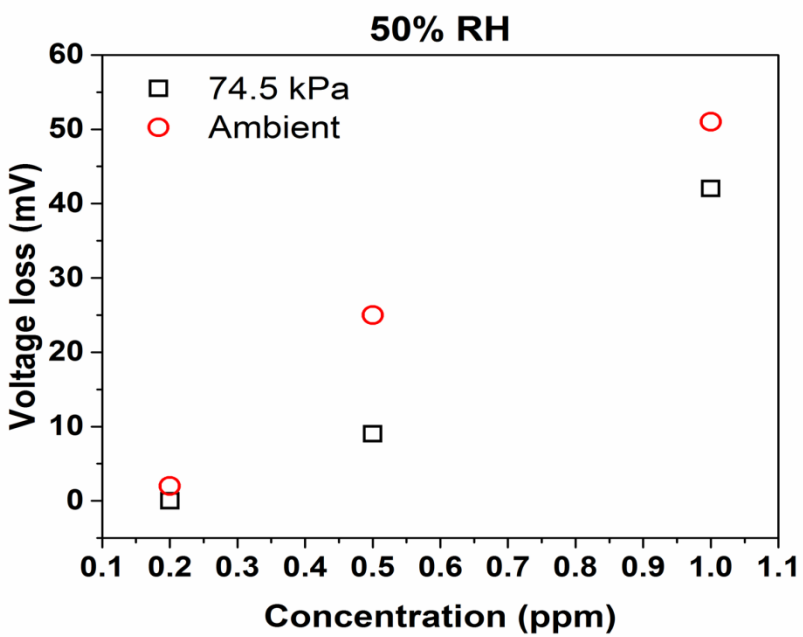
- Testing conditions are controlled: T, RH, P, and gas flows
- Contaminants introduced at the anode inlet (by-pass humidifier)
- Automated data acquisition (LabVIEW)

MEA: 25 cm2, A/C: 0.05/0.10 mg Pt/cm^2
NR211

Fuel stream exhaust gets released to atmosphere.

CO Impact: Constant Dosage(7.5ppm*hr)/RH





Voltage loss versus CO concentration was plotted for both pressures

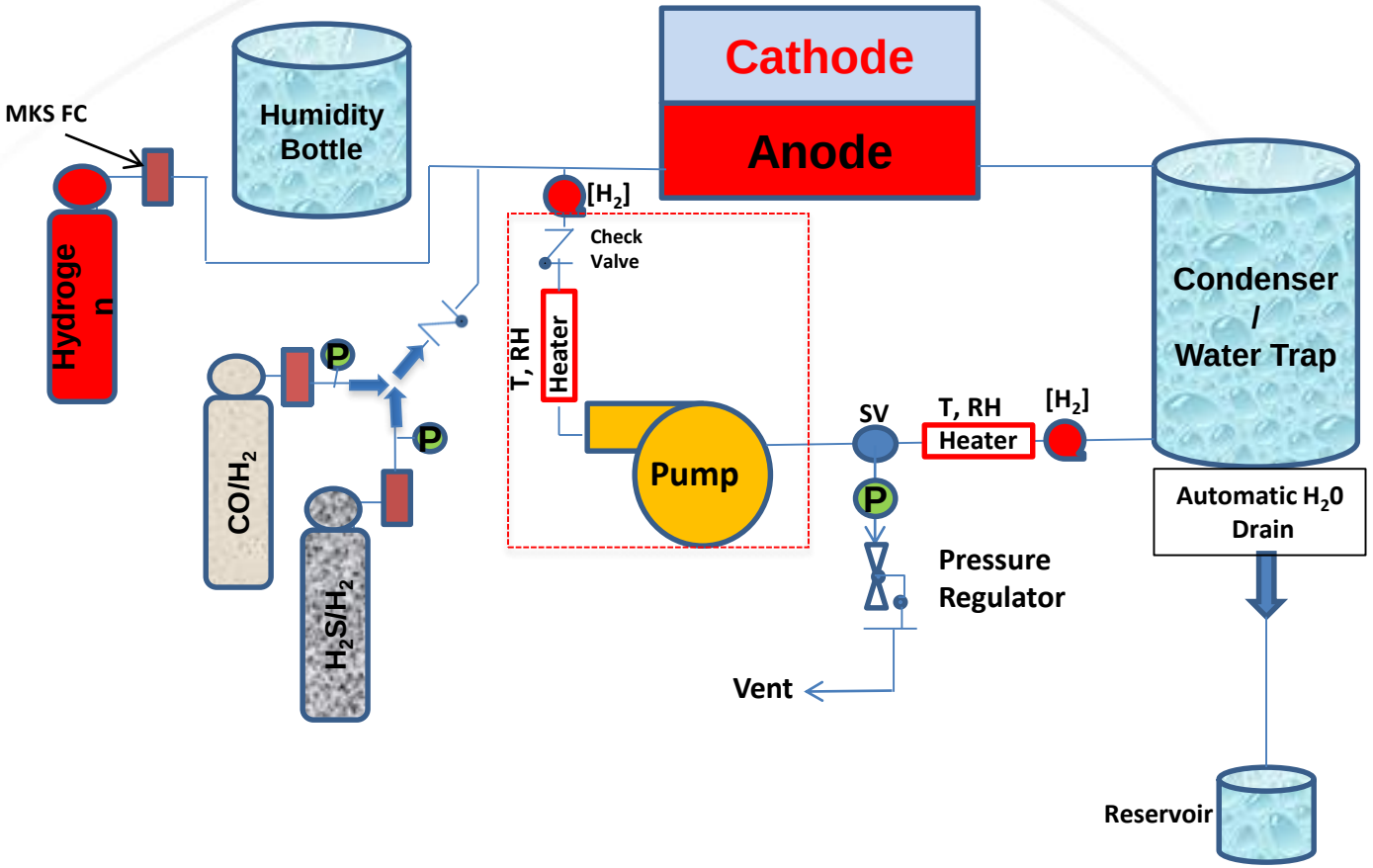
74.5 kPa tolerated 0.2 ppm CO (35hrs)

Ambient pressure showed a 13mV decay @ 100% RH **(Left graph)**

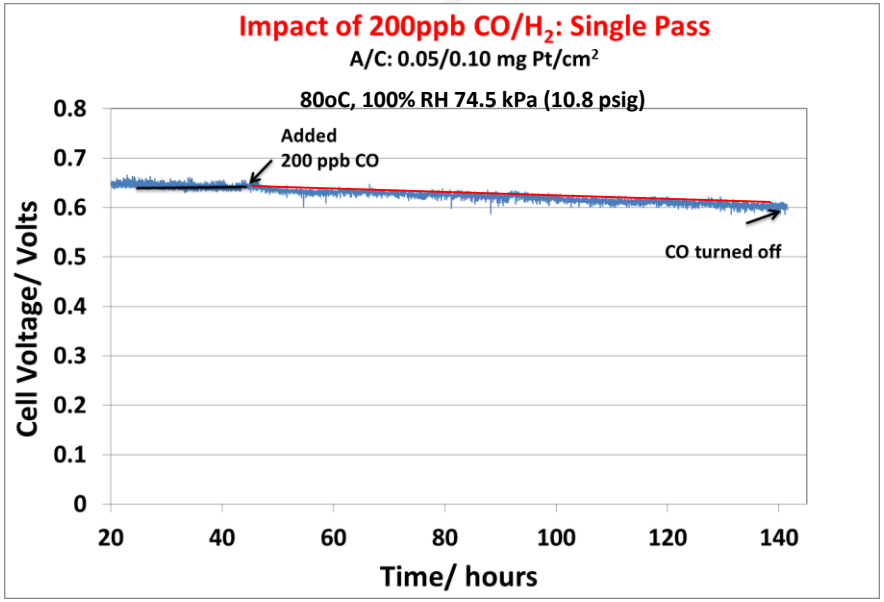
Constant dosage expt's were repeated at 50% RH

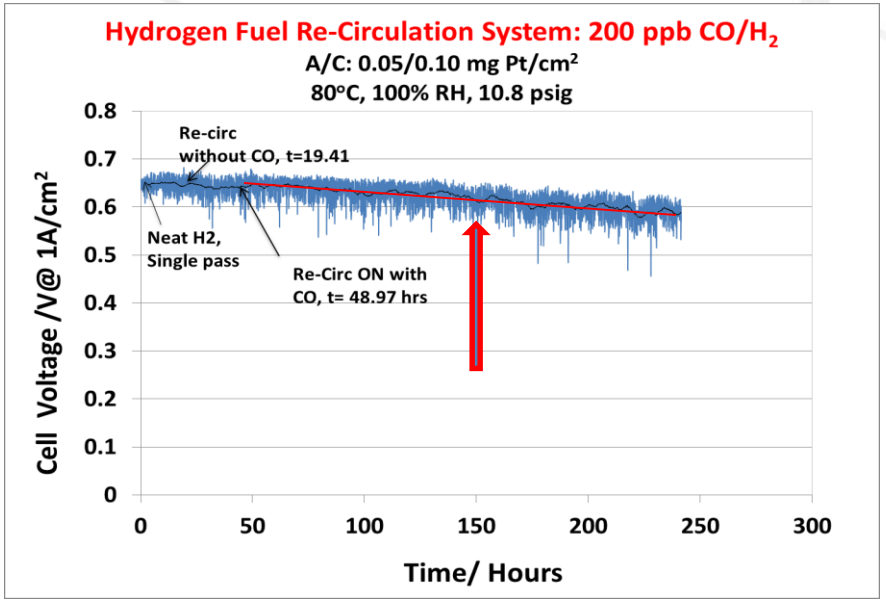
Both pressures were able to tolerate 0.2 ppm CO within the accuracy of the load box **(Right)**

Fuel Re-Circulation System for Fuel Quality Testing



H_2 Recirculation vs Single-Pass with 200 ppb CO/H_2





- **Voltage loss after 100 hrs with single pass is ~ 38 mV.**
- **Fuel Recirculation system loss is ~ 50 mV.**
- **~30% extra voltage loss due to recirculation at anode**

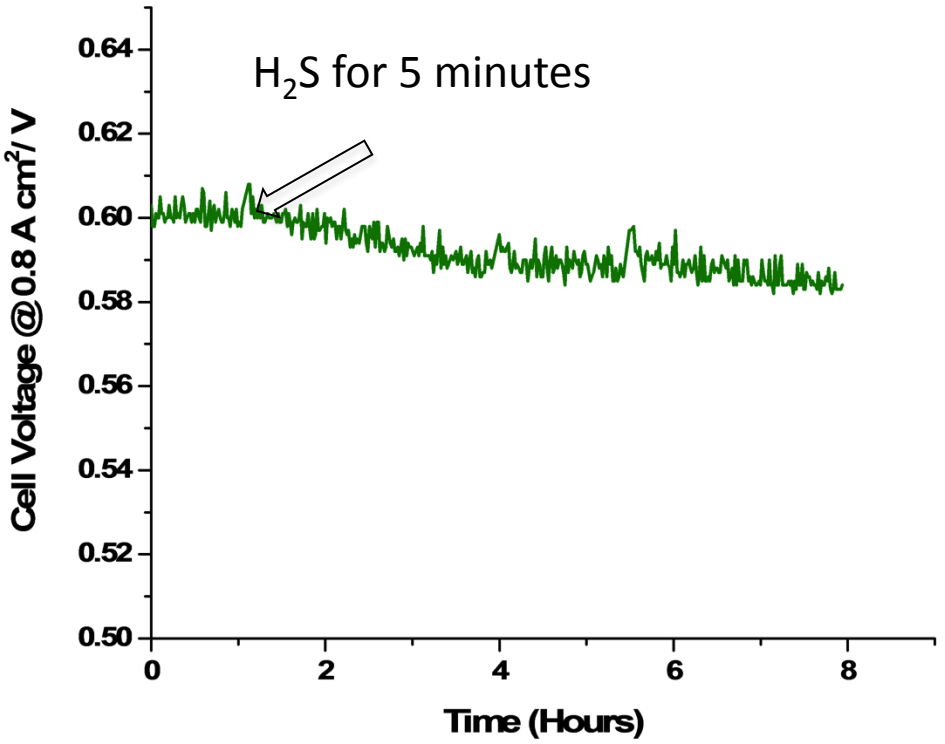
Pre-Dosing Experiments: 200ppb CO in Hydrogen

In re-circ mode, we introduce 4ppb H_2S for 5 minutes.

Afterwards, 200ppb CO is introduced for 7h.

No voltage loss observed during the 5 min exposure to S

Overall voltage losses with CO were approx. 10 mv during the exposure time



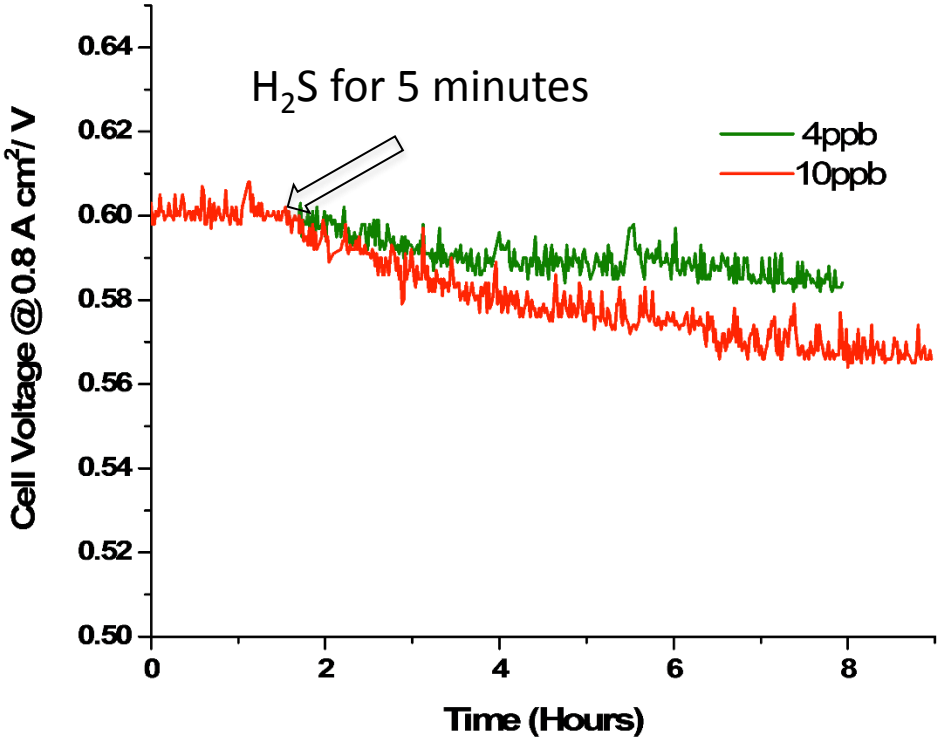
1.2 ppm H_2S for 1 second should have the same effect (dosage controlled)

Pre-Dosing Experiments:

Similar scenario except with 10 ppb H_2S pre-dose.

Losses are enhanced as concentration of pre-dose gas increases. 2X the losses

A system upset containing sulfur can be detrimental to cell performance. At the SAE/ISO levels the CO impacts become more severe.



3 ppm H_2S for 1 second should have the same effect (dosage controlled)

Part II: Fuel Quality Analyzer

Scope

The development of a device to measure impurities in the fuel stream would be useful to the fuel cell community, hydrogen fueling stations and suppliers. Some of the more important qualities of the device:

- Inexpensive
- sensitive to the same impurities that would poison a fuel cell stack (e.g. CO, H_2S, and NH_3)
- quick response time to fuel contaminants

Such a device could be used as an early alert monitor and prevent damage to fuel cell stacks!!!

Approach

- This device operates as an electrochemical pump using a MEA-type Configuration. **(no air or water available).**
- Use similar components to a fuel cell stack (e.g. Ionomer, PGM, and GDLs)
- Identify best materials and their configuration

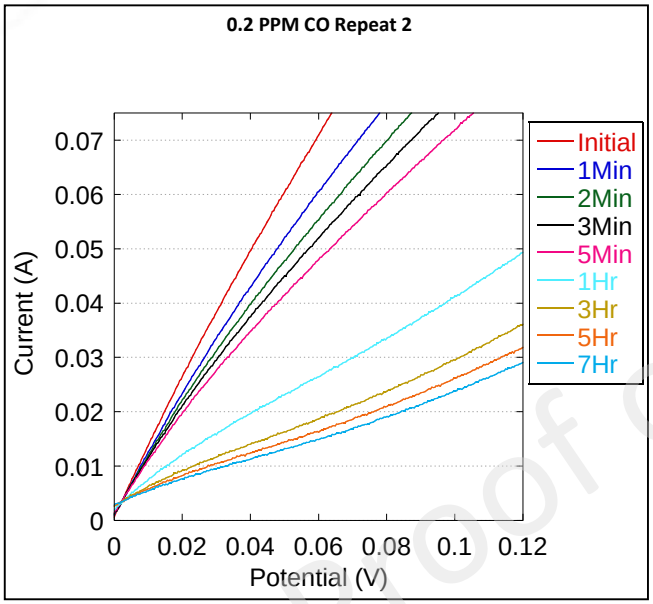
Identifying Desirable Materials

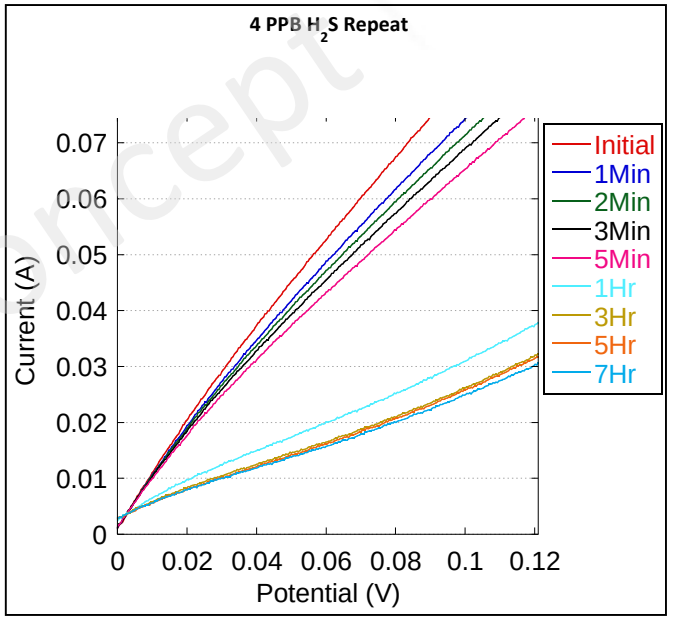
Reference Electrode: Tolerant and Stable

- High surface area materials

Working Electrode: Durable and Sensitive

Engineered electrode provides stable Pt particle sizes and the low loadings desired in an analyzer.





Desired response times obtained for both CO and H_2S at the ISO level!

t < 5 minutes!!!

Developing the Prototype

- **Membrane Hydration Challenging**: Identifying conditions needed for

  constant membrane humidification

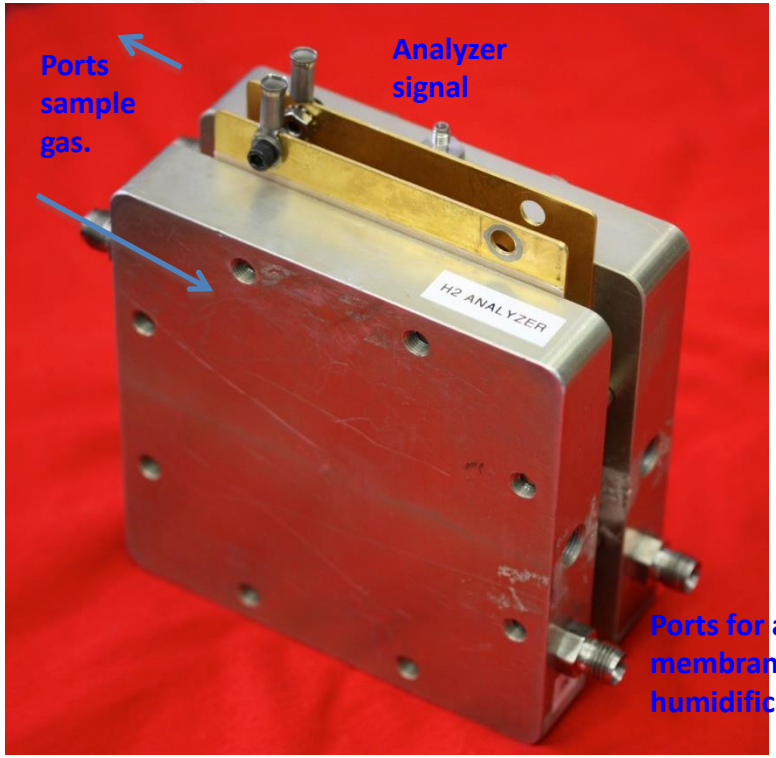
  - Characterize and confirm by measuring HFR and CV
  - Vary flow conditions
  - Vary Membrane thickness
- Determine a **fuel flow-rate** that will not compromise sensitivity or response time

Prototype Developed

About the Prototype:

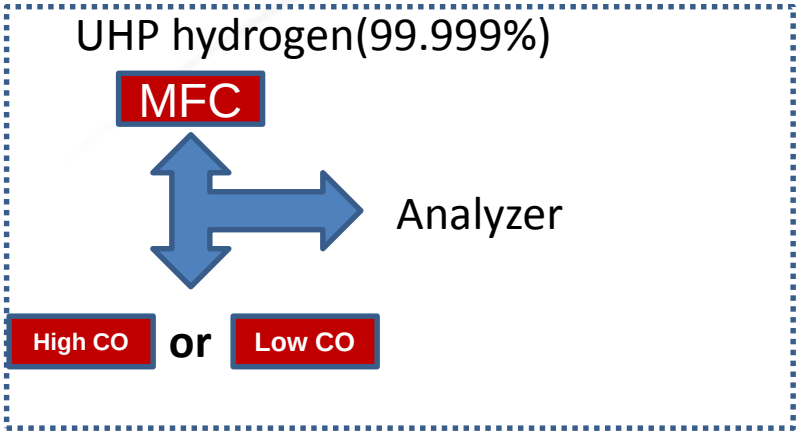
- Incorporate design elements from these experiments into analyzer prototype that uses standard PEMFC hardware and technology.
- Use LANL innovative humidification scheme. Test HFR stability and determine maximum dry gas flow rate.
- Test analyzer with ISO14687-2/

  SAE J2719 contaminant levels



Initial Prototype Results

Automated Gas Set-up

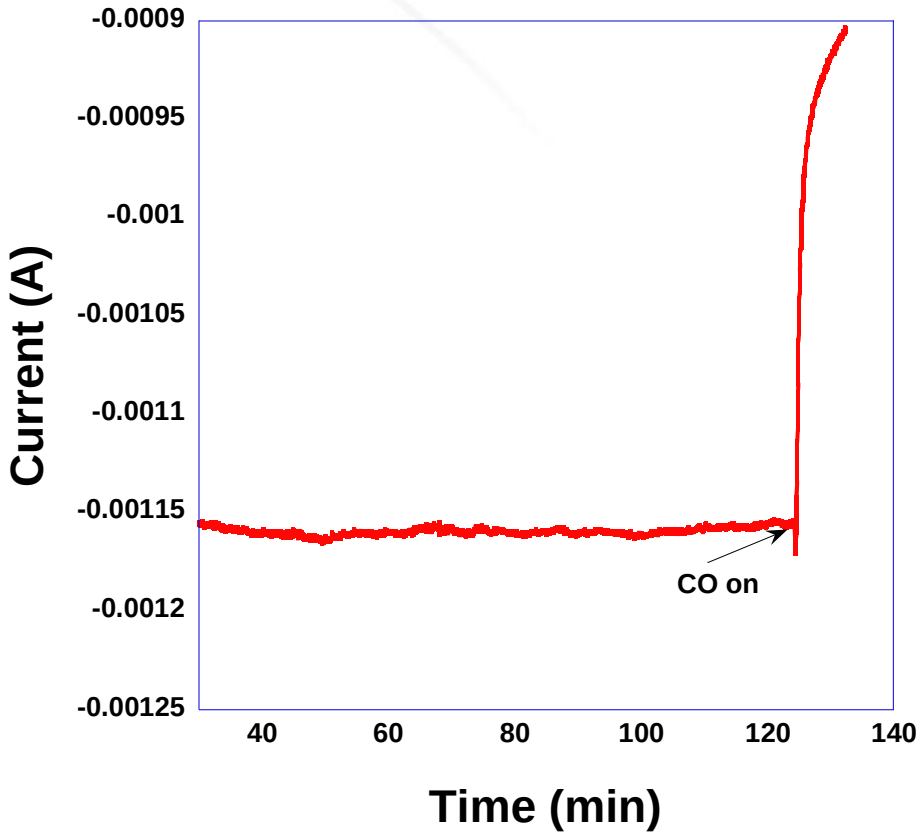


Test conducted at room T

MKS MFC calibrated for both gases

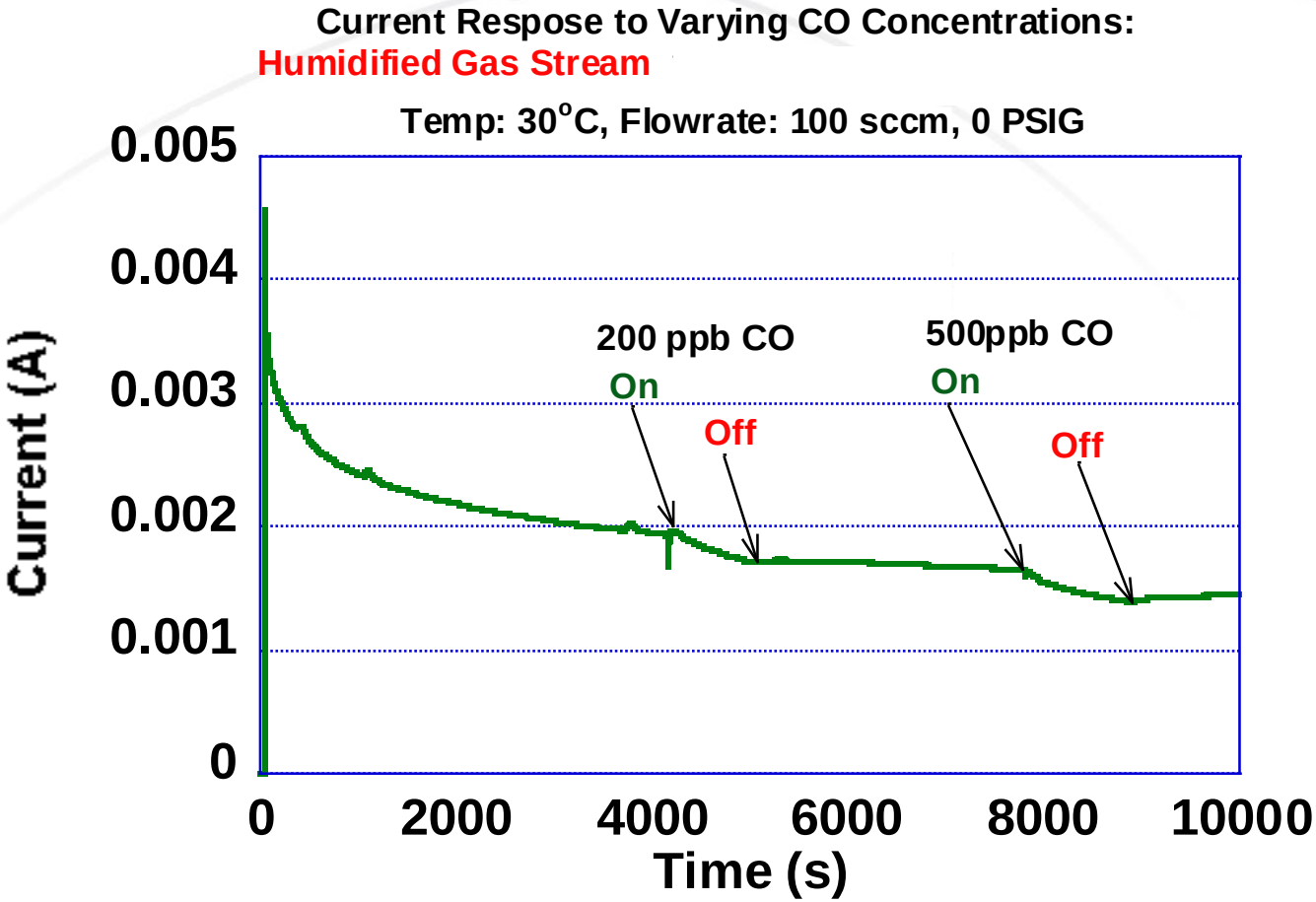
Instance response to 50 ppm CO

Analyzer response to 50 ppm CO



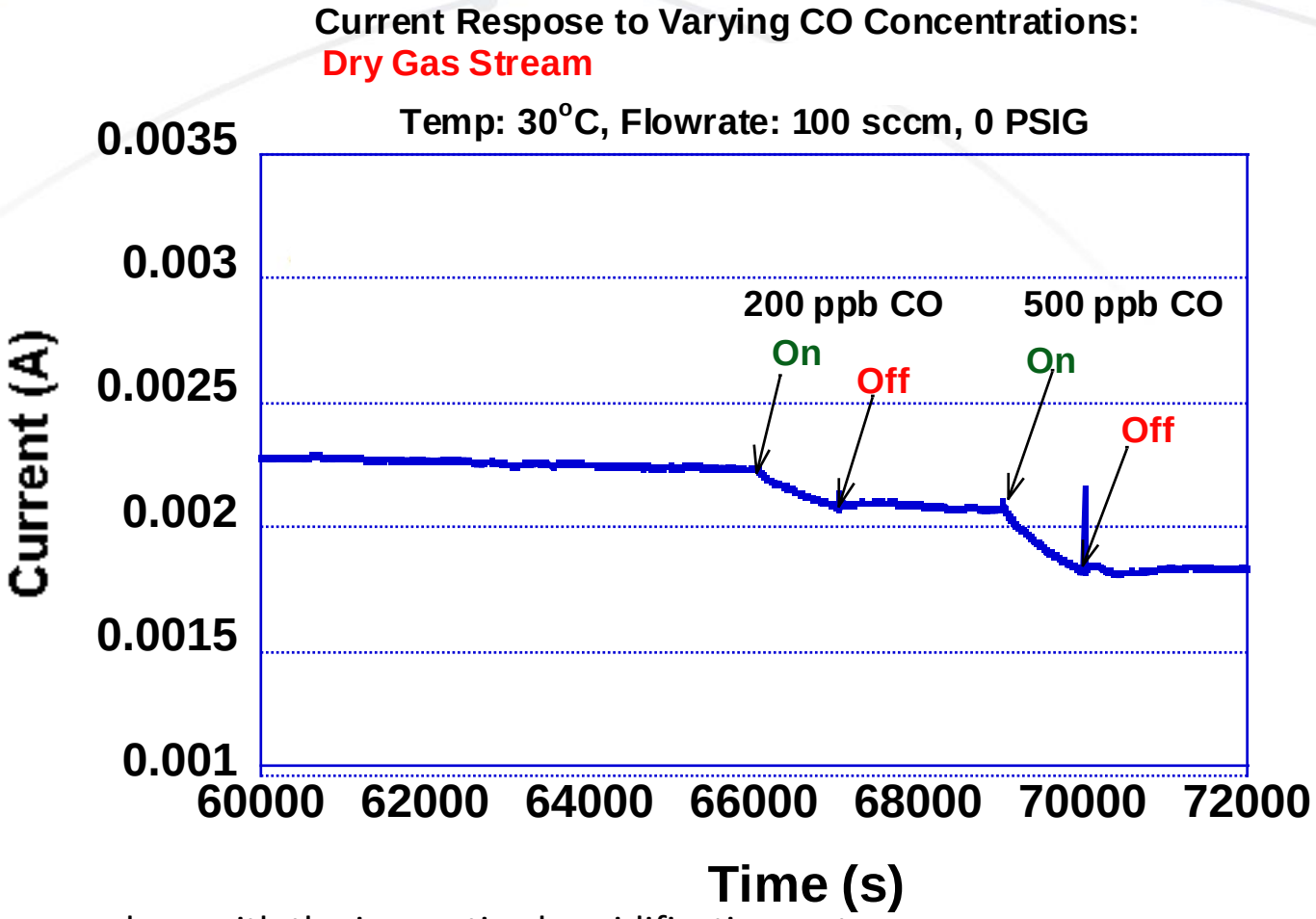
Results showed promise, CO concentration 250 times the ISO/SAE!!!

SAE Level Studies: Baseline



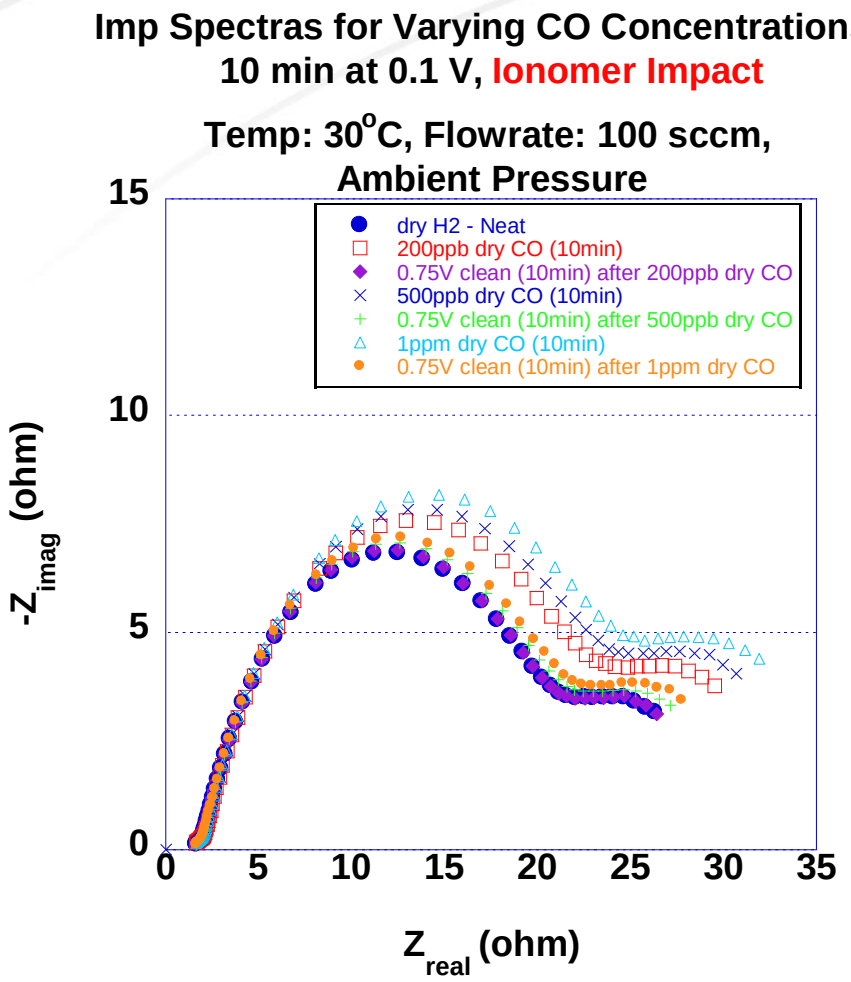
- Baseline conducted for comparison
- Gases were externally humidified
- 0.3V hold , 200 ppb CO and 500 ppb CO exposure shows clear response (current decay)
- No natural recovery observed

Clear Response at ISO/SAE CO Level



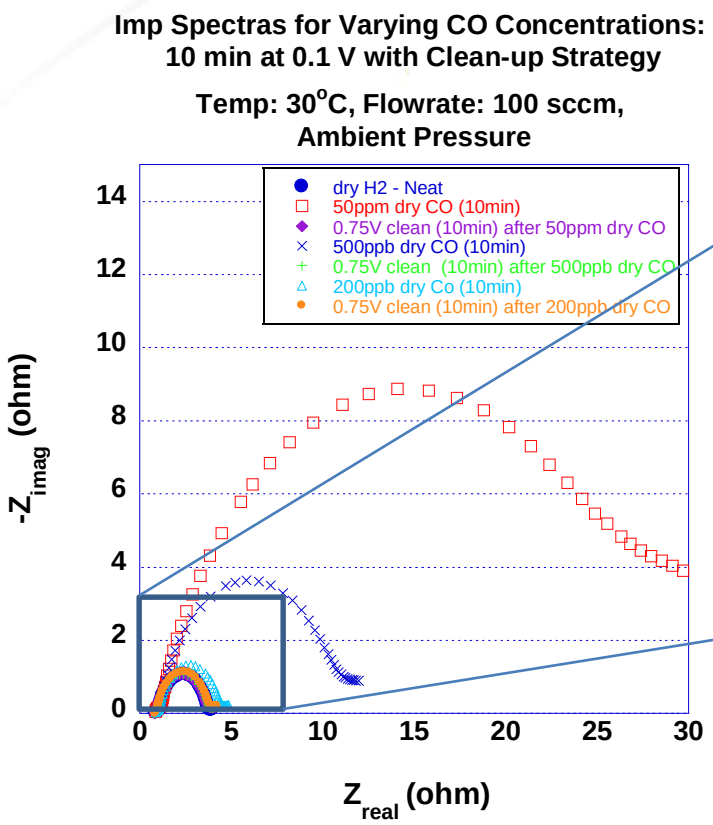
- Dry gases along with the innovative humidification system
- Gas Diffusion Media changed to a less hydrophobic material
- Initial baseline before CO exposure **more stable** than 'Baseline'
- Response to 200 and 500 ppb CO similar to 'Baseline'; larger current decay rate
- No natural recovery observed

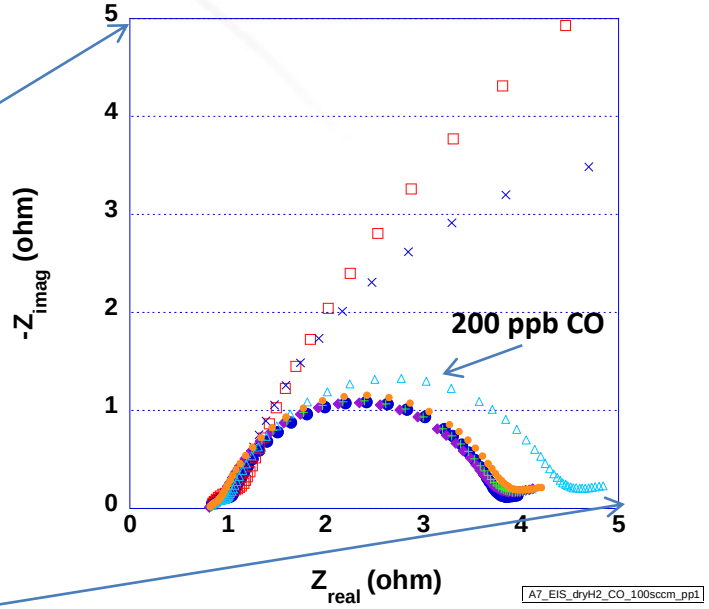
Investigating Clean-Up Strategy



- Impedance Spectras used to investigate the analyzer
- Applied 0.75V pulse for 10 min as a 'Clean-Up' Method
- Analyzer reset after 200 ppb CO
- **Complete recovery not observed at higher concentrations**

Investigating Clean-Up Strategy: Optimization of Electrode Materials



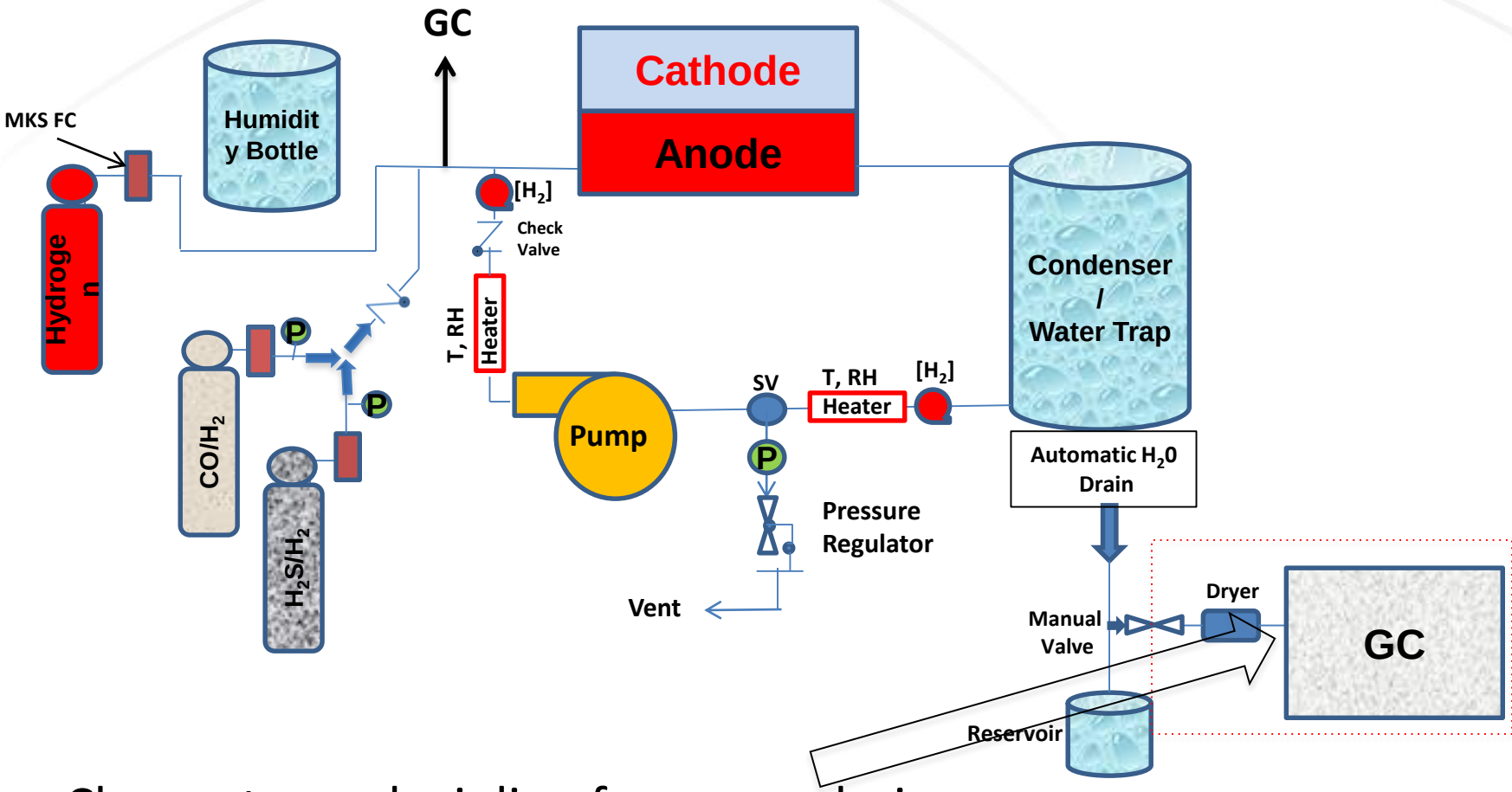


- Ionomer to catalyst ratio changed
- Responses still observed to 200 ppb CO
- 0.75 V applied after CO exposures
- **Clean-up shown at 5 times SAE level!!!**

Future Work

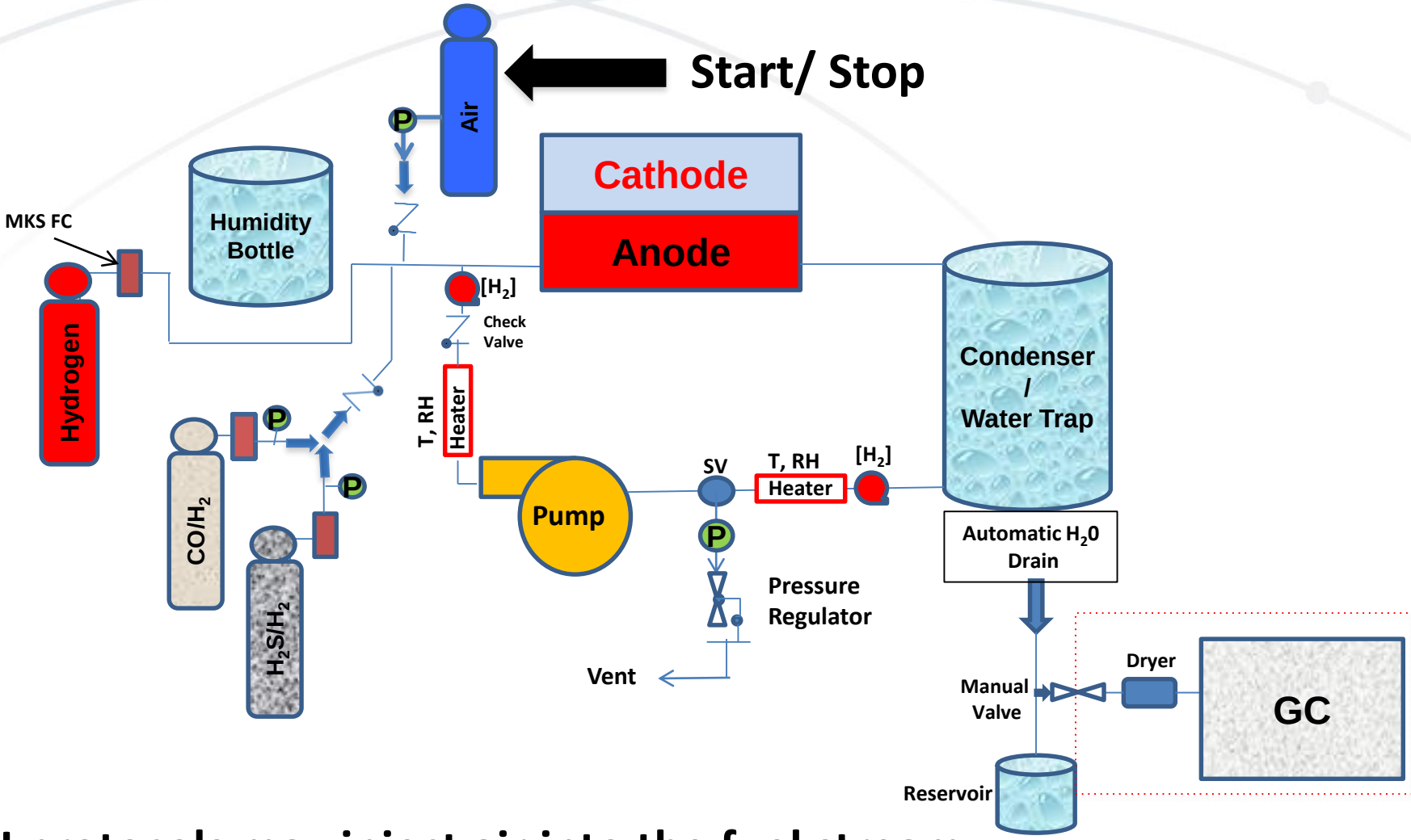
- Modify the Re-Circulation System to include **Gas Chromatography**
- Incorporate Drive cycle and Start-Stop capabilities to mimic vehicle behavior and investigate it as a recovery strategy
- Test with the entire fuel cell specification (minus particulates) and apply drive cycle and start-stop protocol

Fuel Re-Circulation System: Future Work



Add Gas Chromatography inline for gas analysis, mass balance, etc…

Fuel Re-Circulation System: Future Work



SD/SU protocols may inject air into the fuel stream. Durability issue or recovery technique???

Summary

- Parametric Results with CO and H_2S
  - Anode Pt loading plays a critical role in determining H2 impurity tolerance
  - The losses are not observed instantaneously
  - Can SU/SD be used as a mitigating strategy?
- Pre-dosing Experiments
  - During an event, the voltage losses due to 200ppb CO will increase with higher S pre-dosing.
  - The onset of voltage losses appears instantaneously after S exposure.
- Fuel Quality Analyzer
  - Prototype developed
  - Response to ISO/SAE levels (t<5min)
  - Clean-up strategy implemented

Acknowledgements

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- DOE- Will James, Technology Development Manager.
- Jari Ihonen, VTT
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