Hydrogen Fuel Quality

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Los Alamos National Laboratory

2015 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

June 8-12, 2015
Arlington,VA

Project ID: SCS007

Overview

Timeline

- Project start date: 10/1/06
- Project end date: 9/30/15*

* 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: $3325K
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY14: $475K
- Total funding planned for FY15: $475K

Partners/Collaborators

- Japan Automotive Research Institute
- Joint Research Centre- Greece
- CEA- Grenoble, France
- VTT-Finland (FCH JU HyCORA Project)
- National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee Call
- ASTM
- SAE
- CAFP
- CDFA
- Smart Chemistry

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OUTLINE

- **Relevance**: Objectives
- **Approach** and **Technical Accomplishments:**
  1. Contributions to ASTM
     - ❖ Sub-committee Chair D03.14
     - ❖ Update
  2. In-line Fuel Quality Analyzer
     - ❖ Rationale & Approach
     - ❖ Testing Status: CO and H_2S
  3. Hydrogen Fuel Quality Testing
     - ❖ International Collaborations (Established)
     - ❖ Low Loading Results with New MEAs
     - ❖ Re-circulating System
- **Summary**
- **Future Work**

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Relevance to Safety, Codes and Standards:

Objectives

- **Contribute to the goals of ASTM as sub-committee chair for D03.14 gaseous hydrogen fuel efforts.**
- **Develop an electrochemical analyzer to detect low levels of impurities in gaseous hydrogen fuel**
- **To investigate the impacts of contaminants at the levels indicated in the SAE J2719 and ISO TC197 WG12 documents using 2015 DOE loadings.**
- **Collaborate with international partners to harmonize testing protocols and fuel cell impurity testing**

Milestones:

3/31/2015	Regular	Determine response time of Fuel quality analyzer electrode to H_2 fuel with 200 ppb of CO and 4 ppb H_2S. Quantify effect of flow rate on the analyzer response time.	In progress. MEAs with 0.04mg.Pt/cm2 loading have been prepared ad will be evaluated. complete
6/30/2015	Regular	Complete 100 hours of fuel cell testing using anode recirculation system with H2 + 200 ppm CO. Compare performance degradation with and without re-circulation system and quantify effect of anode re-circulation on CO poisoning of PEM fuel cells.	Annual SMART Milestone. Recirculation system should be online in March. In progress
9/30/2015	Regular	Finalize design specifications for proto-type Fuel quality analyzer. Report design to DOE to initiate building of proto-type analyzer in FY16.	Experiments underway to evaluate designs In progress

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1. ASTM D03.14 Hydrogen and Fuel Cells Update

Approach/Objectives: Hydrogen and Fuel Cells is responsible for developing standards, specifications, practices, and guidelines relating to hydrogen used in energy generation or as feed gas to low, medium and high temperature fuel cells.

Accomplishments

- **ASTM sub-committee chair**
- Chaired two ASTM D02/D03 meetings per year
- New Agenda work items:
  - Working with WG-24: Presentation –J. Schneider
  - Tiger Optics: Florian Adler
- Inter-Laboratory Studies:
  - Cavity Ring-Down Spectroscopy - **Status:** additional test sites needed.
  - ASTM D7649 - Test Method for Determination of Trace CO_2, Ar, N_2, O_2 and H_20 in Hydrogen Fuel by Jet Pulse Injection and GC/MS Analysis **Testing complete**
    - ✓ Results received from SmartChemistry

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2. In-Line Fuel Quality Analyzer

Relevance:

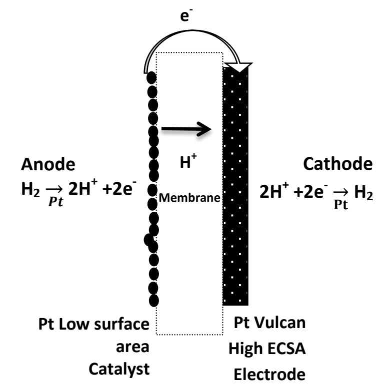
- There is a need for an **inline *hydrogen analyzer to continuously monitor*** impurities and alert the user to any fuel quality issues, ***both on-board in the fuel stream and at the nozzle***.
- To provide a quick response time to prevent damage to multiple vehicles

Concept:

Use a fuel cell type device to measure impurities in the fuel stream. The device should be:

- Sensitive to the same impurities that would poison a fuel cell stack
  - Use same components (Nafion®, Pt and C) as the fuel cell stack
- Orders of magnitude more sensitive to impurities than the fuel cell stack
  - Use extremely low Pt loading and low surface areas
- Durable and low cost
  - Use small area cells, large Pt particle sizes (eliminate carbon), and thick electrolytes

Hydrogen pumping cell



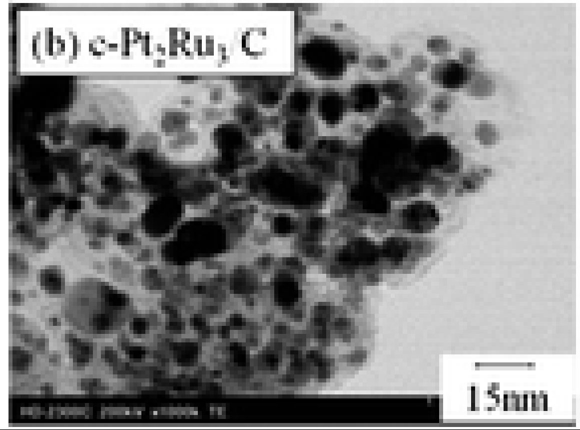
Approach:

It operate as an electrochemical hydrogen pump, using (MEA)-type configuration.

Approach: Electrode materials selections

Reference electrode:

- Pt: 30 wt %, Ru: 23.3 wt %, by TKK., Japan
- Particle size **3.5 nm**
- Carbon black with 5% Nafion® painted decals



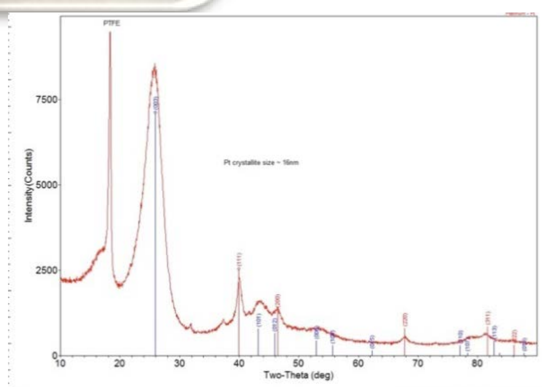
Working electrode:

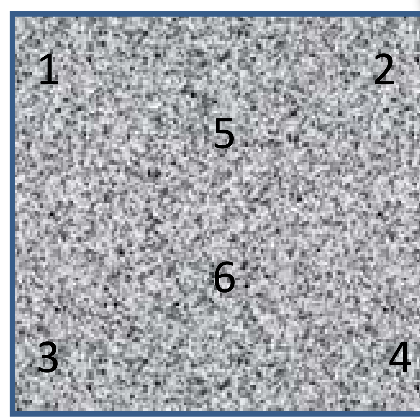
Sputtering System

XRF Calibration test

- Cal Standard: 0.214mg/cm^2 Pt.
- Measured: 0.211 mg/cm^2 Pt.
- Accuracy : 98.5%

XRD
Pt particle size ≈ 16nm





Gas Diffusion Electrode : XRF used to confirm platinum loadings
Use ultra-low loadings ≈ 0.05mg.$_{Pt}$/cm^2

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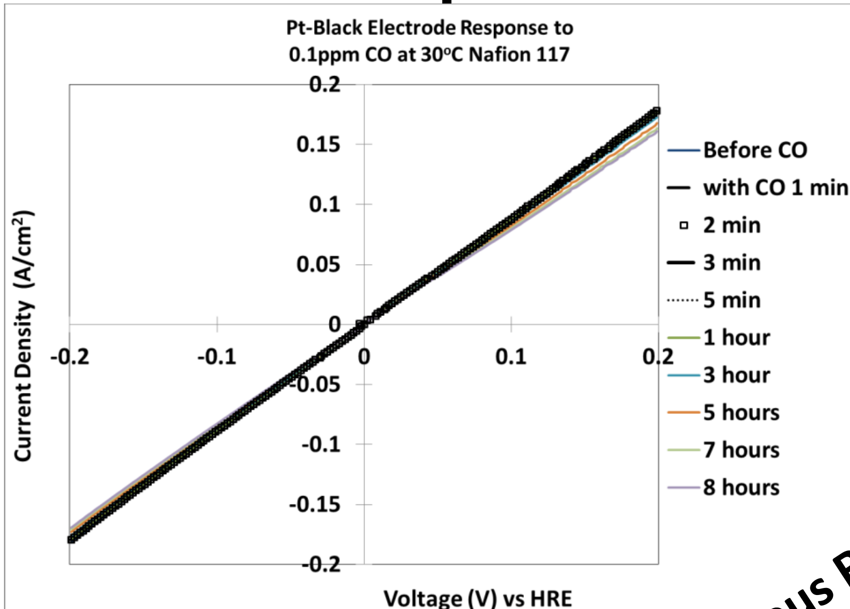
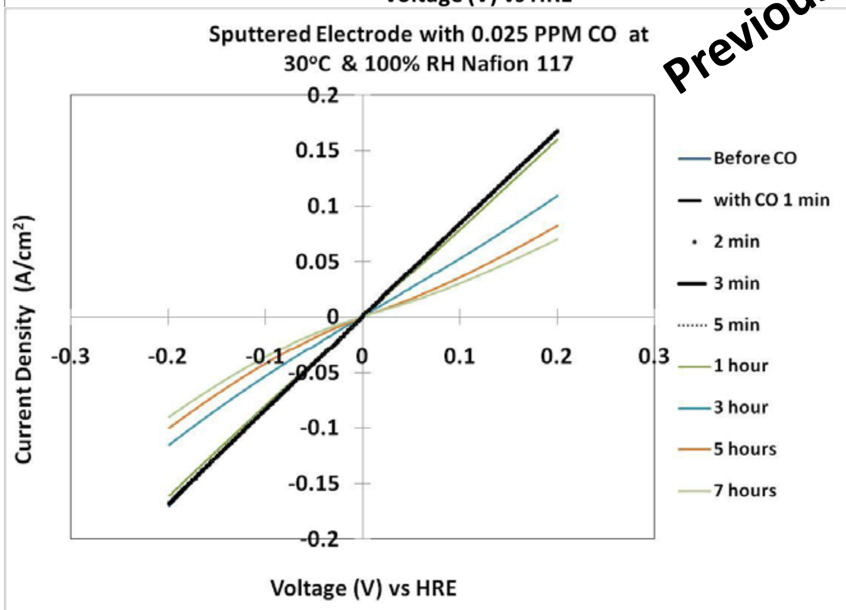
Technical Accomplishments:

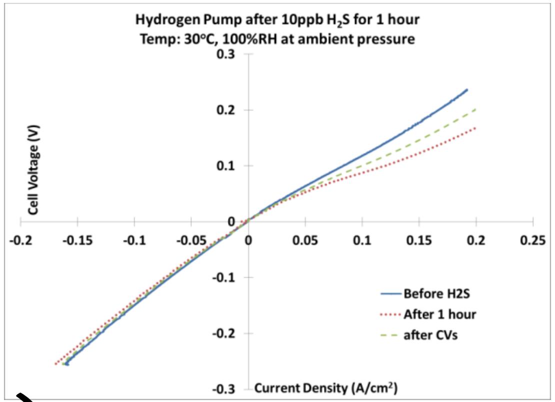
Exposure to **10 ppb H_2S** for 1 and 5hrs; and after CVs.

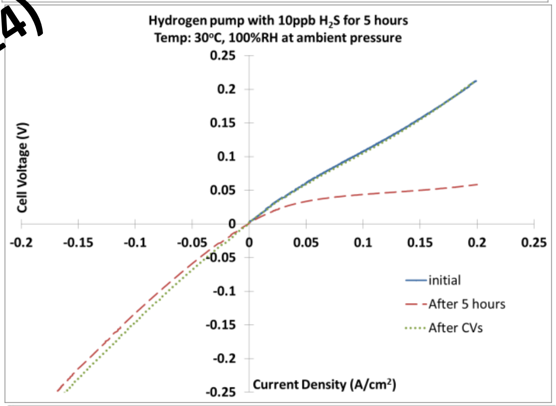
CO results

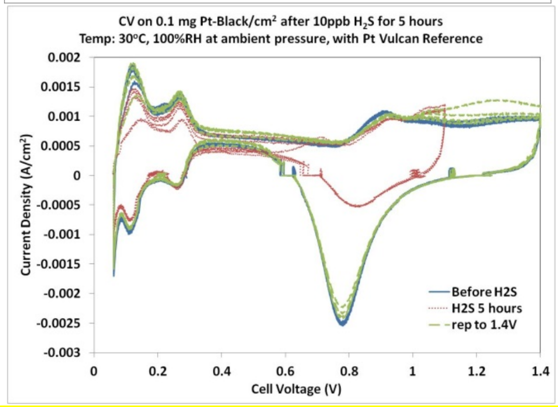




Previous Results (FY14)





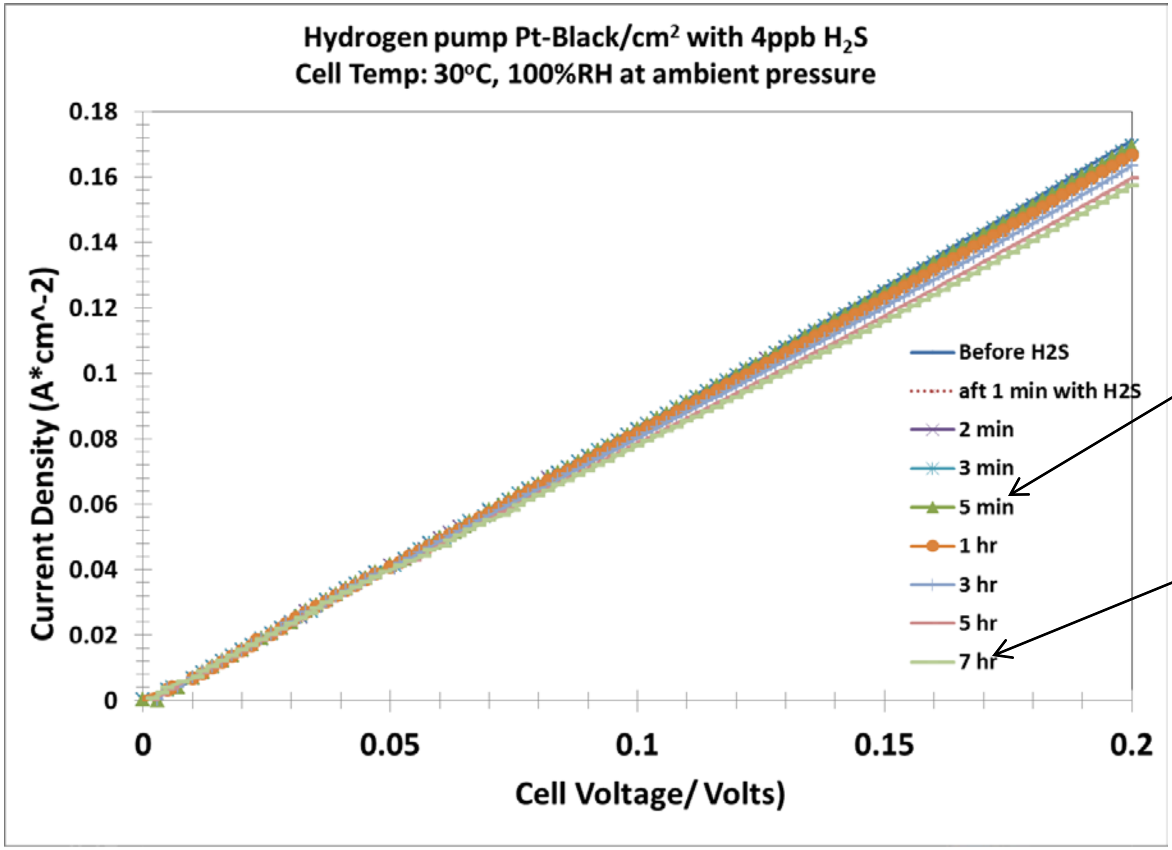


- Pt Black sensitive to 0.1 ppm after 1 hr
- Sputtered sensitive to 0.025 ppm

- Partial recovery after CVs were run up to **1.1V**
- Losses were amplified as exposure time increased
- **1.4 V** need and multiple cycles to reset analyzer

Technical Accomplishments:

Pt-Black Electrode Demonstration to 4 ppb H_2S



SAE J2719 Fuel Specification Limit

Approx. time for two hydrogen fuel fillings

Approx. time to Expend a tank of H_2

4 ppb H_2S response slower and less severe…

How do we decrease the response time and increase sensitivity?

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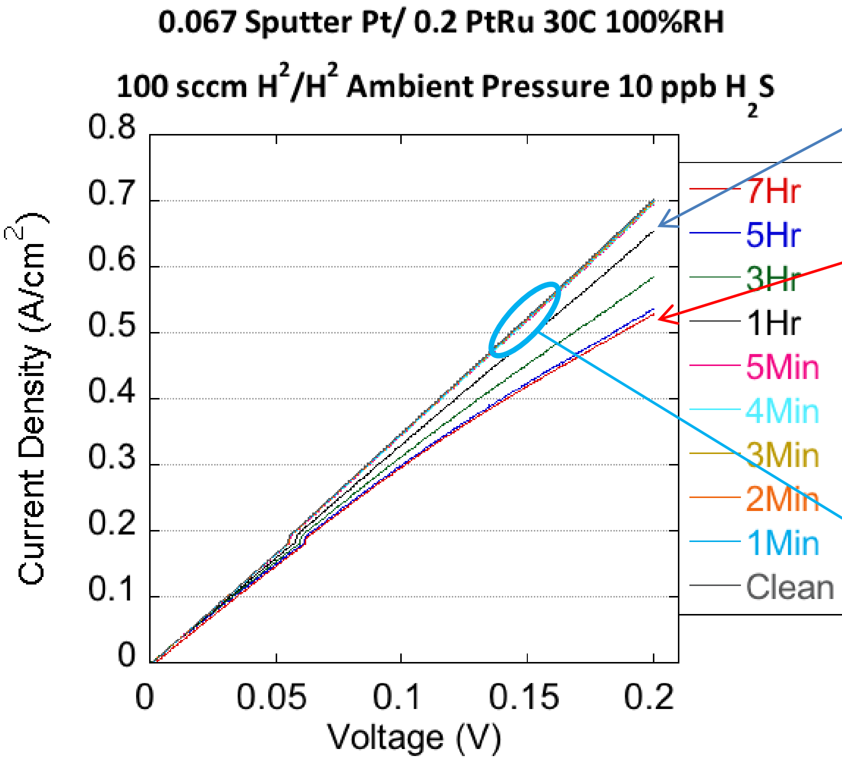
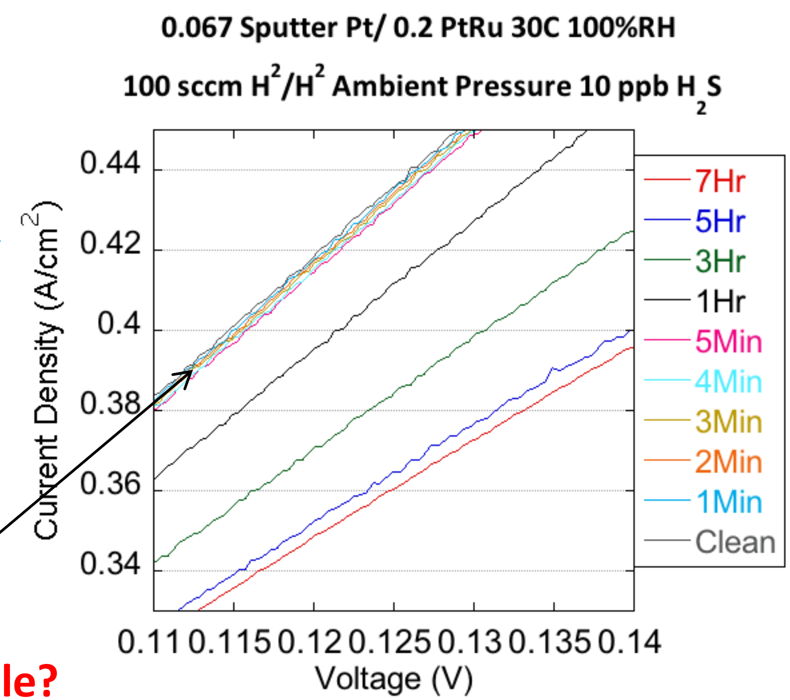
Technical Accomplishments:

Working Electrode Type: Sputtered 0.067 mg Pt/cm^2



Clear response after 1 hr

More pronounced after 7 hrs



Is response in a few minutes possible?

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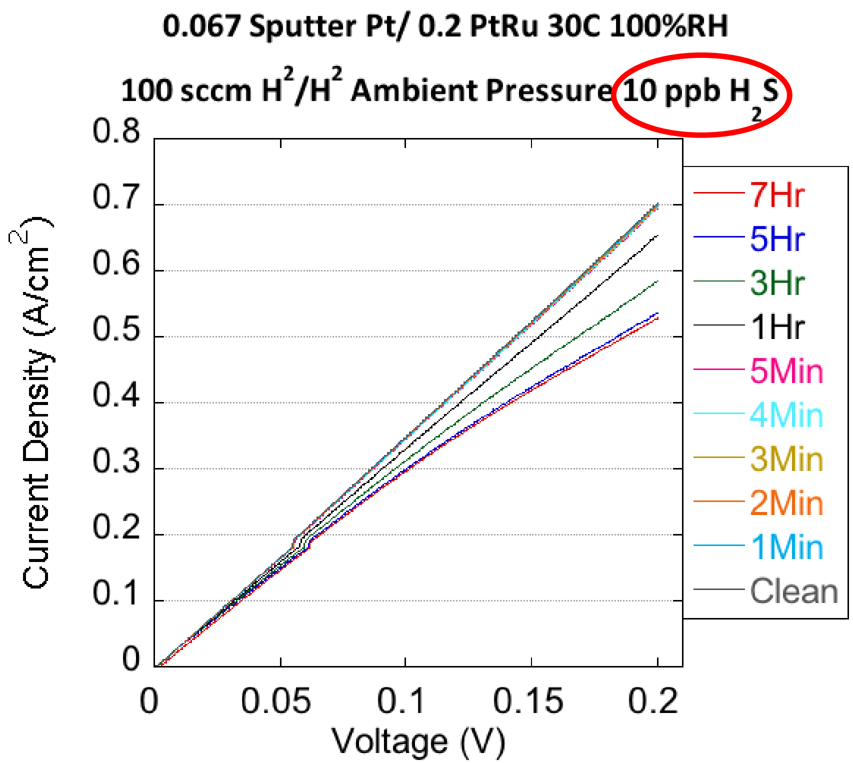
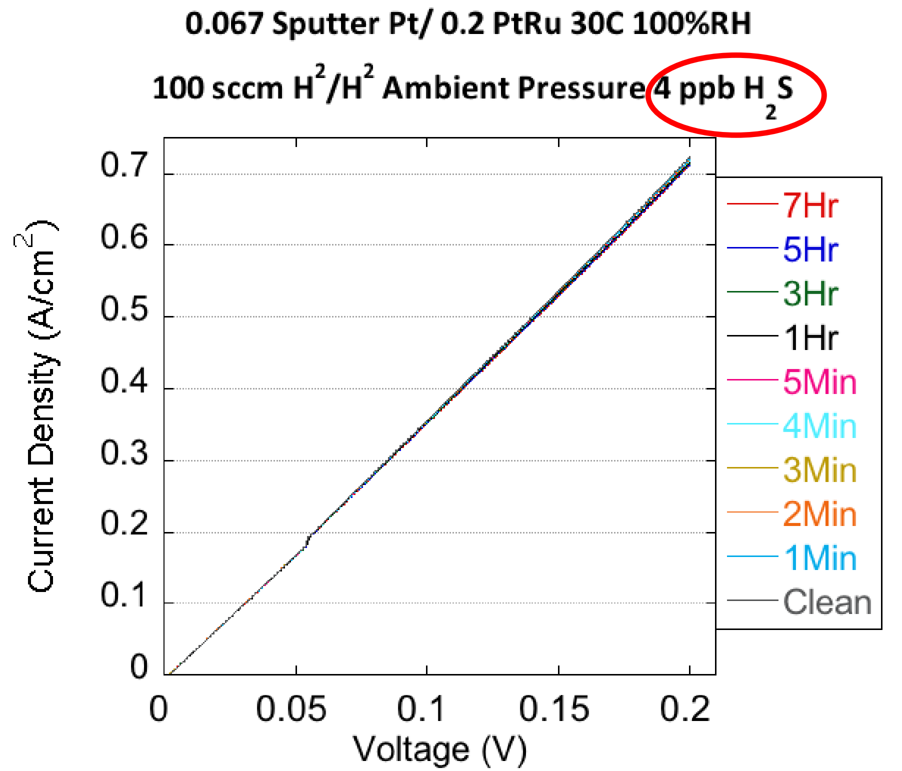
Technical Accomplishments:

Sputtered Electrode: Concentration





Much clearer response was observed at 10 ppb H2S…
At 4ppb, with the same electrode, their is little to no response, even after 7 hours

How do we improve response time at the SAE limit?

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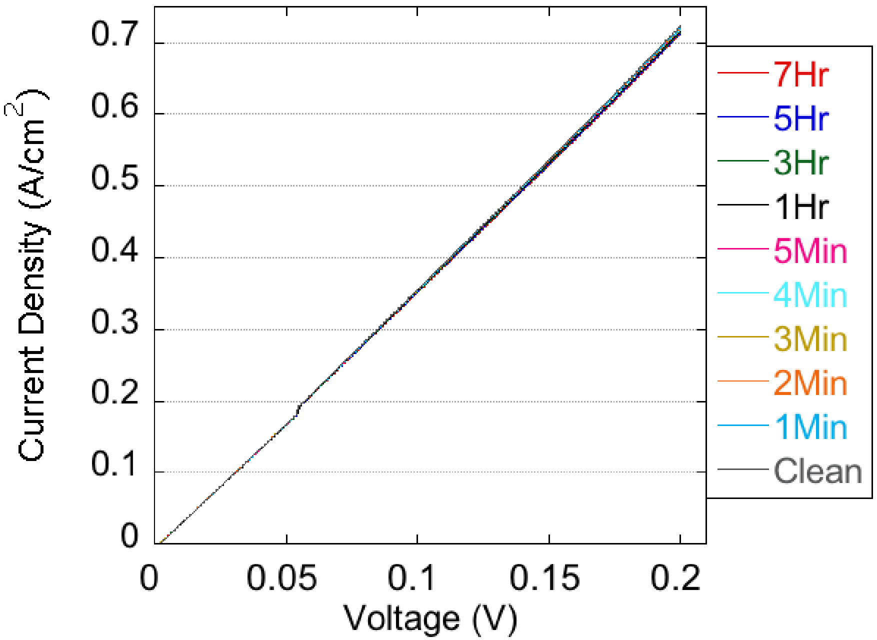
Technical Accomplishments:

Sputtered Electrode: Flow-rate

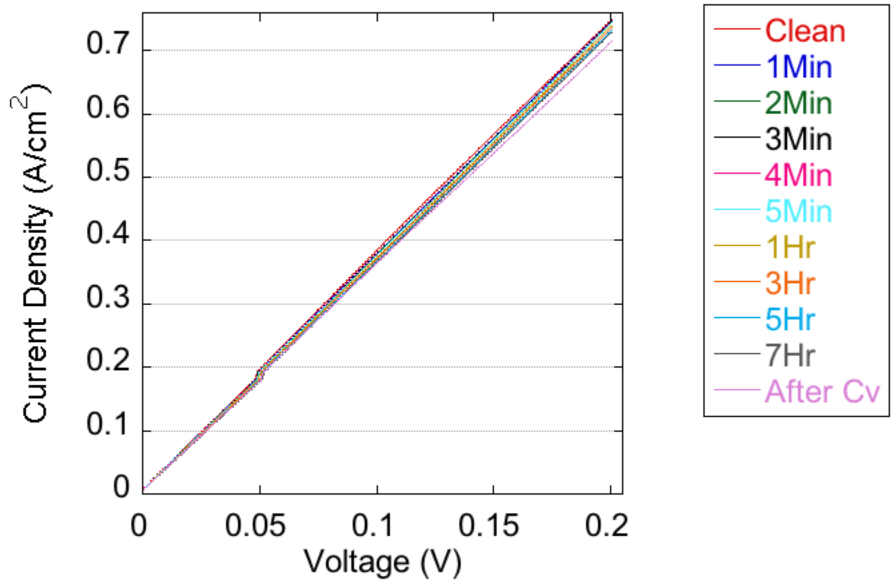
0.067 Sputter Pt/ 0.2 PtRu 30C 100%RH

100 sccm H^2/H^2 Ambient Pressure 4 ppb H_2S



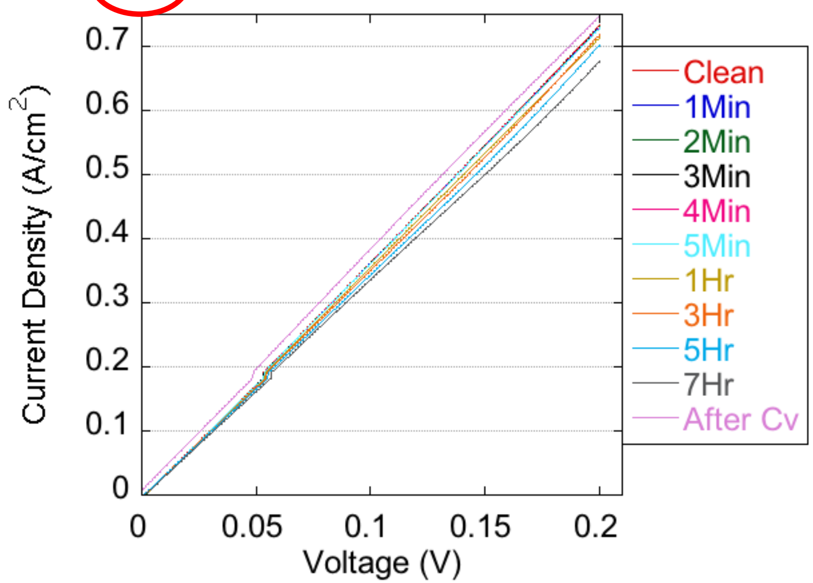
0.067 Sputter Pt/ 0.2 PtRu 30C 100%RH

150 sccm H^2/H^2 Ambient Pressure 4 ppb H_2S



0.067 Sputter Pt/ 0.2 PtRu 30C 100%RH

200 sccm H^2/H^2 Ambient Pressure 4 ppb H_2S



- **Responses increased as flows were increased…**
- **Evident as we see the resistance increasing**
- **Total impurity dosage is critical**

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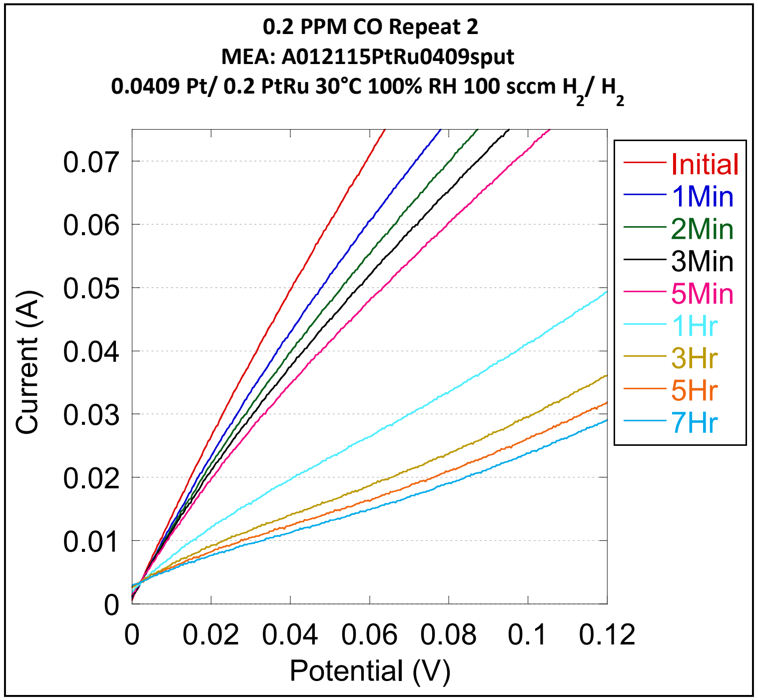
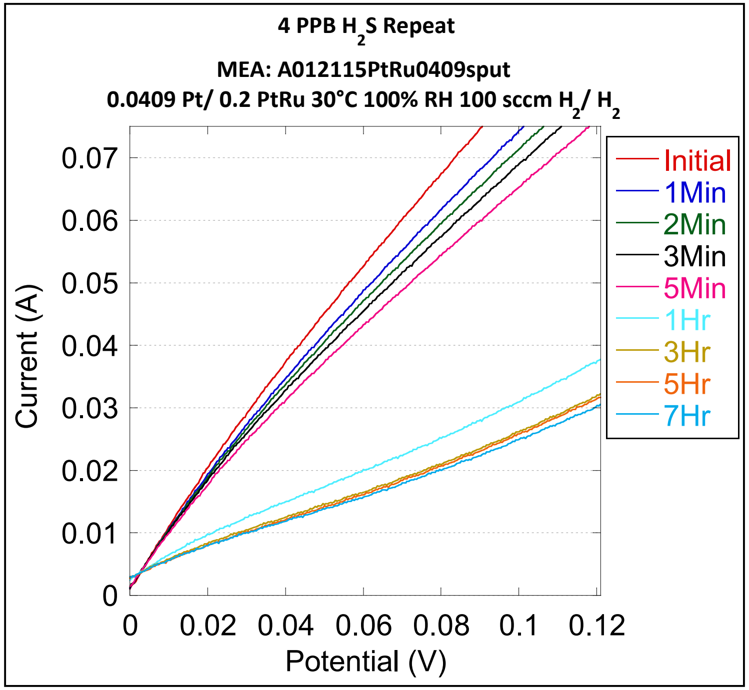
Technical Accomplishments: Sputtered Electrode: Loading

Reduced Loading on working electrode to 0.0409 mg Pt/cm^2





At SAE CO level:

At SAE H_2S level:

Clear response within minutes!!!

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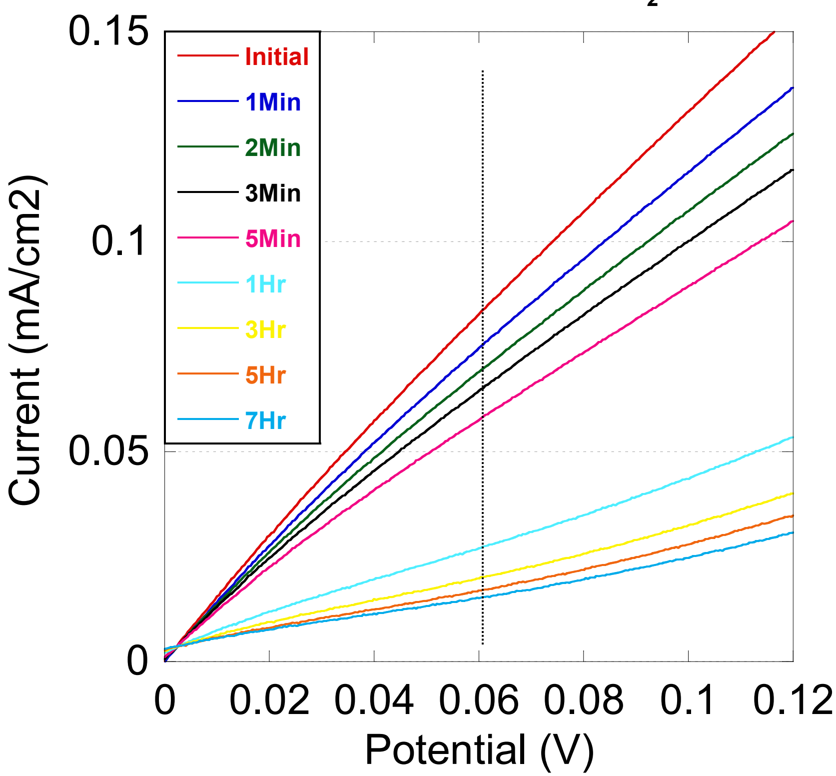
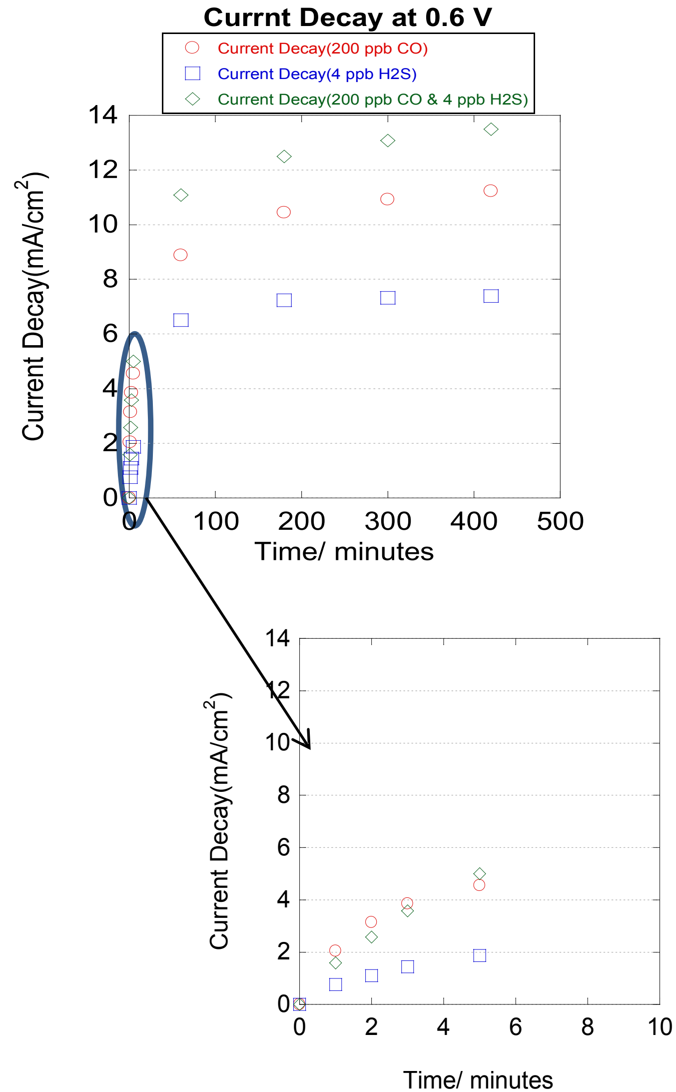
Technical Accomplishments:

Combined: 200 ppb CO & 4 ppb H_2S

0.2 PPM CO & 4 ppb H_2S MEA:

Working Electrode:0.0409 mg Pt/cm^2
100% RH; 100 sccm H_2





Measurements taken at shorter exposure time favors CO adsorption
Decay levels are not additive (as we anticipated)

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3. Hydrogen Fuel Quality Testing

INTERNATIONAL COLLABORATIONS

- LANL-JARI-CEA
  - Baseline Evaluation of MEAs at each facility
  - Impurity testing on low loaded MEAs.
- VTT-Finland/LANL Collaboration
  - Implement identical fuel re-circulation system for impurity testing
- WG11
  - PEFC document on Testing under development, Switzerland, June 2015
- Joint Research Centre- Georgios Tsotridis: Greece, Sept 2015
- Abstract submitted - ICHS 2015 meeting, Japan, October 2015

FUEL QUALITY Underway

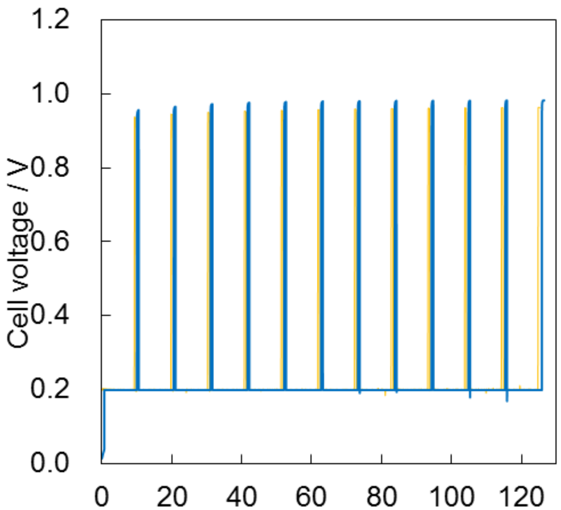
- Test results compared with JARI's MEAs
- New Baseline MEAs obtained
- Materials exchange: sent new MEAs to JARI and CEA
- Implement fuel quality testing with re-circulation system in collaboration with JARI and CEA

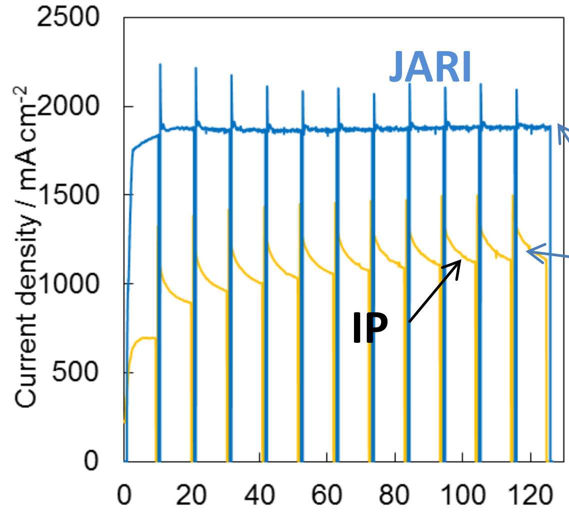
Technical Accomplishments:

Comparison of MEAs measured at JARI Test Site

-both loaded with 0.15 mg Pt/cm^2 (total)

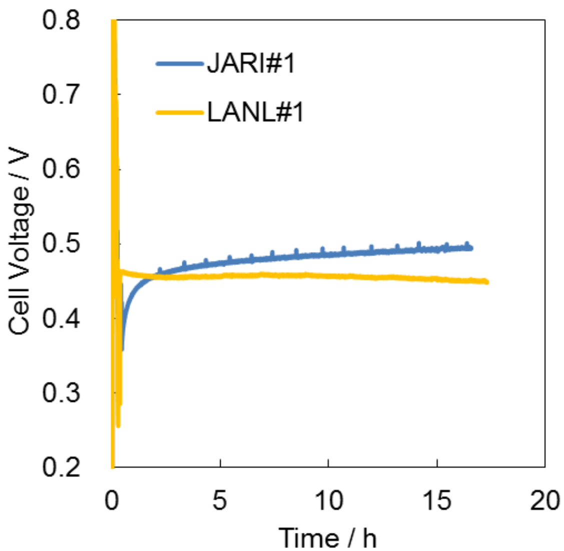
Ion Power Protocol

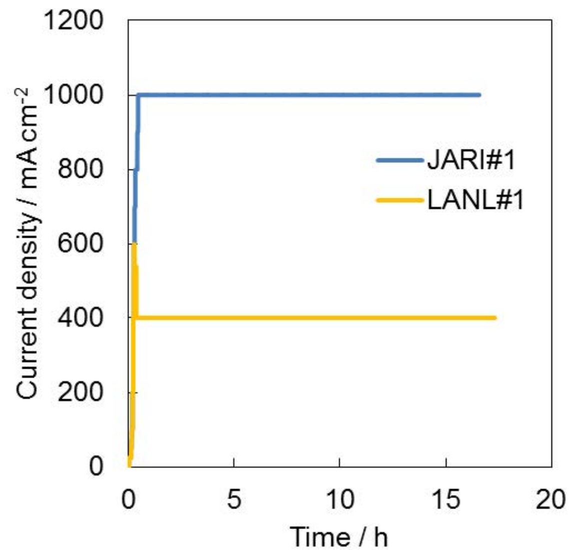




Large performance gaps

JARI Protocol





differences observed regardless of protocol?

Large discrepancies observed in first round of testing

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Technical Accomplishments:

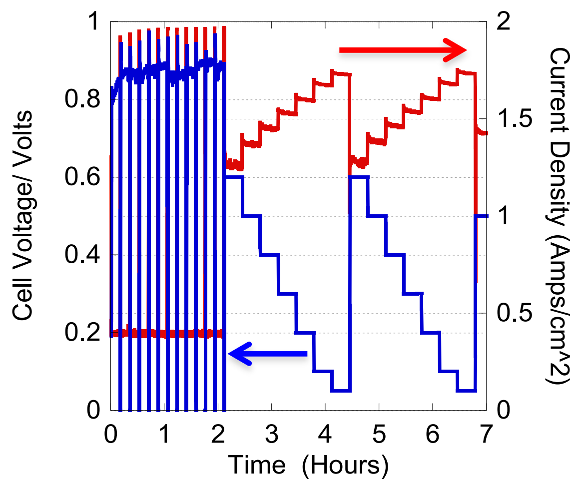
New MEAs with Low Loading:

Reformulated ionomer to catalyst ratio in the electrode

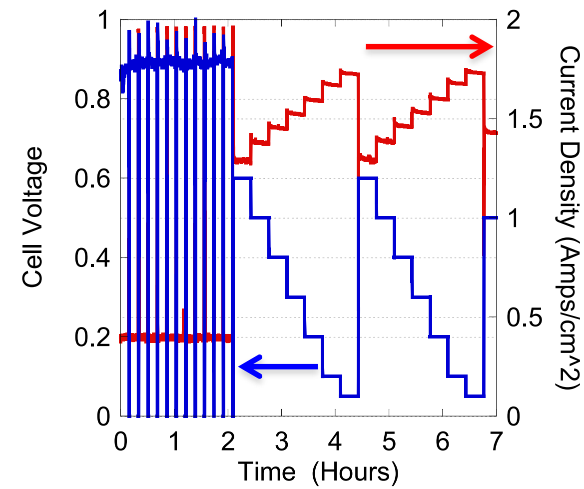
Tests conducted with:
4 different samples
two different sets of hardware
and two different test stands.

Great repeatability demonstrated!

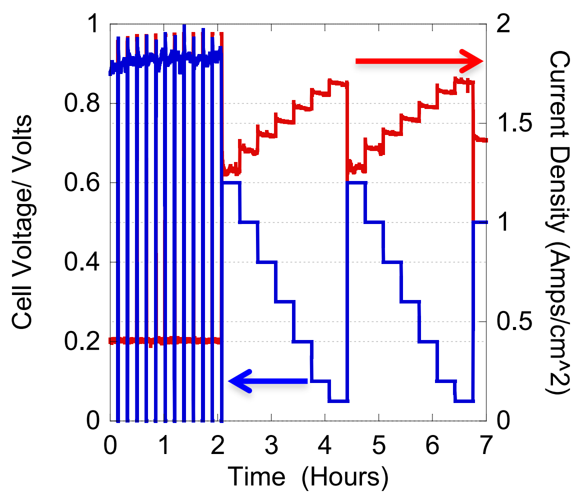
LANL_LOW_LANL_011415B



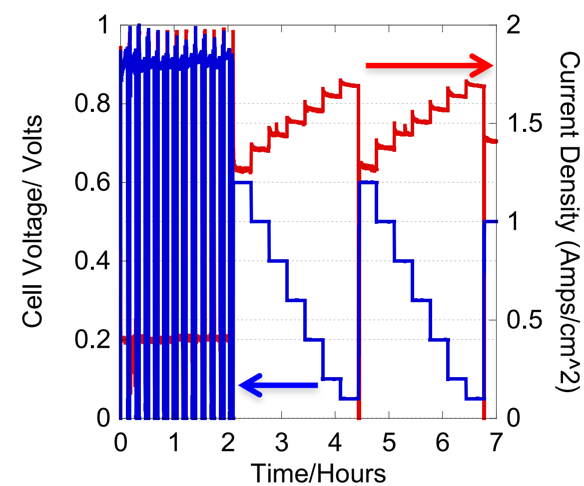
030915A_LOW_IP5LANL



LANL_LOW_LANL_041615



030915B_LANL_LOW_IP#5_LANL



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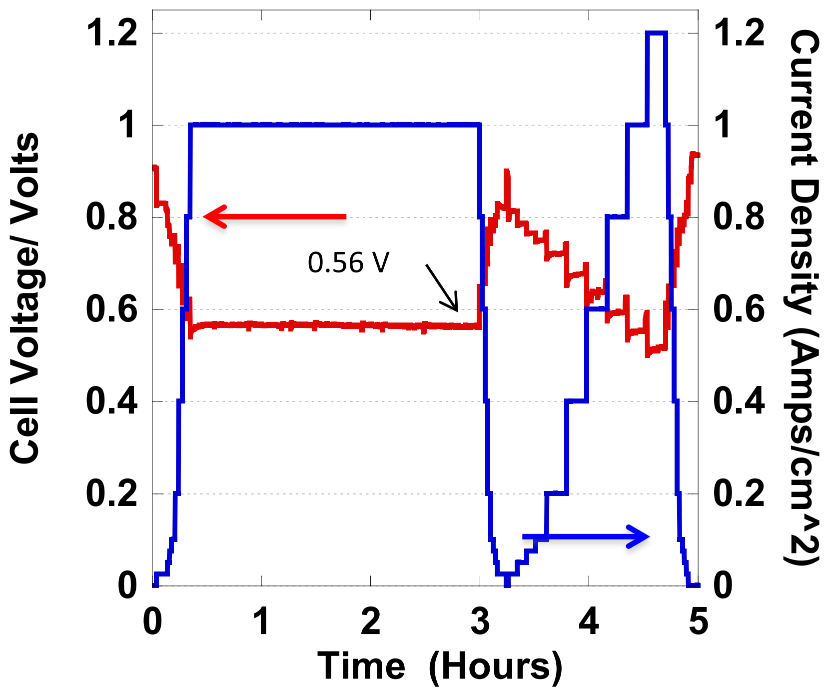
Technical Accomplishments:

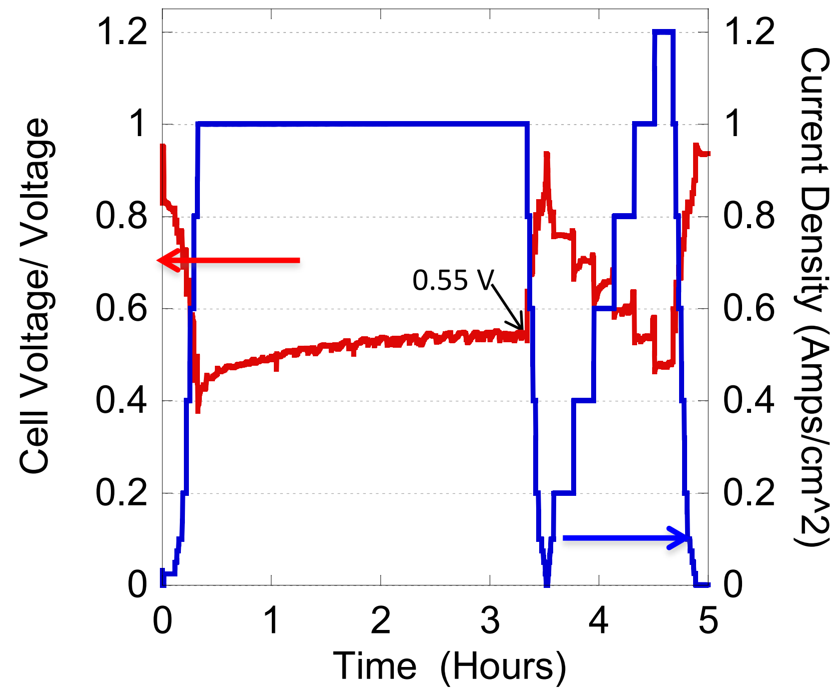
Comparison between MEAs :

Identical Hardware using JARI's Protocol

JARI MEA1_Low Pt



042115_LOW_IP5 JARI HW and Protocol



New MEA yields comparable results with JARI MEA!!!

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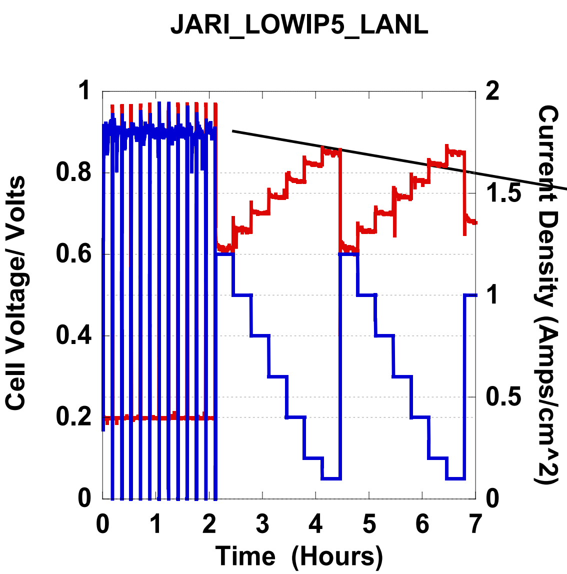
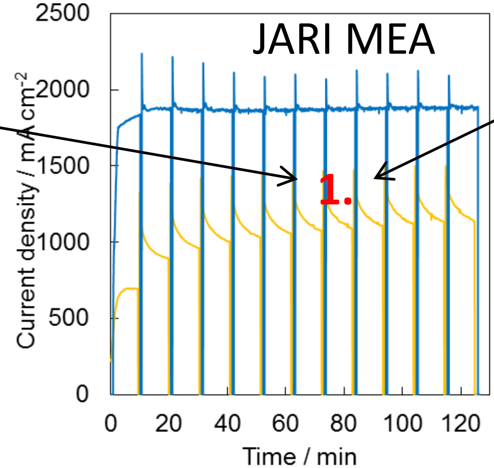
Technical Accomplishments:

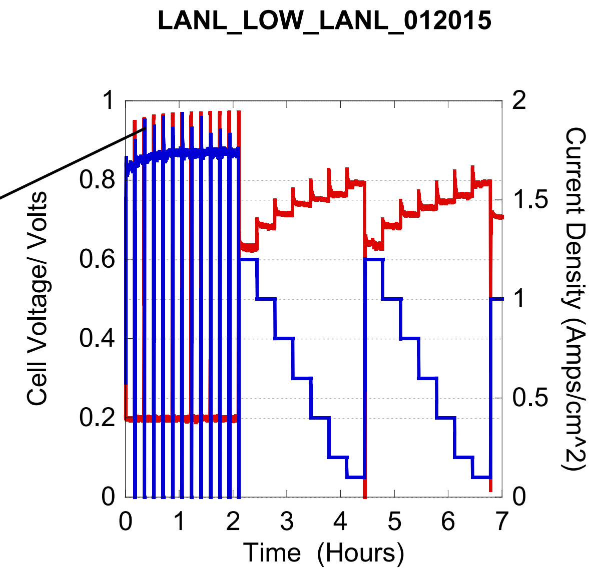
Comparison between MEAs, Hardware & Facilities



(a) JARI Hardware with IP#5



(b) JARI Hardware and MEA



(c) LANL Hardware with IP#5

1. Large performance improvement after changing electrode formulation.
   - Old Ion Power MEA vs New MEA (new ink formulation)
2. Baseline testing shows great agreement between:
   - MEAs (a) vs (b)
   - Hardware (a) vs (c)
   - Facilities (b) and (c)

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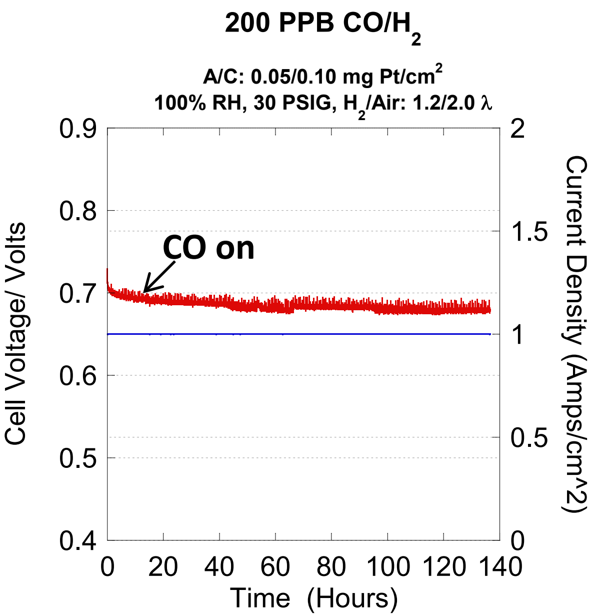
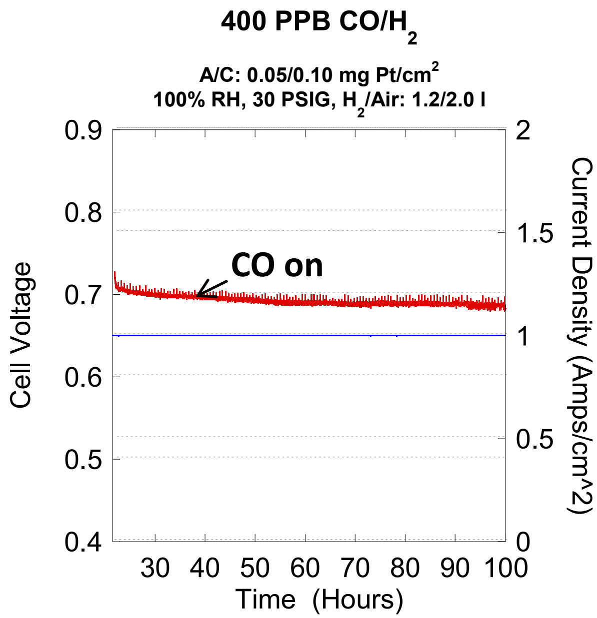
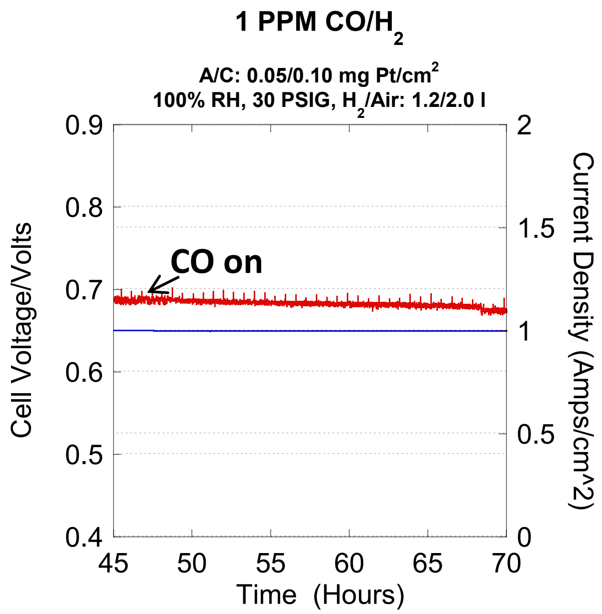
Technical Accomplishments:

New MEAs with Low Loading:

Initial Impurity Results: Identical Dosage CO







Left Figure: 100h of exposure to 200 ppb CO showed **8 mV loss**

Center Figure: 50 h of exposure to 400 ppb CO **18 mV loss**

Right Figure: 20 h of exposure to 1 ppm CO **21 mV loss**

Our current testing plan is to test 2 ppm and 5 ppm CO with identical dosage, plot the voltage loss versus CO concentration. We can then extrapolate the CO tolerance.

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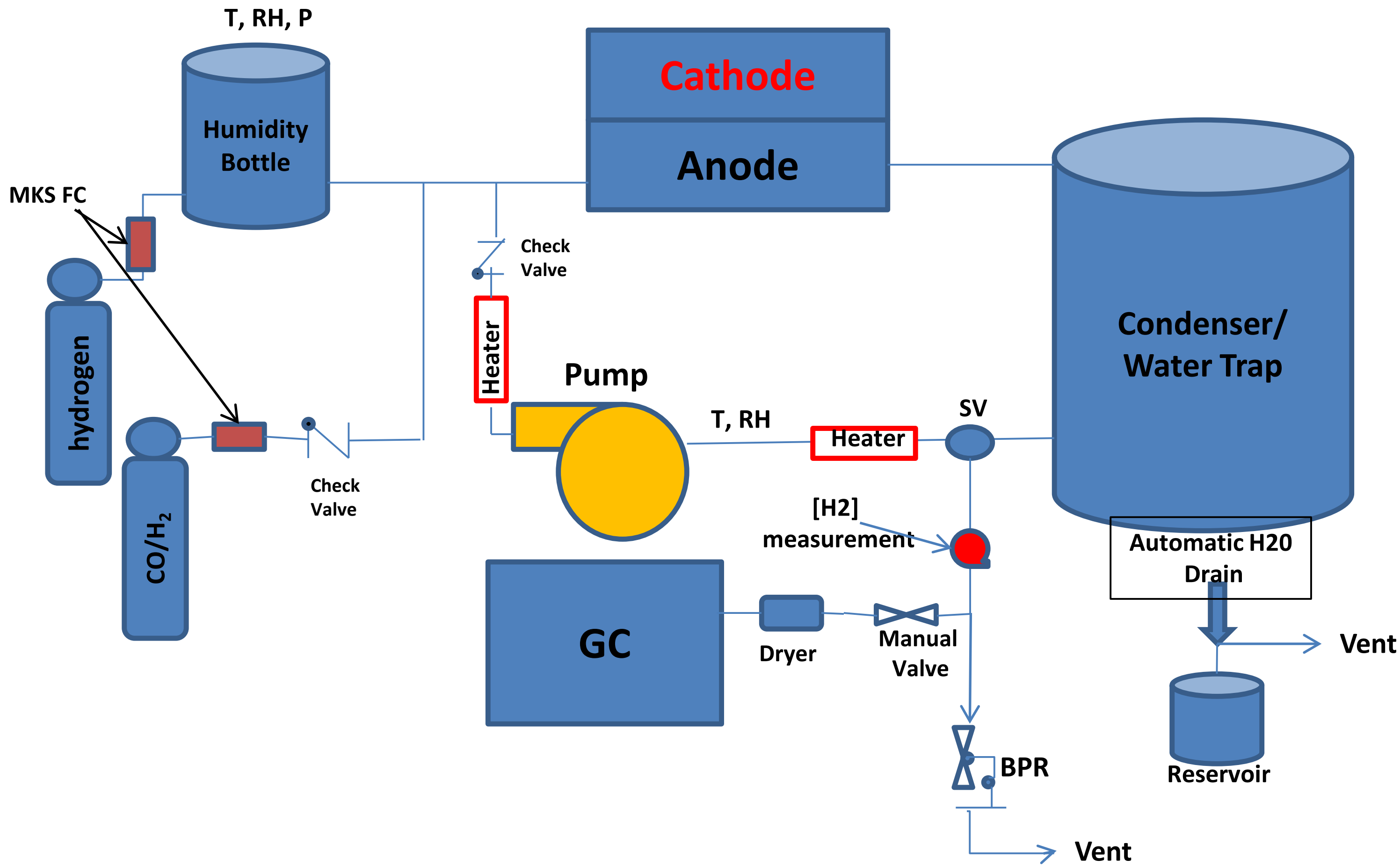
Technical Accomplishments:

New Re-Circulation System for Fuel Quality Testing

Collaborator: VTT-Finland, Dr. Jari Ihonen



- Joint discussions and site visits by Dr. Jari Ihonen
- Newly implemented re-circulation system

Summary

1. ASTM

- ILS 751- *Test Method for Determination of Trace CO_2, Ar, N_2, O_2 and H_20 in Hydrogen Fuel by Jet Pulse Injection and GC/MS Analysis*
  - Testing complete
  - Coordination of results in progress
- Hydrogen Purity Analysis Using a Continuous Wave Cavity Ring-Down Spectroscopy Analyzer
  - Tests sites are needed to conduct -ILS study
  - Presentation on technique scheduled for June 2015 ASTM meeting

2. Hydrogen In-Line Analyzer

- Improvements made to sensitivity
  - Increasing particle size, reducing electrode loading, and increasing flow-rates
- CO and H_2S results
  - Detection at SAE J2719 levels possible in few minutes
  - Analyzer favors CO adsorption in short term exposures
  - CO and H_2S effects are not additive

3. Hydrogen Fuel Quality

- International collaborations underway with JARI,CEA, and VTT
- Low loading tolerance lower than SAE J2719 levels
- Anode recirculation system installed

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Future Work

1. ASTM

- Continue with new standards development- ILS Coordination
- Coordinate a workshop on In-Line Fuel Quality, Dec. 2015 ASTM meeting

2. Hydrogen In-Line Analyzer

- Optimize operating conditions of analyzer to further improve sensitivity
- Work with hydrogen fuel suppliers to better understand S-upsets
- Study impact of humidity
- Evaluate long term durability
- Design and build prototype analyzer by end of FY16 to be evaluated at NREL

3. Hydrogen Fuel Quality

- Continue working with international collaborators
- Initiate an International round robin
- Compare performance degradation with and without **re-circulation system** and quantify effect of anode re-circulation on CO poisoning
- Assess effect of impurities during simulated drive cycle measurements
- Align efforts to work with other Fuel Quality Tests sites: UConn, Hawaii, etc.

Acknowledgements

- **Charles (Will) James Jr, PhD; Technologies Manager**
- Calita Quesada (graduated-NMT) and Fernando Garzon (SNL & UNM)
- Our International Collaborators: JARI, VTT-Finland, CEA
- CSTT, SAE and ASTM D03.14 members

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Publications/Presentations

Tommy Rockward, Calita Quesada, Fernando Garzon, and Rangachary Mukundan, **Platinum Electrode Properties Tailored to Respond to Ultra-Low Concentrations of H_2S in Gaseous Hydrogen Fuel,** Electrochemical Society Meeting, Cancun, Mexico. October 2014

Tommy Rockward, Jacob Valdez, and Rangachary Mukundan, **An In-Line Fuel Quality Analyzer for Detecting Ultra-Low Levels of Hydrogen Contaminants**, (abstract submitted ICHS 2015)

Reviewer's Comments

When asked what the final response time target is, the presenter answered that the target fill time is four minutes; therefore, the response time target is four minutes. While this is an appropriate target, this answer glossed over reality. A response time of four minutes from an hour demonstrates that this technology has a long way to go. The project team successfully reduced the time by a factor of five (five hours to one hour); however, this technology needs another factor of 15 (60 minutes to four minutes). ***We focused on reducing the analyzer's response time to t < 5minutes to avoid damage to multiple fleets and were successful. Results are shown.***

It is recommended that the project include, from the outset, international partners in the efforts (workshop and subsequent experimental activities) on hydrogen storage system cleanliness. Interaction with JARI and the EU should be strengthened, including the identification of commonly agreed loading cycles (stressors) representative for automotive applications, in addition to the harmonized test protocols which should be expanded from MEA to stack level. ***We are steadily increasing our international collaborations: VTT-Finland and Department of Energy-Politecnico di Milano (Italy).***

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