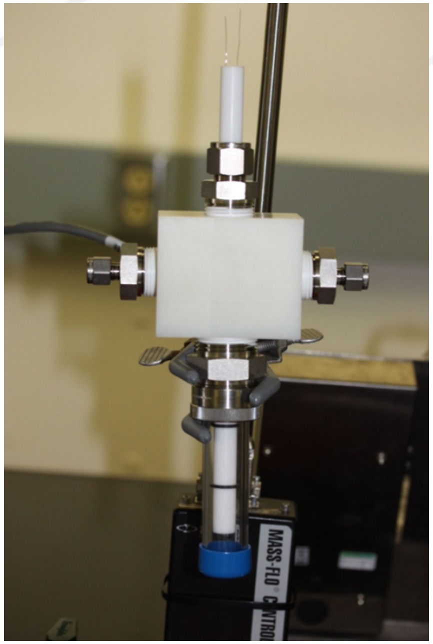
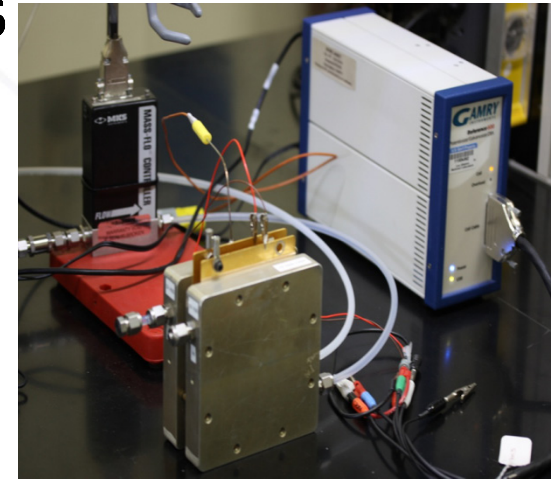
Hydrogen Fuel Quality



The U.S. Department of Energy 2016 Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting



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Team:

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Project ID # SCS007

Overview

Timeline

- Project start date: 10/1/06
- Project end date: 9/30/16*

* Project continuation and direction determined annually by DOE

Barriers

- Barriers addressed
  - I. Conflicts between Domestic and International Standards
  - N. Insufficient Technical Data to Revise Standards

Budget

- Total project funding: 4025K
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY15:700K
- Total funding planned for FY16: 750K

Partners/Collaborators

- Japanese Automotive Research Institute
- National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee Call
- ASTM
- SAE
- Smart Chemistry
- CEA-Liten France
- VTT- Helsinki, Finland
- IEC/TC105/Working Group 11

Project Objective 1: Hydrogen Fuel Quality

LANL has maintained three focus areas for the hydrogen fuel quality part of this project. These focus areas are centered on PEMFC testing, collaborations, and work with the ASTM.

Fuel Quality Testing:

- Utilize MEAs with 2015 DOE target loadings (A/C: 0.05/0.10 mg Pt/cm^2)
- Tests the impact of fuel contaminants at the SAE J2719/ ISO 14687-2 levels
- Disseminate results

Collaborations:

- Develop and maintain US and International collaborations
  - Harmonize testing
  - Protocol and standards development

ASTM:

- Leadership within the D03.14 committee on the development of standards
- Participate in Inter Laboratory Studies (ILS)

Project Objective 2: Fuel Quality Analyzer

Relevance/Impact

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. Such a device could prevent damage to fuel cell stacks provided it is:

- inexpensive
- sensitive to the same impurities that would poison a fuel cell stack
- quick response time to contaminants.

Approach

- This device operates as an electrochemical pump using a MEA-type configuration. **(no air available)**
- Use similar components to a fuel cell stack (e.g. Ionomer, PGM, and GDLs)
- Reduce overall Pt loading and utilize low surface area catalyst
- Identify best materials and their configuration

Outline

- ASTM Efforts D03.14
  - Momentum in the development of Standards
  - Challenges ahead
- Fuel Quality Testing
  - Parametric Studies
  - International Collaboration
- Fuel Quality Analyzer
  - Initial Approach and Findings
  - Prototype Status
  - Results
- Summary
- Future

ASTM Efforts D03.14

- 8 standards are under consideration by D03.14
- New ILS participants: Toyota and PNNL have expressed interest
- New Spreadsheet helps track test-sites
- Next meeting, Bellevue, WA, June 2016
- Inter-Laboratory Studies Underway
  - GC/MS
  - FTIR
- Challenges
  - Data collection
  - Some ILS sites require funding

Fuel Quality Testing

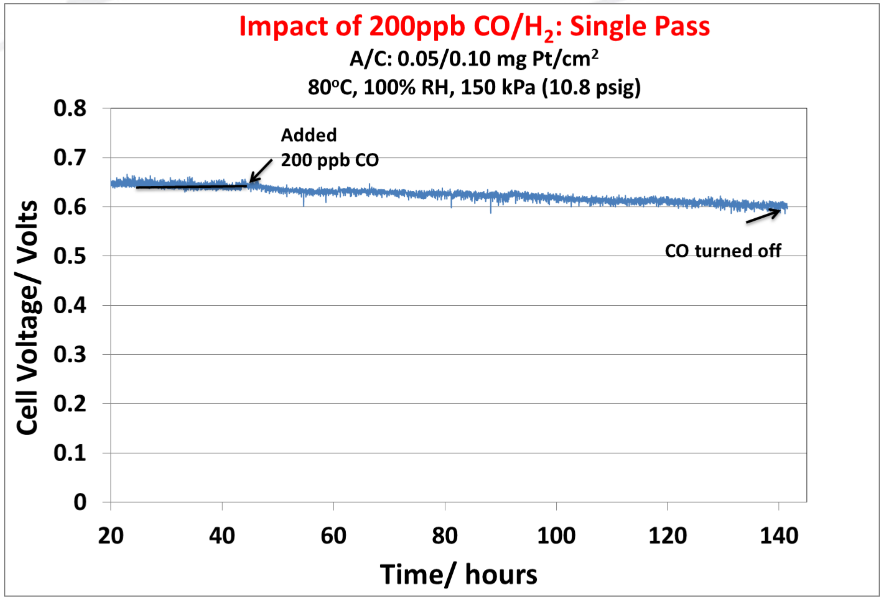
- Parametric studies as a function of operating conditions
  - Determining impurity tolerance under more realistic conditions
  - H_2 fuel recirculation system vs single pass
    - Effect of CO
    - Effect of H_2S
    - Effect of ISO mixture (NH_3, CO, H_2S)
- International Collaborations
  - Standard Testing Protocol for PEFC(IEC/TC105/WG-11)
  - Sulfur Pre-Dose Testing (CEA/LANL)
  - H_2 Fuel Recirculation System testing (VTT/LANL)
  - International Baseline Testing (CEA/VTT/LANL)

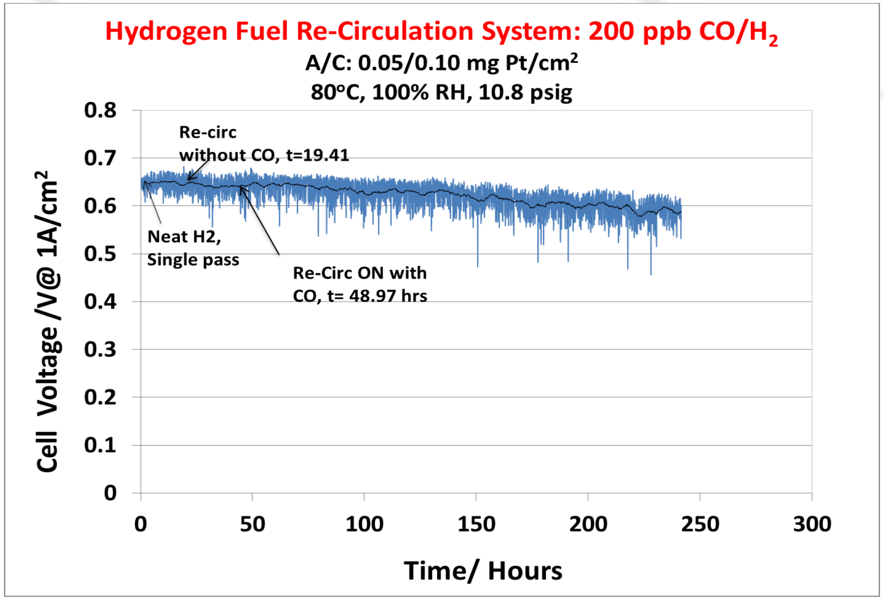
Approach: Parametric Study of CO Tolerance

T: 80 ^{o}C		Tolerance of [CO] in PEM Fuel Cells								completed
Pressure (kPa)		80	150	275	80	150	275	80	150	275
[CO] (ppm)		1	1	1	0.5	0.5	0.5	0.2	0.2	0.2
RH (%)	32									
	50									
	100									

- Is there a need to revise standards
  - Evaluate tolerance on MEAs with low anode loadings (0.05mg_{pt}/cm^2)
  - Compare re-circulation vs single pass
  - Effect of RH and pressure and concentration
- Abstract submitted to ECS (10/2016)
- Create database to provide data for modelers

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

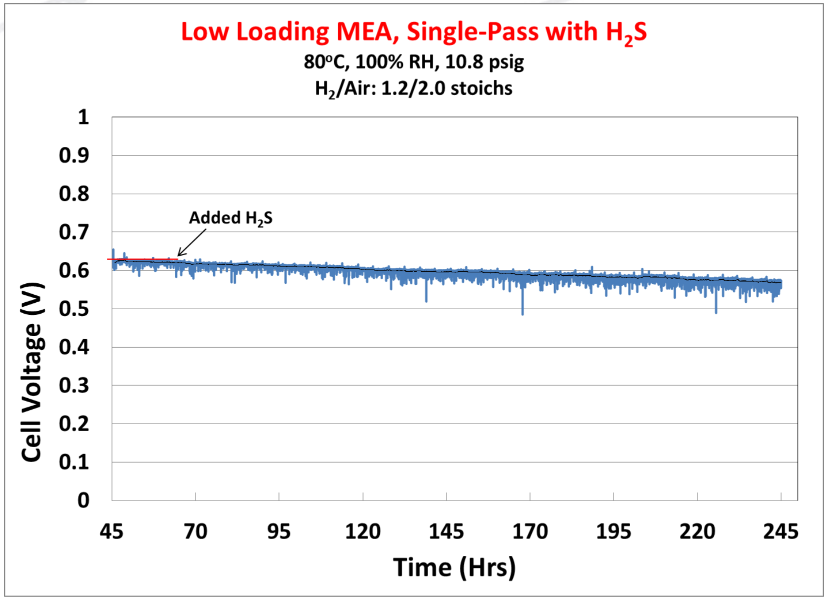


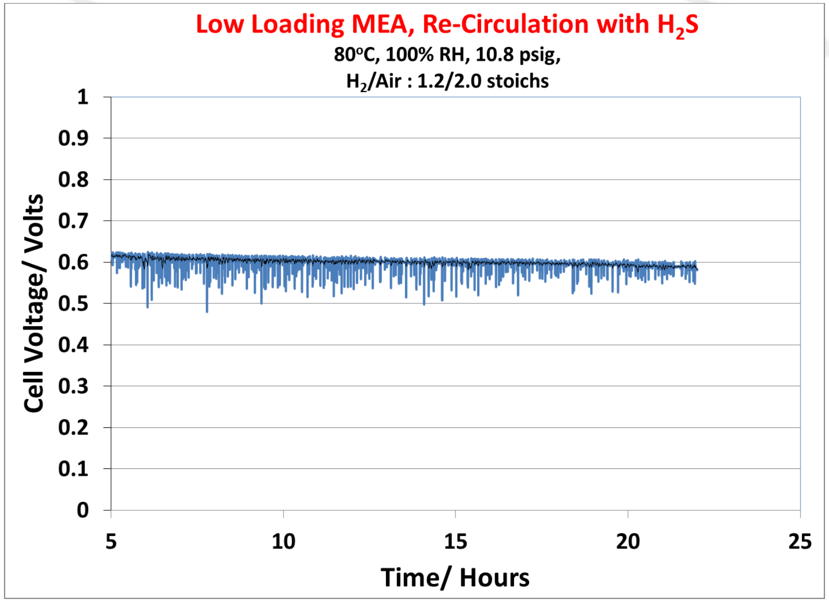


MILESTONE:

- Fuel cell voltage at a current of $1 A/cm^2$ when operating under H_2 + 200 ppb CO with H_2 single pass (left) and H_2 recirculation (right) at 80^oC, 100% RH, and 150kPa
- **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**

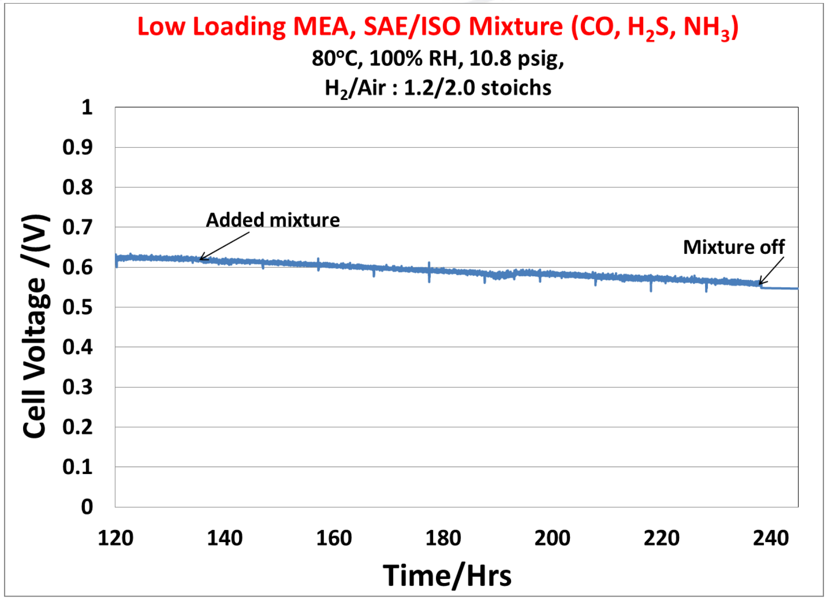
Accomplishments: H_2 Recirculation vs Single-Pass with 4 ppb H_2S/H_2

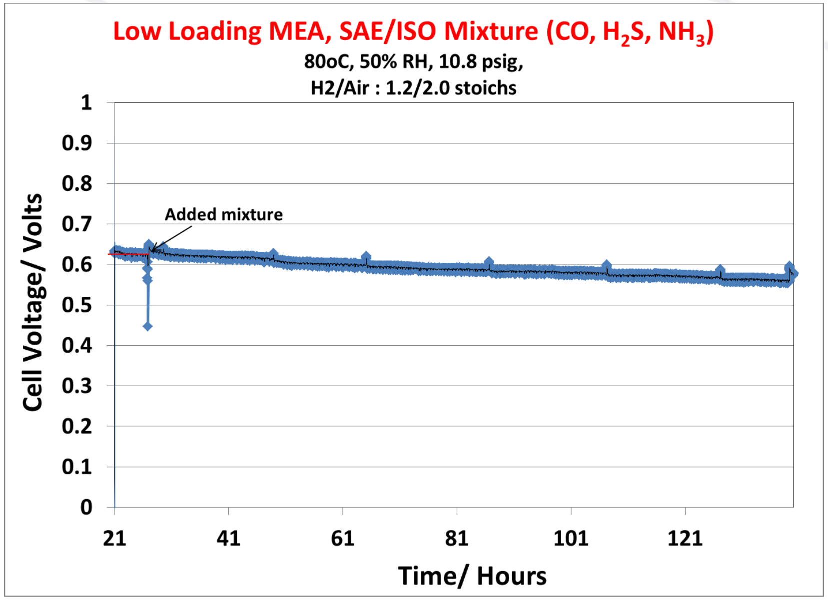




- Fuel cell voltage at a current of $1A/cm^2$ when operating under H_2 + 4 ppb H_2S with H_2 single pass (left) and H_2 recirculation (right) at 80^oC, 100% RH, and 150kPa
- **Voltage loss after 100 hrs with single pass is ~ 31 mV and after 175 hrs is 47mV**
- **Similar losses to 200 ppb CO. Effect of recirculation expected to be similar to CO (underway)**

Accomplishments: Single Pass ISO Mixture: RH dependence





- Fuel cell voltage at a current of 1A/cm^2 when operating under H_2 + mixture: 200 ppb CO, 4 ppb H_2S, and 100 ppb NH_3 with 100 % RH (left) and 50%RH(right) at 80^{o}C, 100% RH, and 150kPa
- **Voltage loss after 100 hrs at 100% RH is ~ 60 mV and at 50% RH is ~ 67 mV**
- **Consistent with previous data describing competitive adsorption between CO and H_2S.**

International Collaborations:

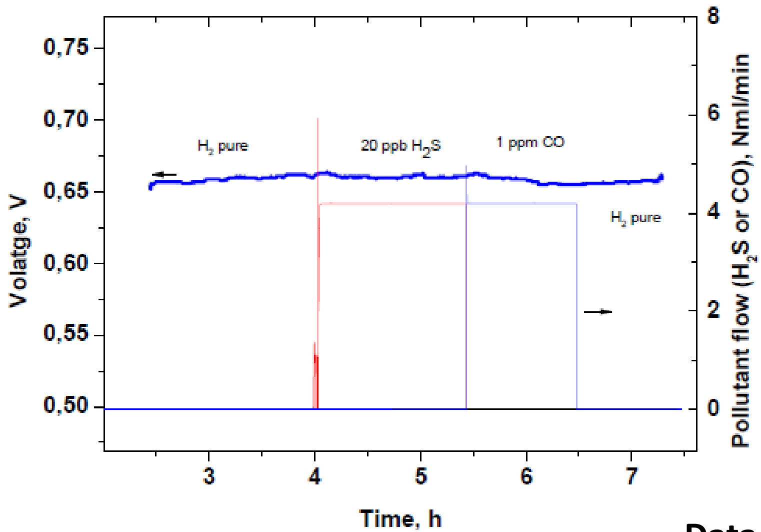
- IEC/ TC197 WG-11
  - International team of experts developing a Fuel cell Testing Document (Status: DTS)
  - Next meeting hosted by DOE/LANL: June 20, 2016 in Washington D.C.
  - Member Countries: Finland, Japan, China, United Kingdom, Italy, France, Switzerland, US
- CEA (Grenoble, France)
  - Pre-dosing Experiments
  - Baseline Testing
- VTT (Helsinki, Finland)
  - H_2 Recirculation System
  - CO poisoning
- Joint Research Centre
  - Test method validation

Collaboration: CEA-LANL Pre-dosing Experiments:

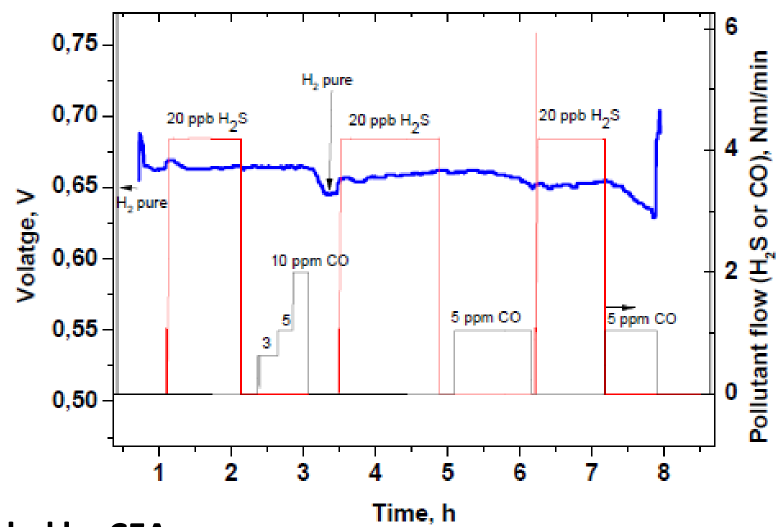
What is the impact of CO in the event of an unexpected exposure to H_2S?

MEA exposed to H_2S then CO:

1st Day Testing



2nd Day Testing



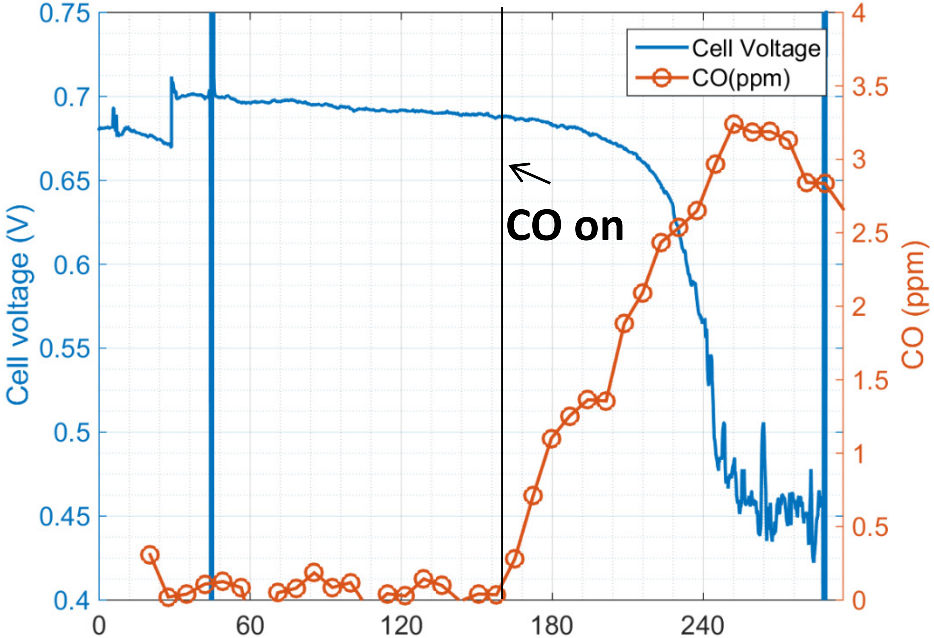
Data provided by CEA

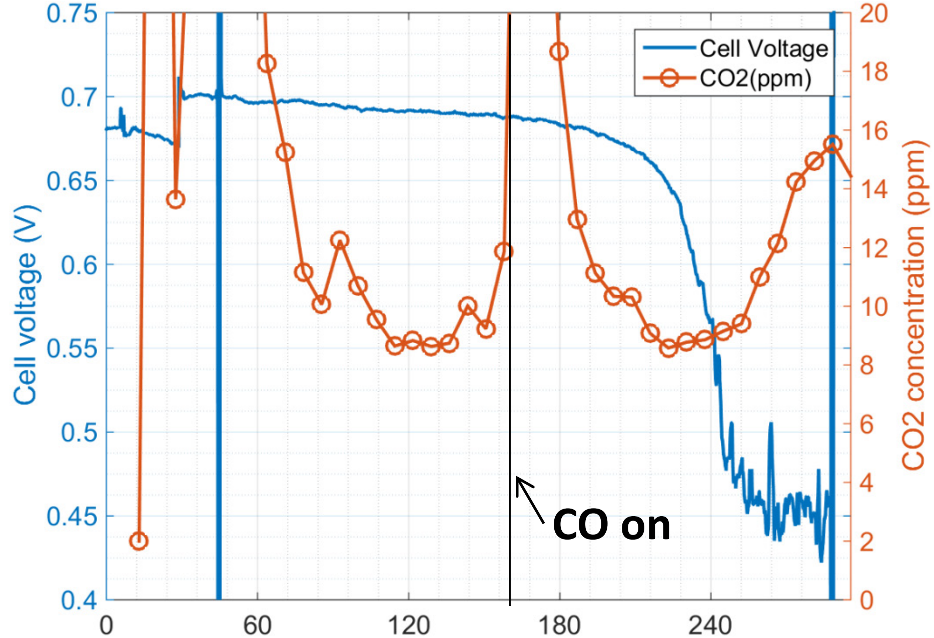
- Higher concentrations used to investigate impact in a shorter time period
- 1st day: After 1h exposure to 20 ppm H_2S shows little response to 1 ppm CO
- 2nd day: Subsequent exposures to CO and H_2S shows both regions are impacted
- H_2S regions are decreasing with successive exposures
- CO impacts become more severe as S coverage increases

Collaboration: VTT-LANL

Scope: Evaluating impact of internal air bleeding on CO by assessing the carbon balance

25cm^2, 80^{o}C, $T_{anode/cath}$: 70^{o}C/77^{o}C
an/cath loading: 0.05/ 0.1 mg Pt/cm^2
H_2/Air: 1.25/2.5 stoichs





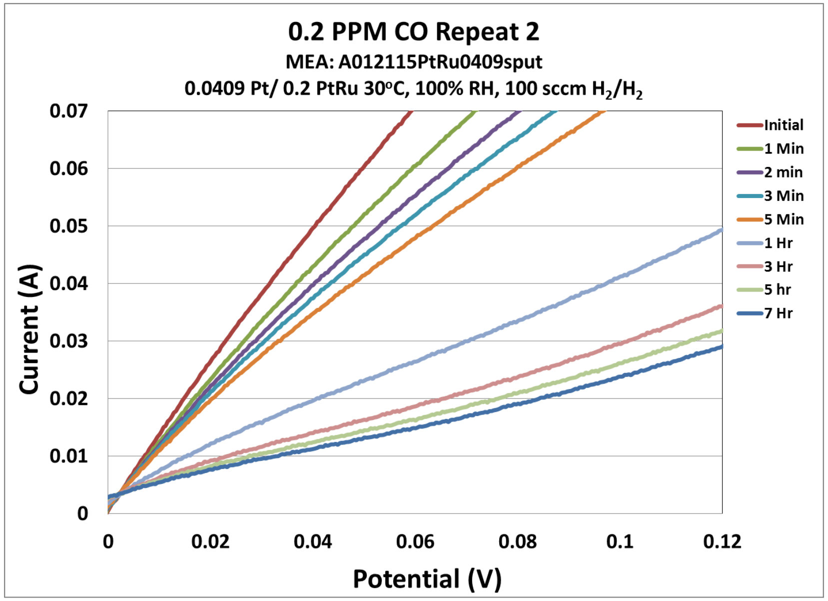
- 1.86 ppm CO/H_2 introduced while cell operated at 0.4 A*cm^{-2}
- For V_{loss} < 30mV, CO_2 concentration increases (CO oxidation)
- Window of opportunity (possibly) exists at the introduction of CO
- Difficulties exist for carbon balancing because pre-existing CO_2 in the system (fuel or oxidant)

Approach: Identifying Desirable Materials

Proof-of-Concept Shown FY15

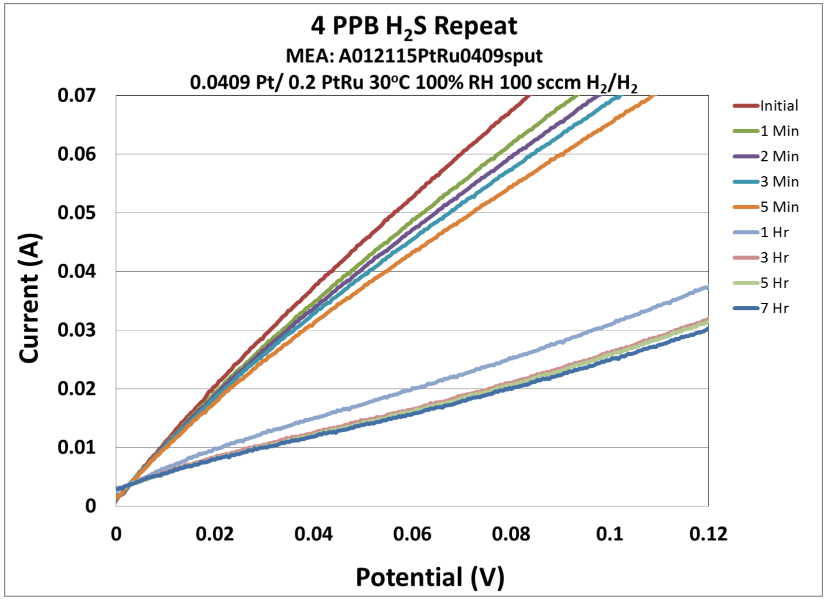
Reference Electrode: Tolerant and Stable

- **Pt: 30 wt %, Ru: 23.3 wt %,** High surface area to mass ratio 3.5nm particle size
- Carbon black with 5% Nafion® painted decals



Working Electrode: Durable and Sensitive

Sputtered low loaded electrode provides stable Pt particle sizes and high sensitivity to impurities.



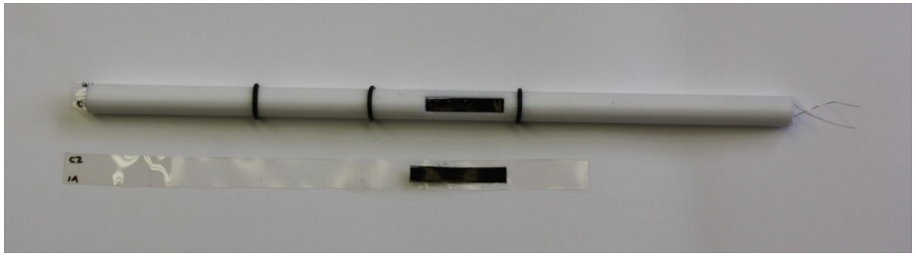
Desired response times obtained for both CO and H_2S at the SAE level!

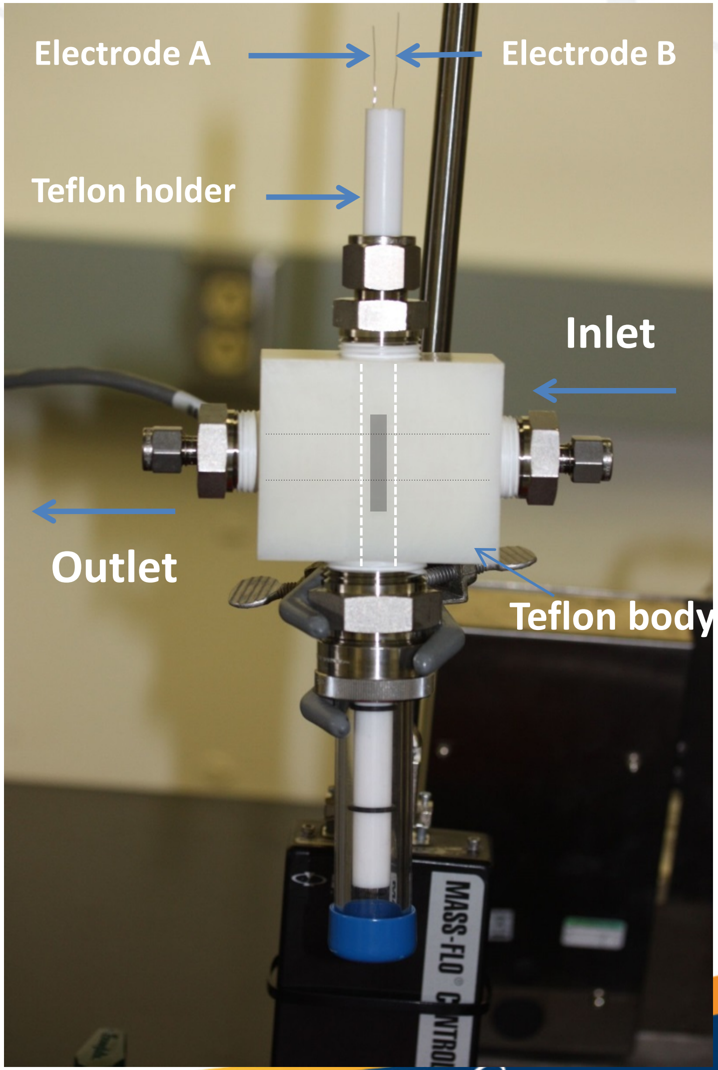
Response time < 5 minutes!!!

Smart Milestone: Developing the Prototype

Approach:

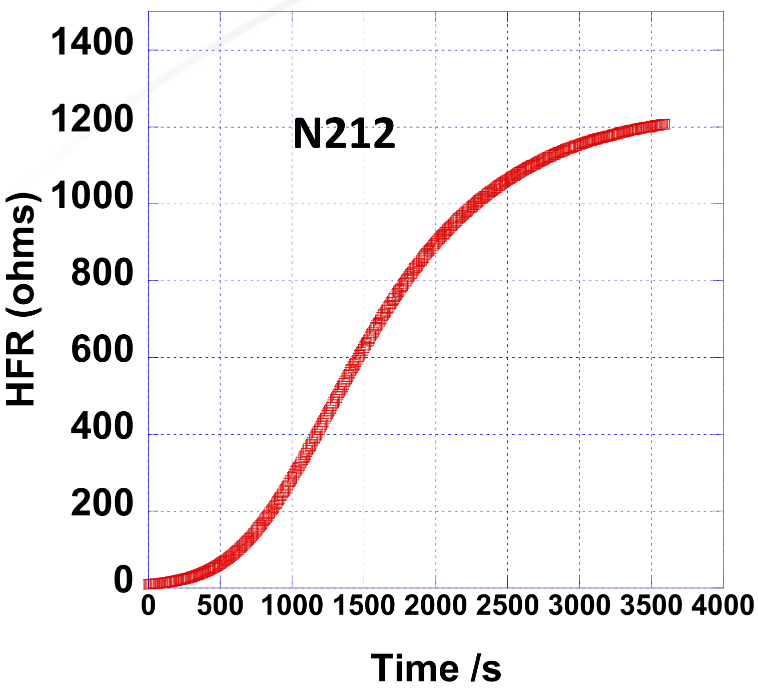
- **Membrane Hydration Challenging**: Identifying conditions needed for constant membrane humidification
  - Characterize and confirm by measuring HFR and CV
  - Vary flow conditions
  - Vary Membrane thickness
- Determine a **fuel flow-rate** that will not compromise sensitivity or response time



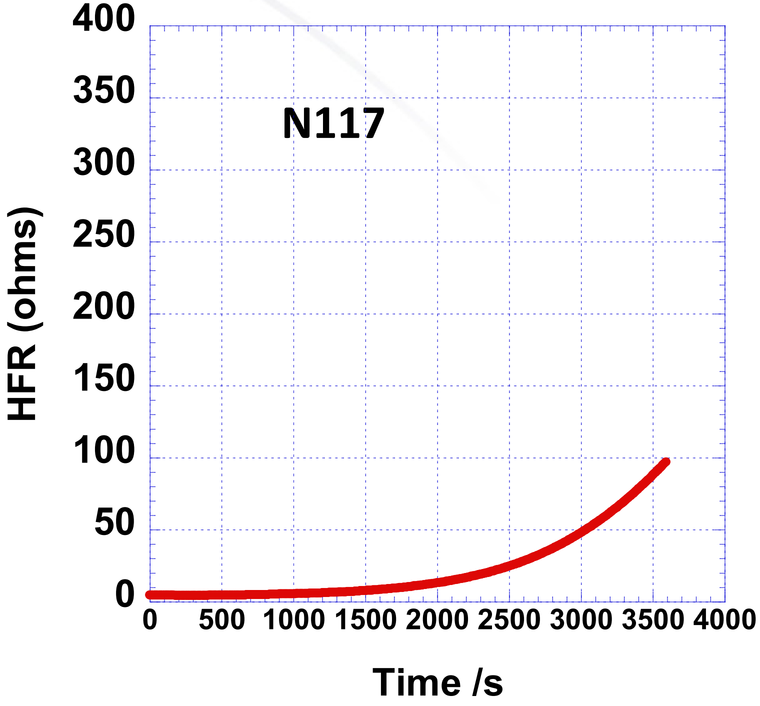


Accomplishments: Membrane Hydration Tests N212 vs N117

N212 membrane HFR at 50kHz - 1L/min N2
HFR_Membranehumidification8

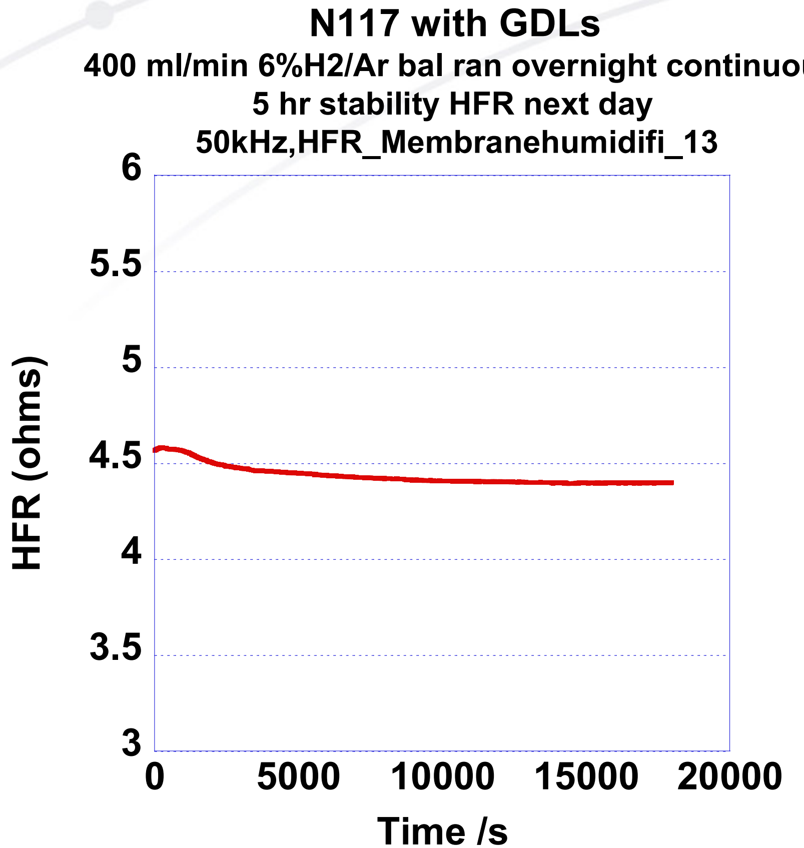


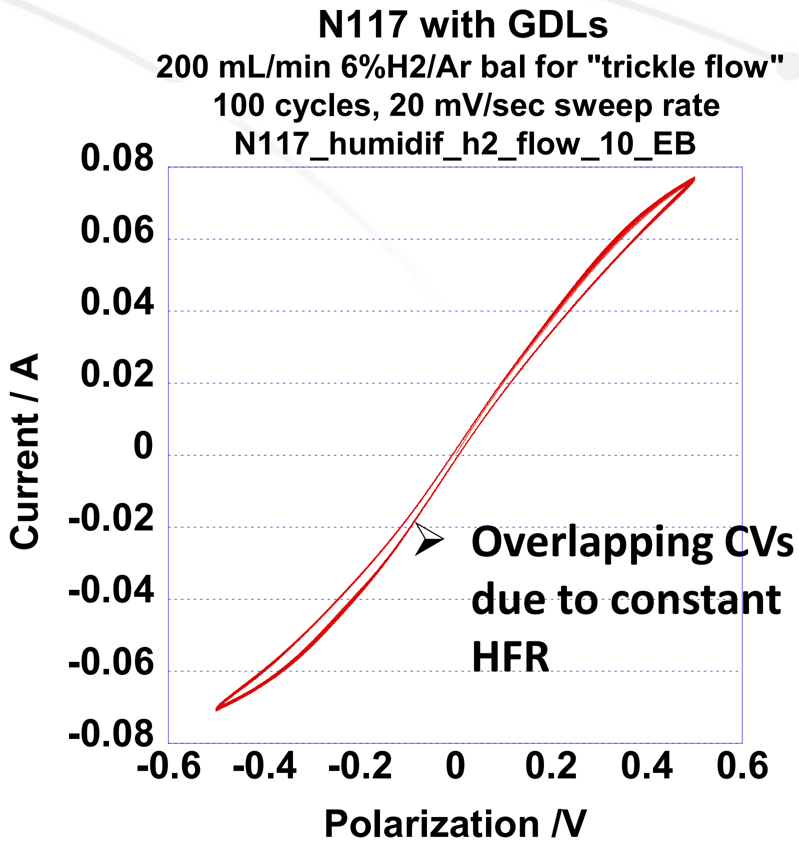
N117 membrane HFR at 50kHz - 1L/min N2
HFR_Membranehumidification8



- Fully saturated membranes yield constant HFR
- Increase in membrane resistivity during flow of dry gas evident.
- Thicker membrane (N117) maintains hydration longer.

Accomplishments: Re-designing the Hydration Scheme





- 400 ml/min of 6% H_2/Ar flow continuously overnight
- HFR reasonably stable (left)
- **GDLs added: 1<u>00 cycles</u> are shown overlapping (constant HFR achieved?)**

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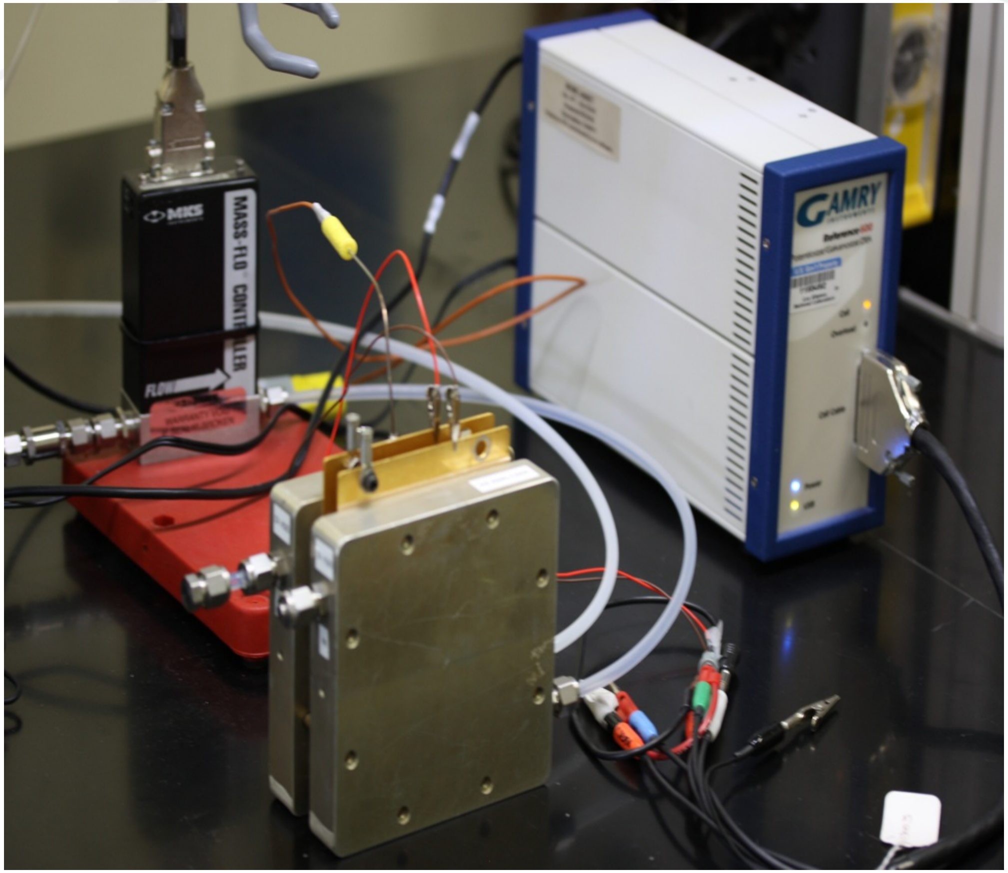
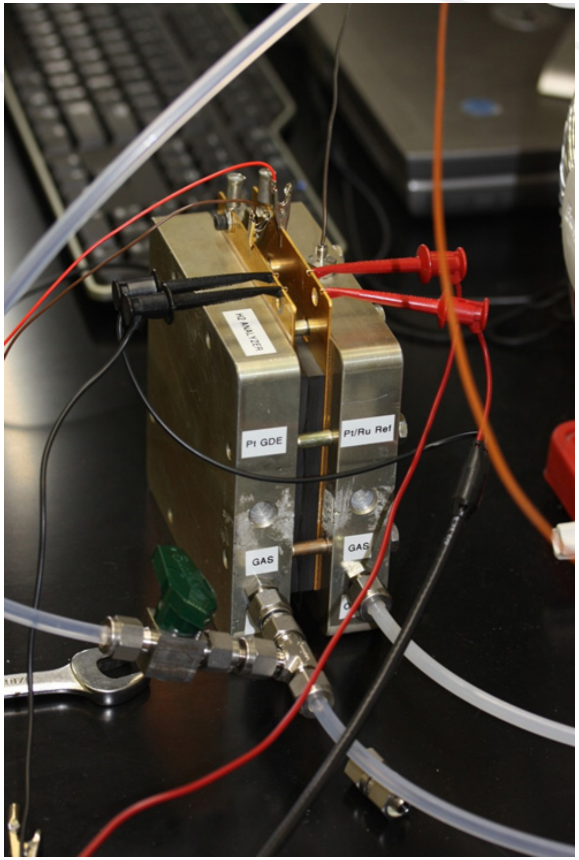
Prototype Developed: Validation underway



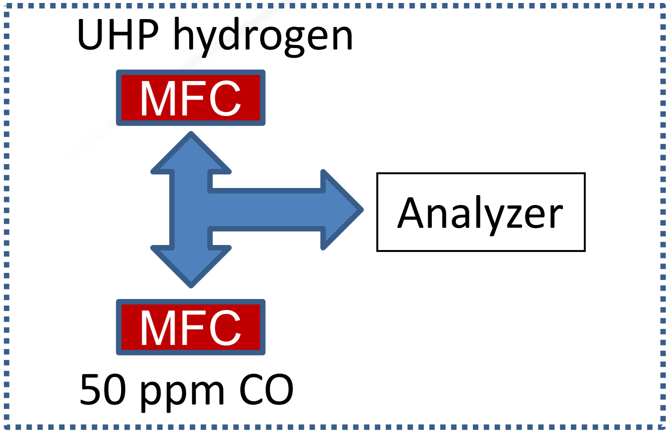


Newly designed prototype developed. IP protection initiated for membrane hydration system

Testing is underway!!!

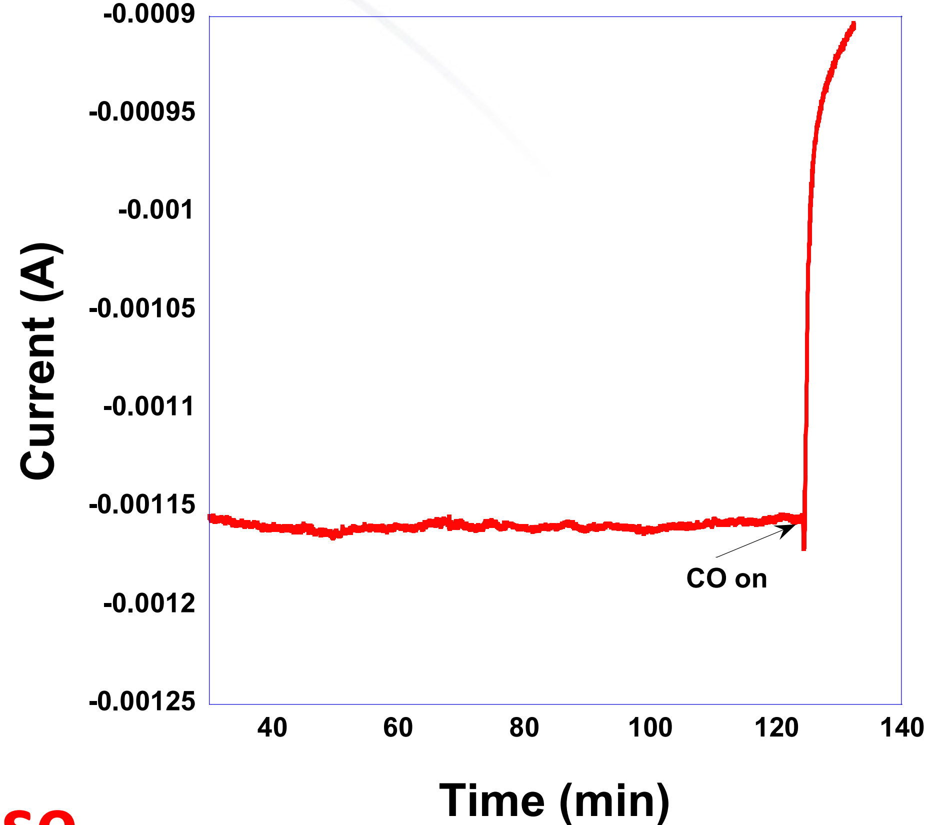
Preliminary Prototype Results

Gas Set-up



Test conducted at room T: 22°C
MKS MFC calibrated for both gases
Instance response to 50 ppm CO

Analyzer response to 50 ppm CO



Initial results show promise,
Next step is to test at SAE/ISO levels!

Summary

1. ASTM
    - Several test methods have been published
    - Spreadsheet helped identify interested test-sites with capabilities for conducting ILS
    - Testers are looking for support
    - ASTM can purchase samples but does not provide funding

2. Hydrogen Fuel Quality
- International collaborations underway (CEA, VTT, JRC)
    - Baseline testing complete
    - H_2 Impurity testing on-going and should continue (HyCoRA Project funding extended)
    - Re-Circulation testing comparisons made with single-pass results

3. Hydrogen In-Line Analyzer
- Demonstrated hydration scheme allows for constant baseline measurements
- Instant response observed at 50 ppm CO

Future Work

1. ASTM
   - Continue to support D03.14 efforts
   - Identify test sites with the capabilities and interest
2. Hydrogen Fuel Quality
   - Continue working on the CO Tolerance Chart
   - Continue testing re-circulation vs single-pass
   - Continue International collaborations (CEA, VTT, JRC)
     - Complete PEM FC testing protocol document
     - Complete round robin testing
     - Confirm the delivery of FC stack for impurity testing
1. Hydrogen In-Line Analyzer
   - Test using SAE/ISO limits (CO and H_2S)
   - Test response times for varying CO and H_2S concentrations
   - Correlate the response signal with CO and H_2S concentrations

Acknowledgements

- **Charles (Will) James Jr, PhD; Technologies Manager**
- Our International Collaborators: JRC, VTT-Finland, CEA, WG-11
- CSTT, SAE and ASTM D03.14 members

Reviewers Comments

“The project weaknesses are the apparent lack of urgency with ASTM and apparent lack of collaboration with the academic labs that developed the initial data. Recommend evaluating effectiveness of chairing ASTM sub-committee. “

The challenge of finding test sites has been overcome and now funding surfaces as an issue. The sub-committee chair cannot appropriate funding.

“Future work may be reasonable and worthwhile; however, little detail is provided in the presentation. Decision points are nor described. Risks, barriers and challenges are not described.”

The AMR is a snap-shot of the Project approaches, accomplishments, and future direction. Sub-tasks are typically expanded during and throughout the year in dedicated presentations and or forums. The critical assumption made by the presenting team is that the reviewer(s) participates in those activities. Details have been presented to the Codes and Standards Tech Team (CSTT). Project ahead of schedule with all milestones.