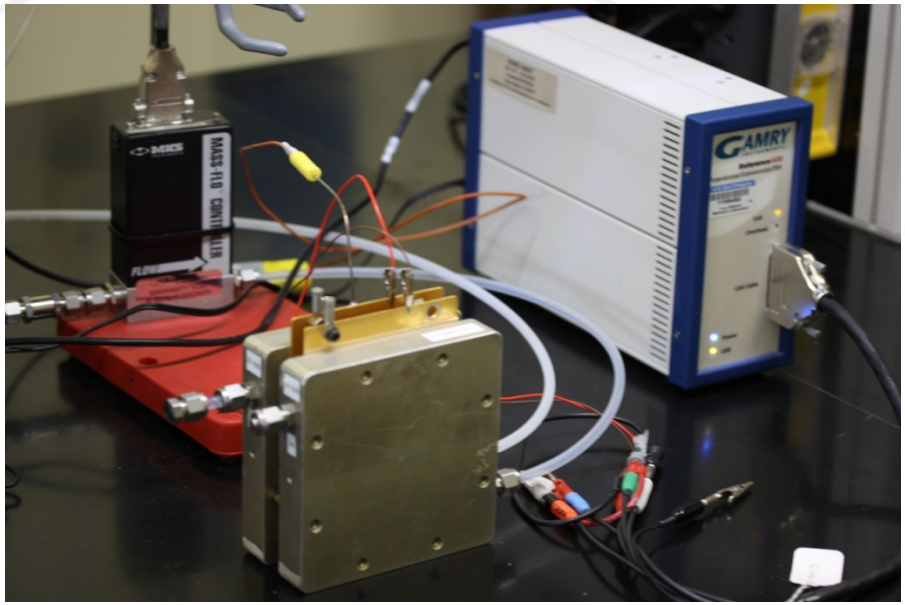
Fuel Quality Assurance Research and Development and Impurity Testing in Support of Codes and Standards



Team:

E. Brosha, R. Lujan, R. Mukundan, T. Rockward **(presenter),** C. Romero, S. Williams, M. Wilson

June 13-15, 2018

#SCS007

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Overview

Timeline

- Project start date: 10/1/06
- Project end date: 9/30/18*

* Project continuation and direction determined annually by DOE

Barriers

- Barriers addressed
  - G. Insufficient Technical Data to Revise Standards
  - K. No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

Budget

- Total project funding: $5125K
- Funding received in FY18: $350K (For Fuel Quality Analyzer)
- Total funding planned for FY19 $350K (For Fuel Quality Analyzer)

Partners/Collaborators

ATS
H2Frontier
SKYRE (Formerly Sustainable Innovations)
HYDRAITE members

Outline

- Project Background: Relevance and Approach
- Prototype development: Timeline
- Analyzer Research : Fundamentals
- Proposed Operating Mode
- Considerations for Testing in Real-World Conditions
  - Gen 1 Analyzer Electronics Development
  - Testing Partner Identified
  - Field Trial Planning
- Summary
- Future Work

Project Background: Relevance

Problem:

Certain contaminants in the hydrogen fuel steam can cause irreversible damage to Fuel Cell systems and therefore should be avoided. An in-line fuel quality analyzer can significantly improve the reliability of the Hydrogen Infrastructure

Objectives:

1. Develop a low cost fast response device (analyzer) to measure impurities in a dry hydrogen fuel stream at or above the SAE J2719 levels.

Analyzer Targets:

SAE J2719 Limit	Filling Time
200 ppb CO	~ 5 min

2. Test the analyzer in real-world environments

3. Develop a better understanding of the analyzer's workings to identify best materials and device configurations for improved analyzer performance

Project Background: Approach

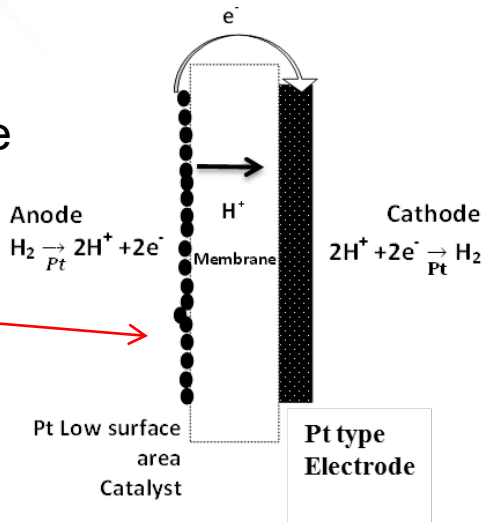
A miniature fuel cell can be used in the hydrogen stream to detect impurities that can be harmful to the fuel cell stack

However, no continuous source of oxygen or water available at the filling station

Device operates as an electrochemical hydrogen pump using a MEA-type configuration. Measure pumping current before, during and after contaminant exposure**. (No Oxygen required.)**

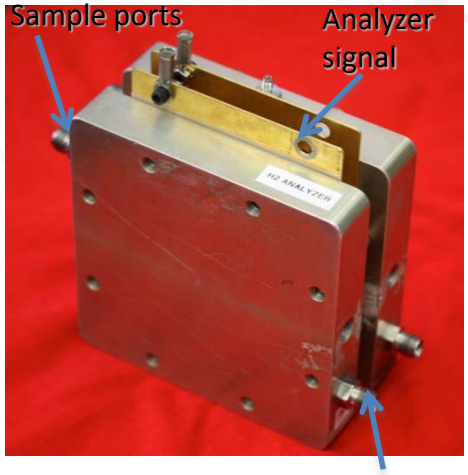
Provide hydration via a ***Wicking Scheme***

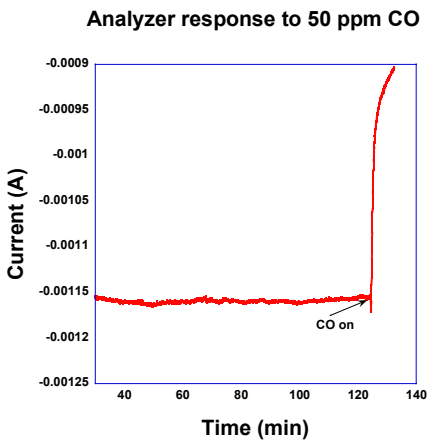
Develop understanding of working mechanism and improve analyzer by identifying the best materials and their configuration



Developing the Prototype: Timeline

- **FY 15: Proof-of-Concept demonstrated**
  - Identified electrode materials for a stable Reference Electrode (RE) and a durable and sensitive Working electrode (WE)
  - Desired response times obtained for both CO and H_2S at the SAE J2719 levels.
- **FY 16: Prototype Developed and Tested**
  - Membrane hydration tests determined thicker membranes were more stable and less sensitive to flow-rate.
  - Analyzer prototype uses standard PEMFC hardware and technology (upper right)
  - Analyzer responds to 50ppm CO (lower right)
- **FY 17: Provisional Patent Applied for in November 2016**
  - Analyzer responds to SAE levels of CO
  - Docket No. 127686/LANS (S133399)
- **FY 18: System installed in Field**





Analyzer Research : Fundamentals (FY18)

Accomplishment

Development of External Humidification System

- Nafion® membrane hydration characteristics evaluated
  - Role of membrane thickness, Gas diffusion layer composition, and gas flow rate examined
- Wicking system developed to provided necessary hydration for stable baseline
  - Membrane conductivity stabilized at levels comparable to humidified stream

Enhanced Electrode Performance

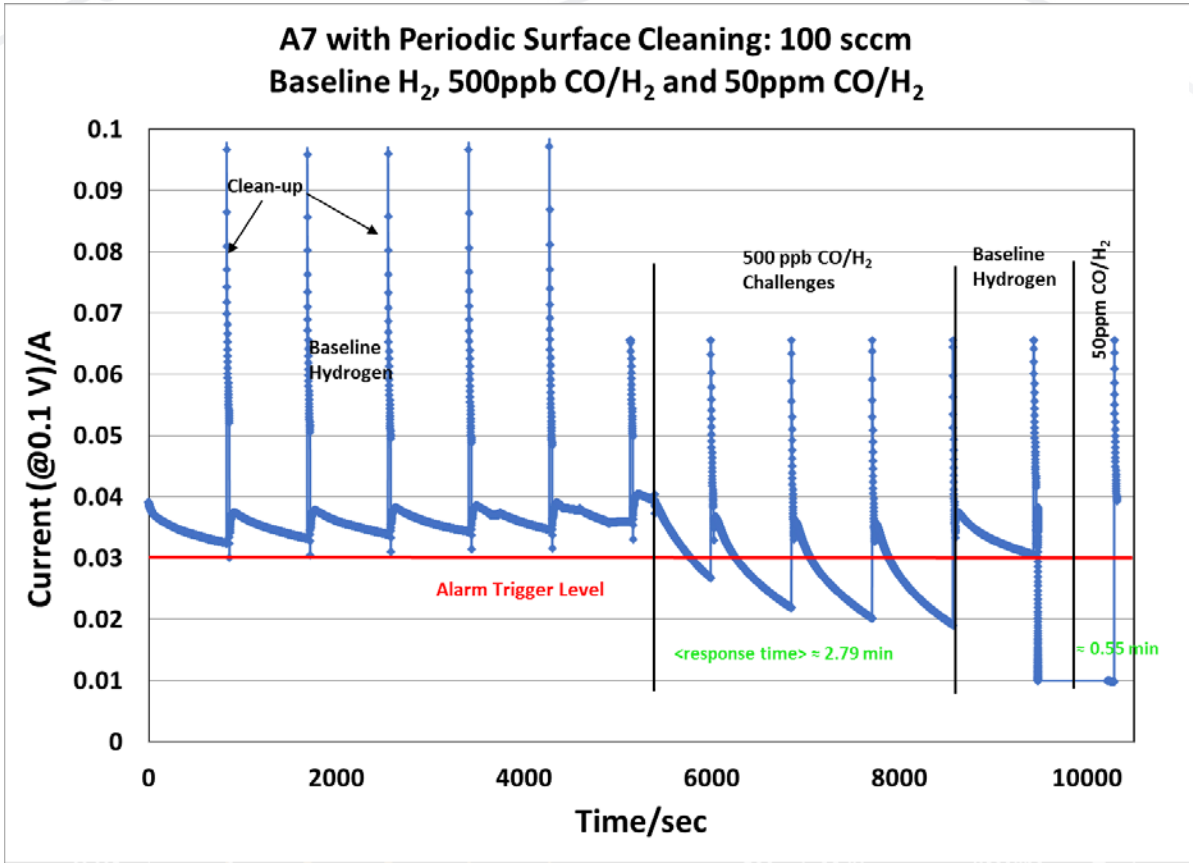
- Role of ionomer in the electrode elucidated
  - Ionomer improved access to Pt within the electrode (larger baseline currents)
  - High ionomer content resulted in excessive conditioning times
- Optimized conditioning time and improved Analyzer Signal/Noise

Implemented Clean-Up Strategy

- Evaluate Adsorption/Desorption characteristics of CO
  - External voltage effective in resetting the analyzer and desorbing the CO
- Optimized clean-up voltage: time and frequency

Proposed Operating Mode Demonstrated: 100 sccm H_2

Accomplishment



Ave. Response Time:

500ppb CO: **2.79 min**

50ppm CO: **0.55 min**

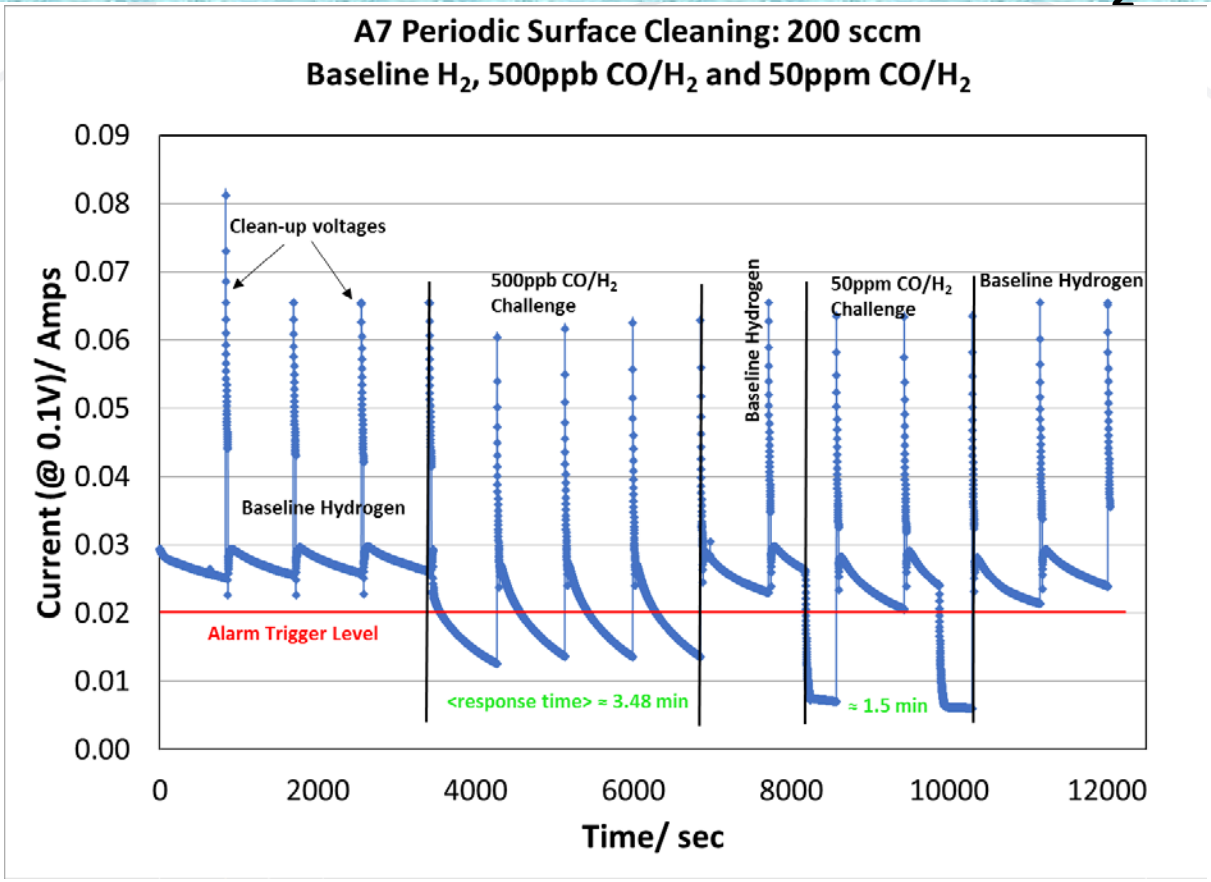
Dec 2017 Milestone

Investigate the causes of drift in the baseline current of the analyzer in order to identify the mechanism of current degradation and develop strategies to stabilize the baseline.

- Apply periodic cleanup voltages (1.5V for 30s) and measure current during 15 minute recovery intervals. (**Current kept in operating window)**
- **Alarm trigger level can be set (e.g. 30 mA).**
- **Response time for both concentrations are < 5 min (goal).**
- **Analyzer current loss tracks CO concentration.**

Proposed Operating Mode Demonstrated: 200 sccm H_2

Accomplishment



Ave. Response Time:

500ppb CO: **3.48 min**

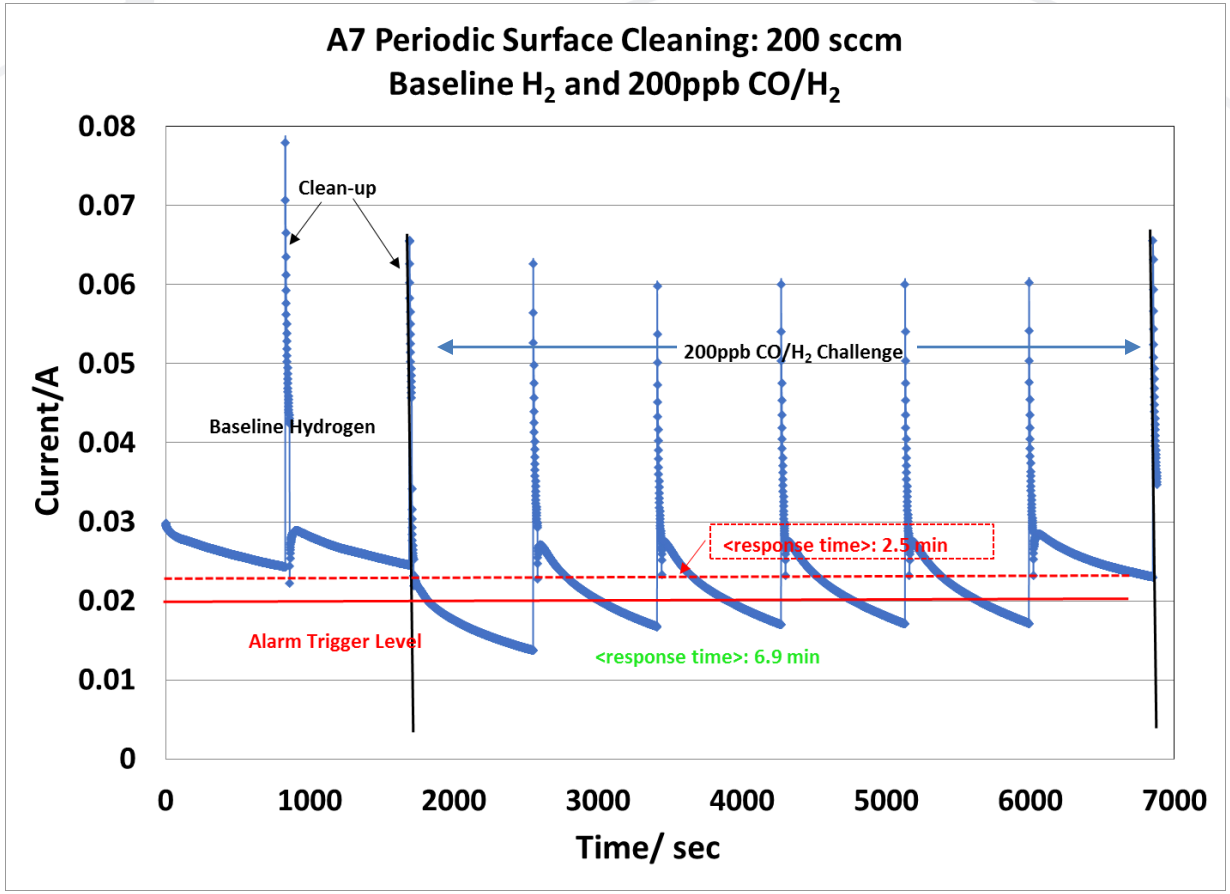
50ppm CO: **1.5 min**

Current decays with higher flow rates due to membrane drying which increases High Frequency Resistance (HFR) or membrane resistance.

- Higher H_2 flow rate demonstrated using identical clean-up strategy.
- **Response time< 5 min (goal)**.
- Total current loss similar for 100 and 200 sccm flow rates
- Response time increases slightly as a function of flow rate (under investigation)

Proposed Operating Mode Demonstrated: SAE Level

Accomplishment



Ave Response Time: **6.9 min**

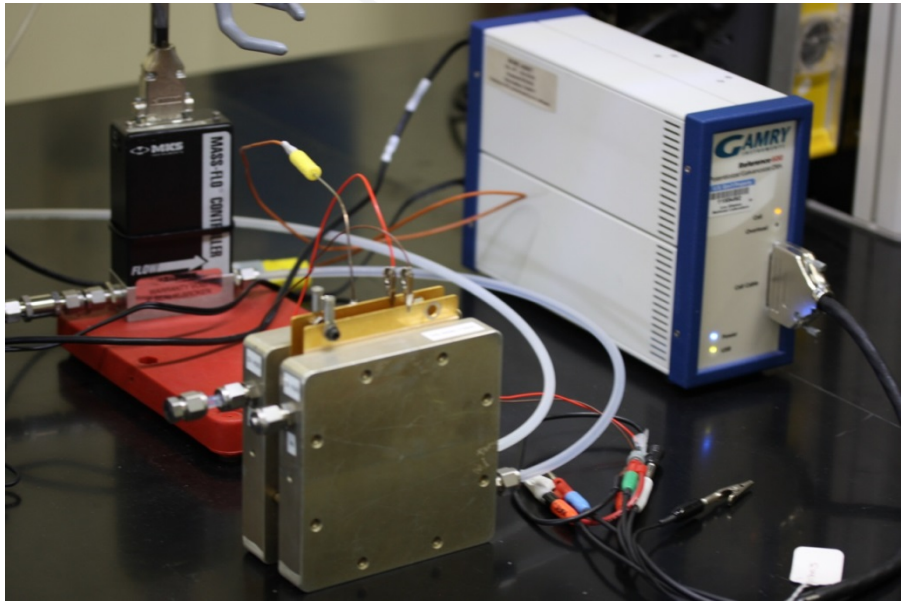
Adjusted Trigger Level
Ave Response Time: **2.5 min**

Note: Flow here is 200sccm. The effect of flow rate on response time is under examination. Controlled by changing humidification (more drying at higher flow rates).

- Sensitivity to 200ppb CO demonstrated.
- Analyzer response time > 5 min. **(goal not met)**
- **Adjusting trigger level allows 200ppb CO to alert in 2.5 min.**

Approach: Considerations for Testing in Real-World Conditions

- Operation in the field may presents challenges not captured with laboratory testing. For example,
  - Sensitivity in the field
  - Maintaining stability
  - Analyzer cell lifetime
  - Durability issues

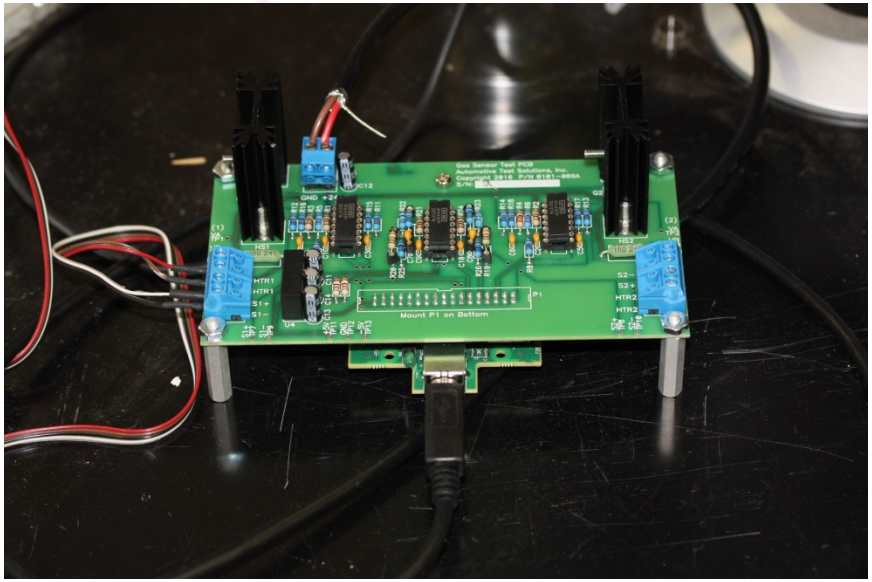


Analyzer set-up to be tested in the field

Expected to provide feedback to the research direction

Gen 1 Analyzer Electronics Development

- **<u>FY2017 Milestone</u>**.
- Worked with **ATS**, Albuquerque, NM to develop sensor control electronics for NMSBA project.
- Modified circuit (**digital based with LabVIEW VI control and current/voltage logging**) and tested with H_2 analyzer.
- Newly developed clean-up strategies required voltages outside the power capabilities of this design. Also, higher resolution DAQ necessary to maintain high system sensitivity.

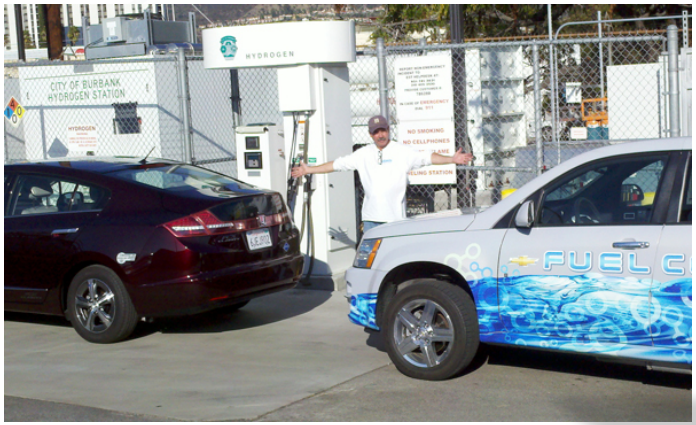


Decision: postpone electronics development until field trials testing are complete.

Goal : Better understanding of the analyzer requirements before Gen 2 circuit design.

Collaborator: Testing Partner for Analyzer Field Trials

H2 Frontier Inc
Hydrogen Generation, Storage & Delivery Systems



- Dan Poppe at H2Frontier volunteered access to the Burbank CA station for Analyzer Field Trials experiments.
- Collaboration established in 2014
- Experiments conducted remotely from LANL.

LANL, LLNL, and H2F capture R&D 100 award for hydrogen safety sensor work (previous SCS project)

Collaborator: H2Frontier Produces Hydrogen On-site

- Methane reformer is in service at this H2F station.
- On-site H_2 storage.
- Pressure Swing Adsorption bed used to purify H_2.
- Non-Dispersive Infrared (NDIR) CO analyzer presently used to check for CO contamination.
- High concentrations of CO reported during reformer start-up.

LANL staff visited to discuss the installation and planning in July 2017

Installation Stages (Progress)

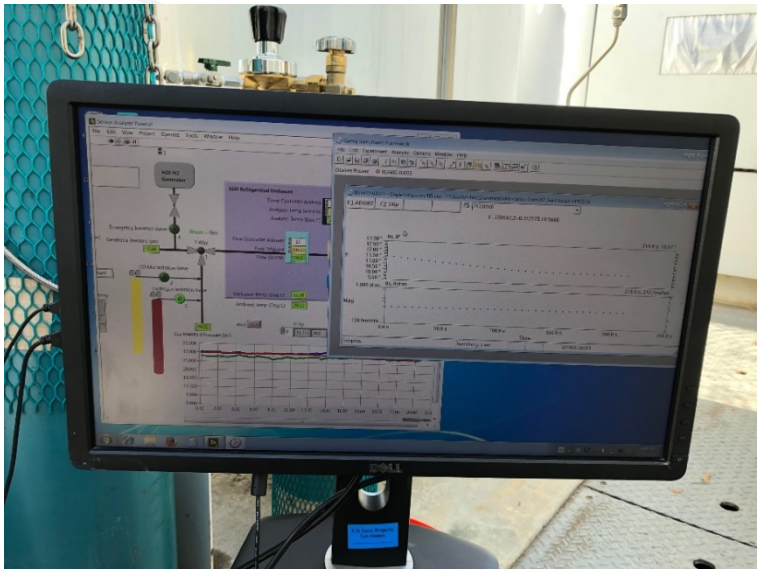
Constraints

- Temp control critical
  - Enclosure T could easily be > 120° F.
  - T drifts could impact response, stability, and or sensitivity
  - Potentiostat has maximum operating temperature limit.
- Flow control is important.
- Internet access required to remotely control experiments
- Certified gases

Solutions

- Refrigerated enclosure controls temp.
- Analyzer will be placed inside this enclosure.
- Gamry potentiostat will fit in available space
- Access ports available for H_2

Analyzer Installed and Tested in Field (March 18)



Accomplishment

Installed analyzer and potentiostat in temp controlled enclosure

Implemented new DAQ and valve control system for MFC operation

Baseline tests were performed on-site

Remote access software used to monitor and control experiments from Los Alamos

Proposed Future Work: Field Experiments

- Verify temperature stability, MFC stability, etc.
- Measure Analyzer baseline using high purity H_2 remotely.
- Test Analyzer response to 1ppm CO/H_2 test gas and calibrate response and verify baseline recovery after cleanup potential is applied.
- Switch source gas from certified gas bottles to H2F station supply from reformer.
- Coordinate with station operations during reformer start-up.
- Test Analyzer periodically

Any proposed future work is subject to change based on funding levels.

Proposed Future Work: Research & Development

- Improve our understanding (based on field trials feedback):
  - Signal/Noise and methods to improve that
    - Flow fields, catalyst, electrode and membrane optimization
  - Effect of other contaminants present in the field
    - Extend analyzer to H_2S and NH_3
    - Extend analyzer to include impedance capability (fixed frequency)
  - Possible elimination of humidification system by using advanced membranes.
- Develop Gen 2 electronics
  - Based on results from field trials , look for Industrial partners to transition this work

Any proposed future work is subject to change based on funding levels.

Reviewer's Comments

"The timescale for the analyzer in real stations is unclear, and it appears to be a long way off."

LANL's team has installed the analyzer at H2Frontier in Burbank, CA., and is operating the system remotely.

"The only weakness of this project is that there is not enough time and money to support the work at a faster pace."

LANL's staff is efficiently working towards meeting the agreed upon milestones with the current funds allocated by the FCTO in an expeditious manner.

"It is recommended that the project team expand international collaborations with similar projects."

PI attended the HYDRAITE meeting (Ulm, Germany) in order to gauge interests from the international community.

Summary

- Prototype improved in several iterations
  - Component modification to stabilize membrane hydration
  - Ionomer content varied for baseline stability and improved conditioning
  - Clean up strategy implemented to reset analyzer
- Sensitivity to 200ppb CO in dry H_2 has been demonstrated
- Patent filed for technology
- Field trials location identified, system installed and testing is under way
- Analyzer fundamental R&D is on-going to improve understandings
- Gen 2 electronics development after field trials testing

Acknowledgements

LANL staff would like to thank:

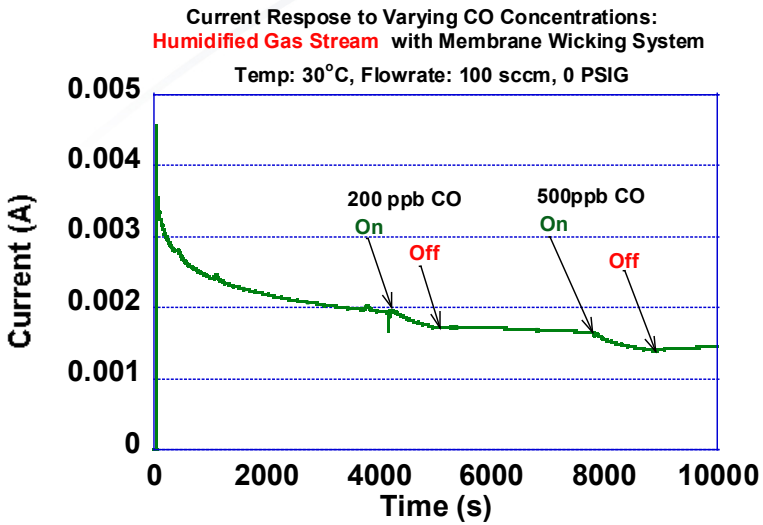
- DOE-EERE Fuel Cell Technologies Office
  - Laura Hill and Will James : Project Managers Safety Codes and Standards
- Codes & Standards Tech Team
- The Audience…

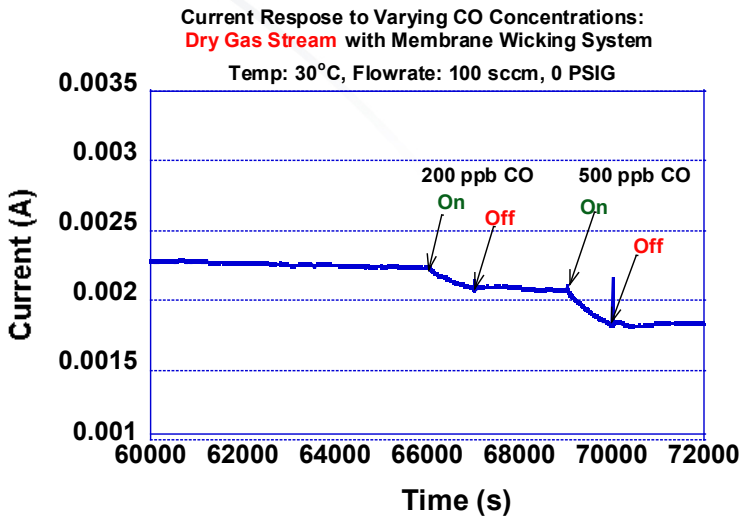
Additional Slides

Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

Analyzer 3 vs 5: Improved Humidification

0.039 mg Pt/cm^2; Low Pt, 0.2 mg Pt/Ru (RE) T: 30°C, P: 0 psig, Flowrate: 100 sccm



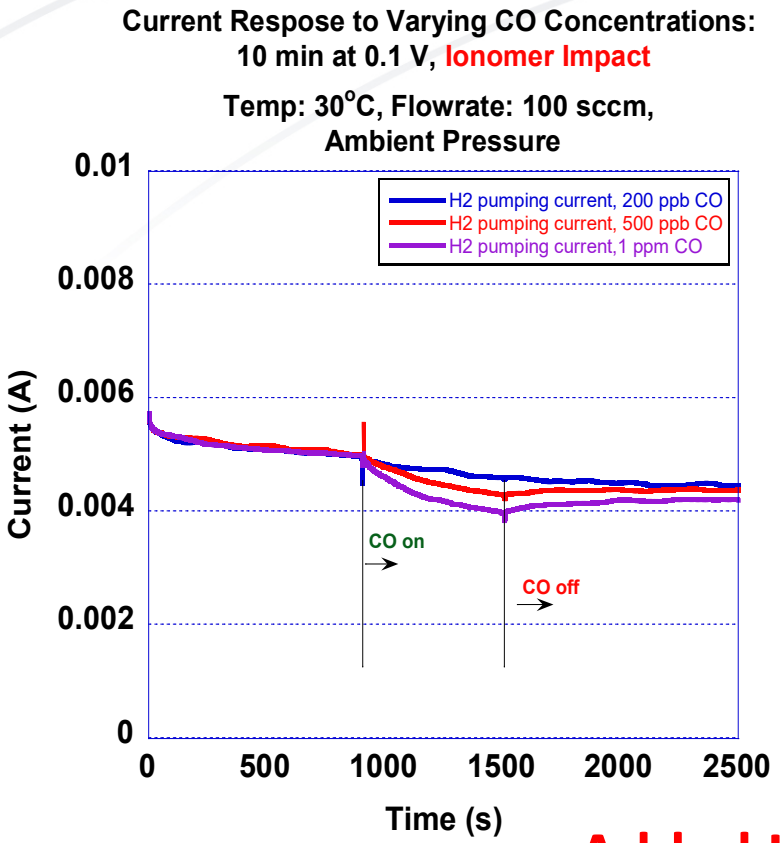


- Baseline experiments
- Gases were externally humidified
- 25 BC GDL
- CO exposure shows clear response
- No natural recovery observed

- Dry gases with wicking humidification system
- GDL changed to a less hydrophobic material
- More stable than 'Baseline'
- Responds to 200 and 500 ppb CO
- No natural recovery observed

Accomplishments FY17

Analyzer 6: Stabilizing the Baseline



- Membrane wicking humidification system with GDE/GDL wicking tabs
- ~ 1 mg/cm^2 Ionomer applied to Pt sputtered electrode/ **Working electrode**
- Current decay rate increases with CO concentration (10 min)
- **Still little to no natural recovery**

Added Ionomer to the WE

- Electrode resistance is very high without ionomer and any water in the electrode altered electrode resistance significantly
- Ionomer added to help stabilize electrode water content

Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA

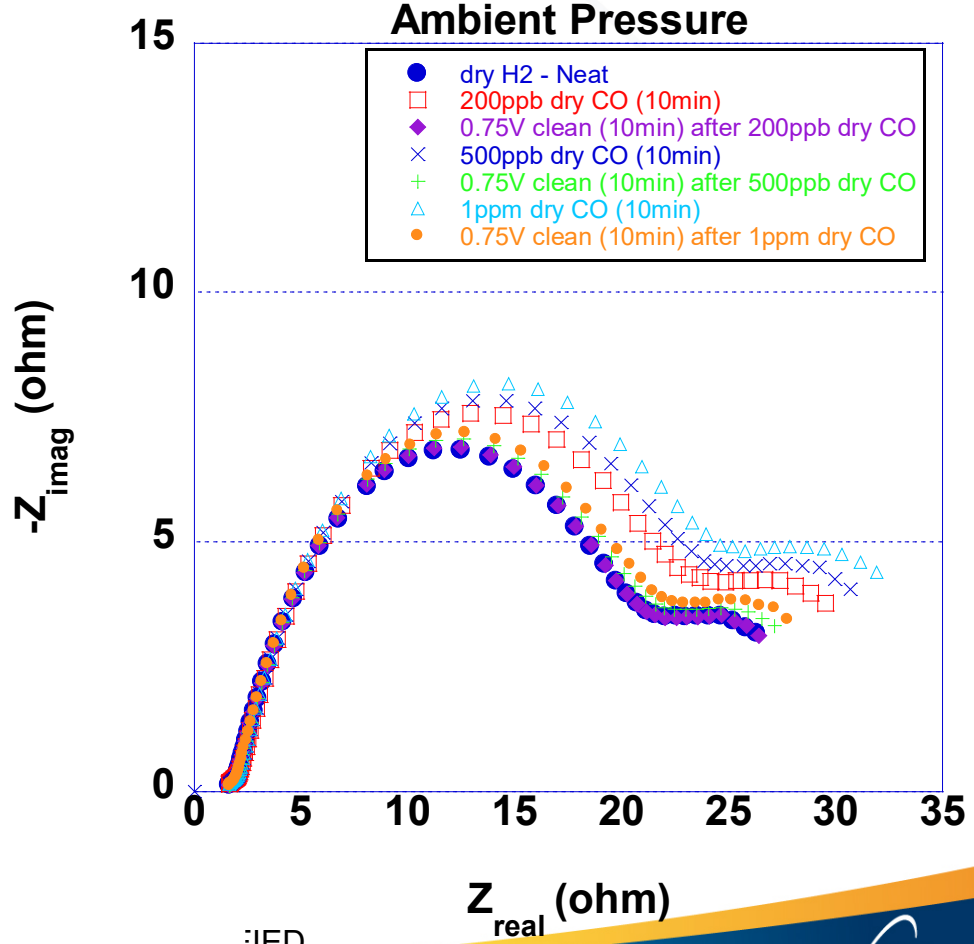
A6: Applying Clean-Up Strategy

How to reset the analyzer?

- Applied 0.75V as a 'Clean-Up' Method
- Analyzer reset after 200 ppb CO
- **Recovery not complete at highest concentrations**

Imp Spectras for Varying CO Concentrations: 10 min at 0.1 V, Ionomer Impact

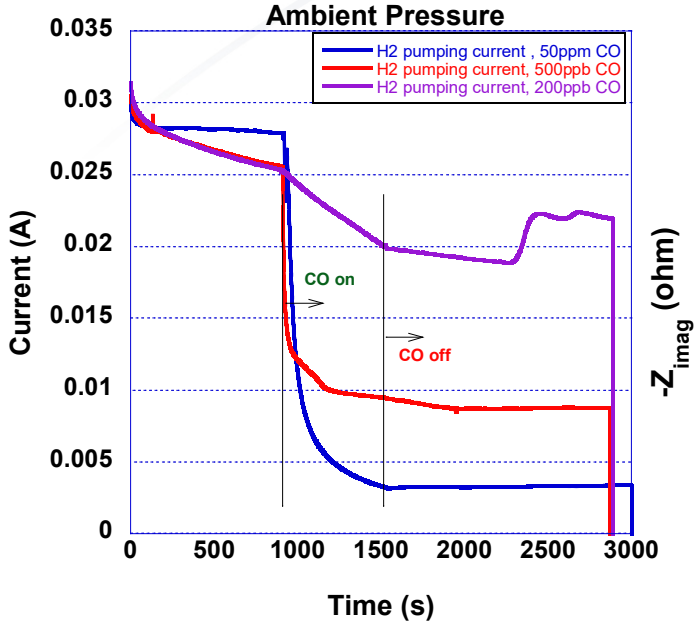
Temp: 30°C, Flowrate: 100 sccm, Ambient Pressure



A7: Lowering Ionomer content in the electrode Improves Response

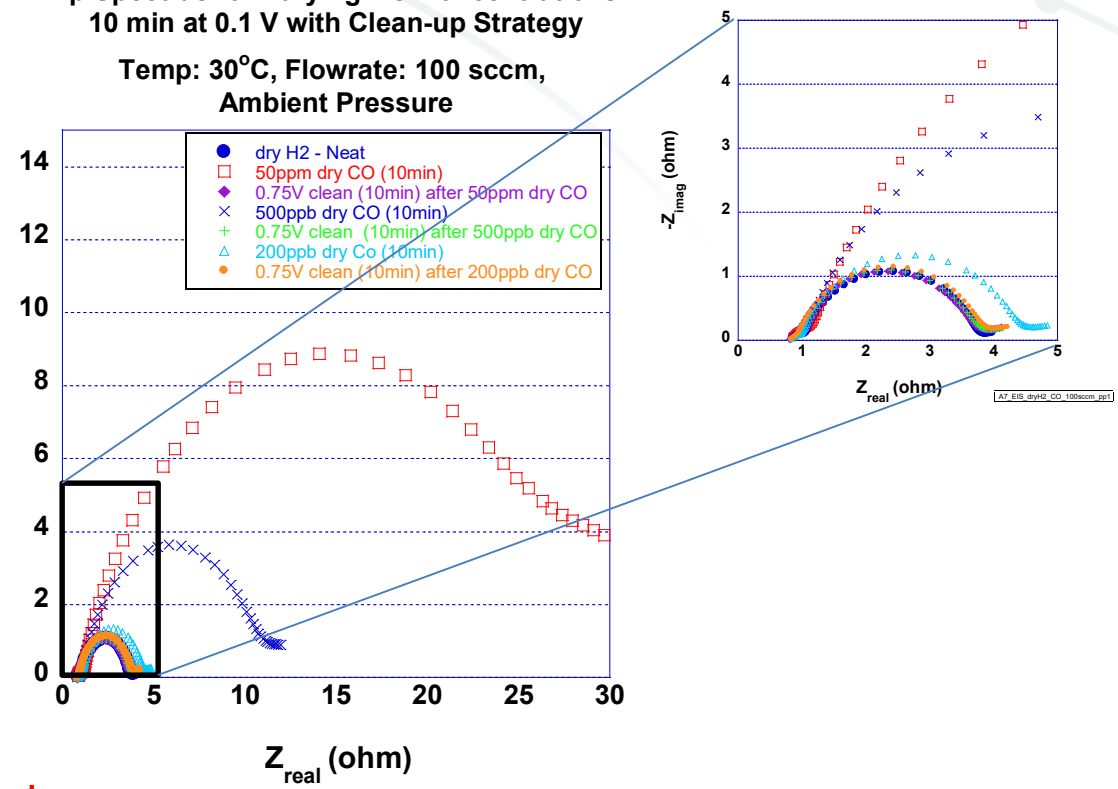
Current Respose to Varying CO Concentrations: 10 min at 0.1 V

Temp: 30°C, Flowrate: 100 sccm, Ambient Pressure



Imp Spectras for Varying CO Concentrations: 10 min at 0.1 V with Clean-up Strategy

Temp: 30°C, Flowrate: 100 sccm, Ambient Pressure



- Reduce Ionomer by a factor of 10
- **Response is almost instantaneous (minimal conditioning)!!!**
- **1 order of magnitude improvement in electrode resistance (access to more Pt sites)**
- Activation steps and baseline are being explored

- Responses still observed to 200 ppb CO
- 0.75 V applied after CO exposures

Clean-up shown at 5 times SAE level!!!

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