Hydrogen Fuel Quality

Tommy Rockward (PI), C. Quesada, F. Garzon, and R. Mukundan

Los Alamos National Laboratory

June 18, 2014
Washington, D.C

Project ID: SCS007

Overview

Timeline

- Project start date: 10/1/06
- Project end date: 09/2014*

* Project continuation and direction determined annually by DOE

Budget

- Total project funding: $2,850K
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY13: $475K
- Total funding planned for FY14: $425K

Barriers

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

Partners/Collaborators

- Japanese Automotive Research Institute
- European Union
- National Hydrogen and Fuel Cell Codes and Standards Coordinating Committee Call
- ASTM
- Air Liquide
- CAFP
- CDFA
- Smart Chemistry
- Advanced Biofuels
- Shimadzu

OUTLINE

- **Relevance**: Background and Milestone
- **Approach** and **Technical Accomplishments:**
  1. Contributions to ASTM
     - ❖ Sub-committee Chair D03.14 Update
     - ❖ Inter Laboratory Study 775
  2. In-line Fuel Quality Analyzer
     - ❖ Rationale & Approach
     - ❖ Testing Status: CO and H_2S
  3. Hydrogen Fuel Quality
     1. ISO Results with Anode: 0.03 mg Pt/cm^2
     2. CO Tolerance
  4. International Collaborations (Established)
     1. JARI
        - ➢ Exchange of Protocols , Materials, and Personnel
        - ➢ On-going tests
     2. European Union:
        - ➢ Collaboration Areas
        - ➢ Recirculation System
- **Future Work**

Relevance

Objectives:

- **To carry out the duties of ASTM sub-committee chair for D03.14 gaseous hydrogen fuel efforts.**
- **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**
- **Develop an electrochemical analyzer to detect low levels of impurities in hydrogen fuel.**

Milestones	Due Date	Status
Quantify CO tolerance limit of conventional Pt/C based MEA with total Pt loading of 0.15mg-Pt/cm^2	3/31/14	completed
Demonstrate H2S sensitivity of 10ppb in In-Line Fuel Quality Analyzer	6/30/14	completed
Quantify CO tolerance limit of NSTF MEAs with total Pt loading of 0.15mg-Pt/cm^2	9/30/14	On-going

Los Alamos NATIONAL LABORATORY EST. 1943

1. **ASTM D03.14 Hydrogen and Fuel Cells**

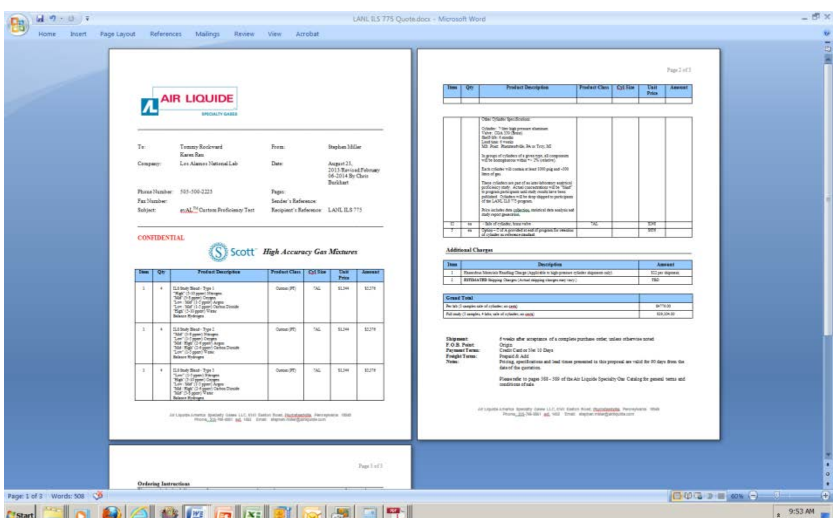
Approach:

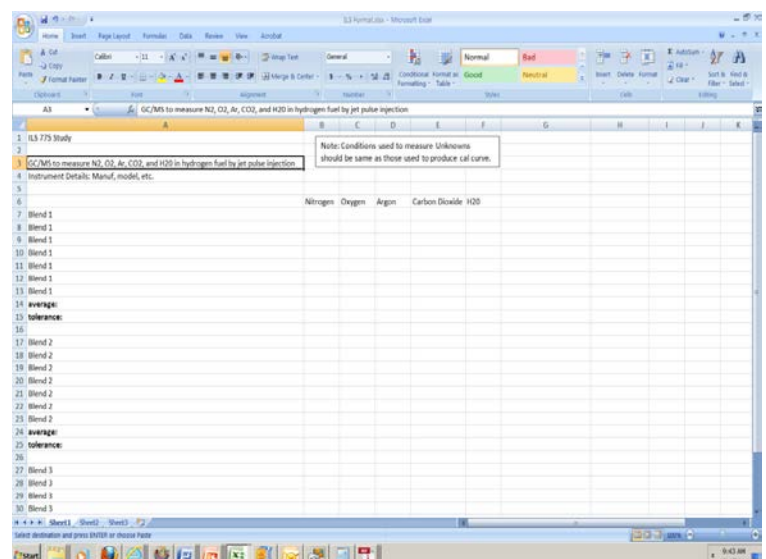
ASTM sub-committee chair: Hydrogen and Fuel Cells is responsible for developing standards, specifications, practices, and guidelines relating to hydrogen used in energy generation or as feed gas to low, medium and high temperature fuel cells.

- Procured Gas samples to be used in ILS 775
- Conference calls for testing and data reporting
- Proposed data report format
- Balloting Items

Accomplishments:

- Chaired D02/D03 Meeting held in Tampa, FL (Dec 2013)
- **Coordinated test labs for ILS 775**, 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





Los Alamos
NATIONAL LABORATORY
EST.1943

Relevance

2. Inline Fuel Quality Analyzer :

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***.

- The importance of ***qualifying the hydrogen fuel grade*** for PEM fuel cell systems has surfaced as a priority in order to assure fuel cell's viability.
- **Our focus** is to ***tailor electrode materials/configuration*** for a dispersed platinum-type membrane electrode assembly (MEA) to be employed ***as a stripping voltammetry analyzer.***
- **Expectations:** The MEA will be more sensitive to impurities and more durable to harsh conditions than a regular fuel cell MEA and will serve as a dosage monitor for impurities that have the potential to poison a PEMFC.

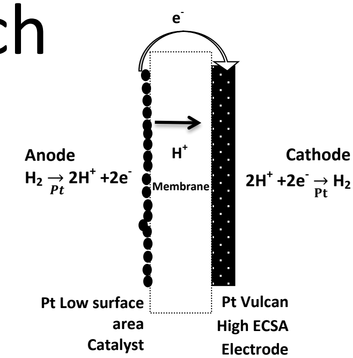
Approach

2. Inline Fuel Quality Analyzer : *Materials Selection/Testing*

- Materials Selection/Sample Preparation:
  - Low surface area, resistant to voltage cycling and sensitive to contaminants **(CO shown in FY 13**)
  - Test Analyzer with different electrode configurations and catalyst
- Various tests:
  - H_2/H_2 Experiments 0~0.1V
    - 5cm^2, 30^{o}C , 0 psig, 100% RH
  - Sensitivity Test: Investigated other electrode materials such Pt-black, and Pt-Ru
  - H_2S Results: Exposure to 10 ppb H_2S and clean-up strategy
  - Probing the surface: H_2/N_2 CVs 0.06 -1.1 or 1.4V before and after Impurity exposure

Approach

2. Inline Fuel Quality Analyzer: Approach



Principle:

Membrane electrode assembly (MEA) similar to a fuel cell.

Operating as an electrochemical hydrogen pump.

Focus for FY14:

Sputtered electrode provides stable Pt particle sizes and the low loadings desired in an analyzer. Vary electrode: Pt black catalyst (no C-support), Pt-Ru, Sputtered Pt Electrode.

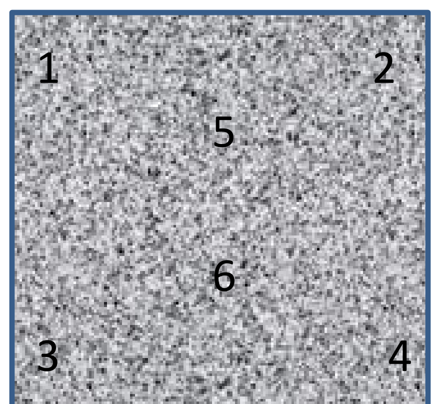
Test in-line Analyzer in the presence of H_2S.

Gas Diffusion Electrode XRF Results

Sputtering System

XRF Calibration test

- Cal Standard: 0.214mg/cm² Pt.
- Measured: 0.211 mg/cm² Pt.
- Accuracy : 98.5%



XRD confirm 16 nm particle sizes

Sputtered Sample results at points:

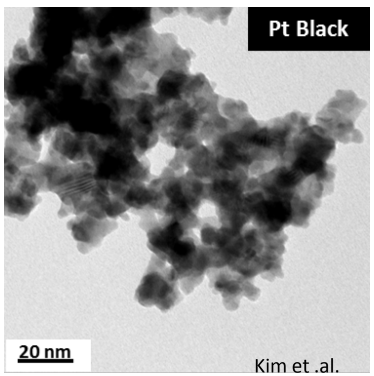
- location 1: 0.08766mg/cm² Pt.
- location 2: 0.09926mg/cm² Pt.
- location 3: 0.09803mg/cm² Pt.
- location 4: 0.09396mg/cm² Pt.
- location 5: 0.101mg/cm² Pt.
- location 6: 0.100mg/cm² Pt.

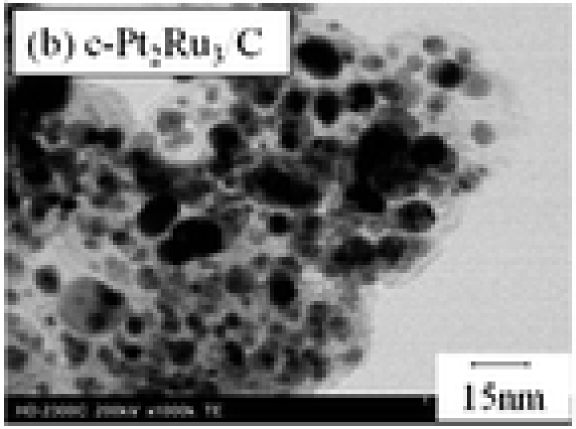
Los Alamos NATIONAL LABORATORY EST. 1943

Inline Fuel Quality Analyzer: Prepared Samples: Varying Working Electrodes

- Pt black
- Alfa Aesar HiSPEC ™ 1000 by Johnson Matthey
- Particle size of 6.3 nm
- Water-based ink
- Hand painted directly onto membrane
- Gas diffusion layer
  - SGL 25BC carbon paper

- Pt: 30 wt %, Ru: 23.3 wt %, by TKK., Japan
- High surface area to mass ratio 3.5nm particle size
- Carbon black with 5% Nafion® painted decals
- Gas diffusion layer
  - SGL 25BC carbon paper

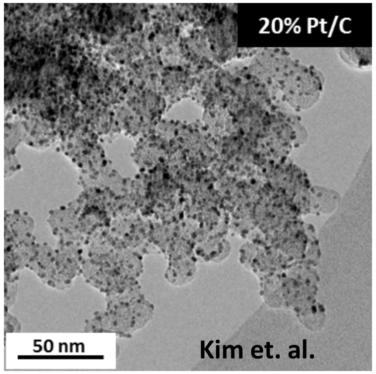




Sato et.al.

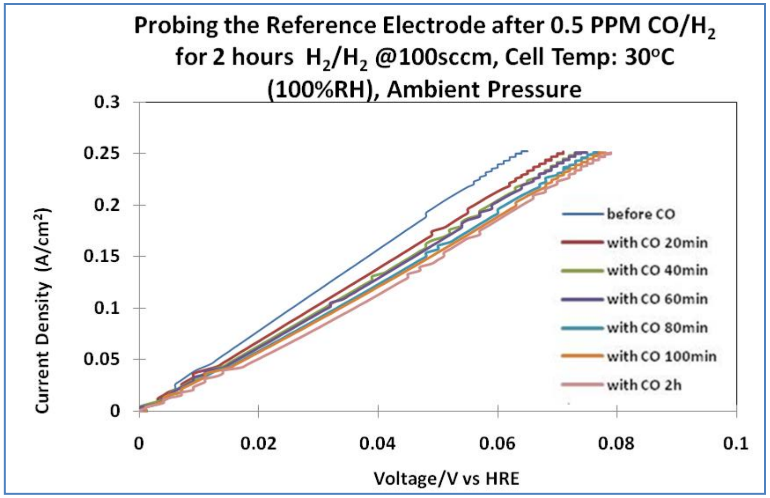
Counter/ Reference electrode

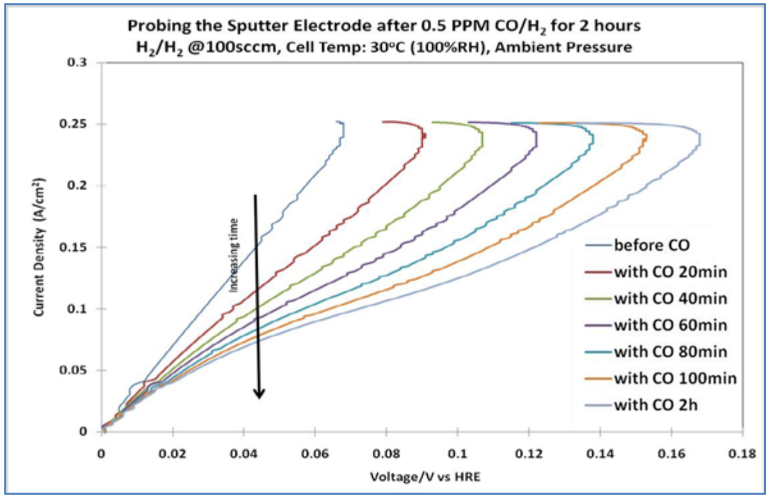
- **High surface area** to mass ratio 2.5nm particle size
- 0.2 mg Pt/cm^2 loading
- Vulcan carbon with 5% Nafion® painted decals
- Gas diffusion layer
  - SGL 25BC carbon paper



2. Reference Electrode vs Sputtered: **Sensitivity to CO**

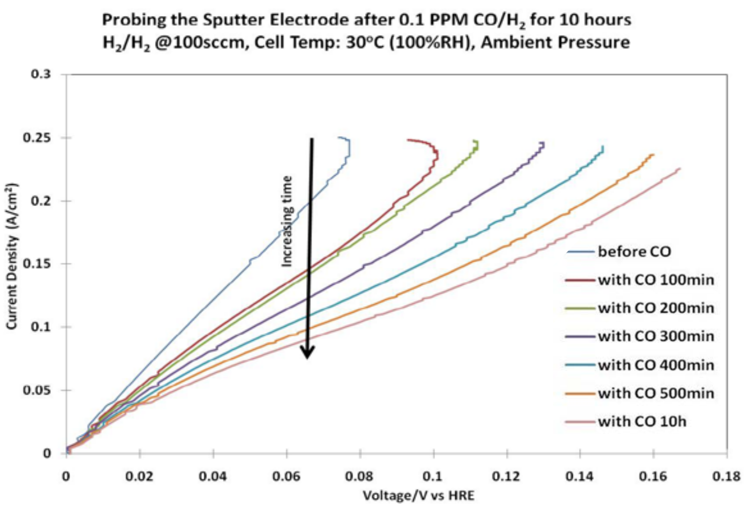
FY13 Results

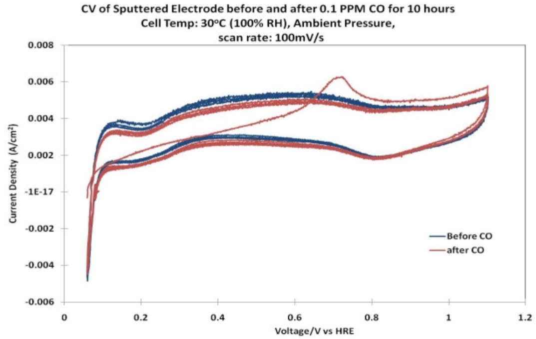




- Sensitivity improved by utilizing low surface area platinum(Sputtered Electrode).

: Exposure Time and CO Concentration



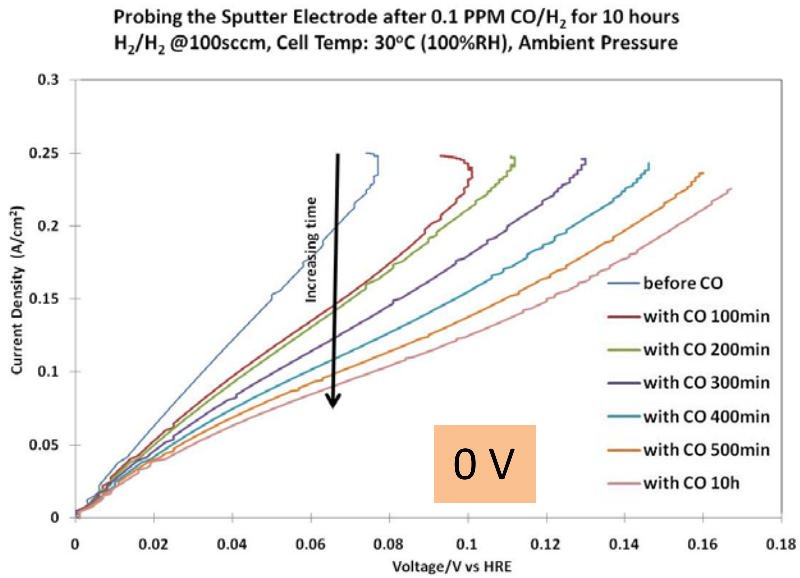


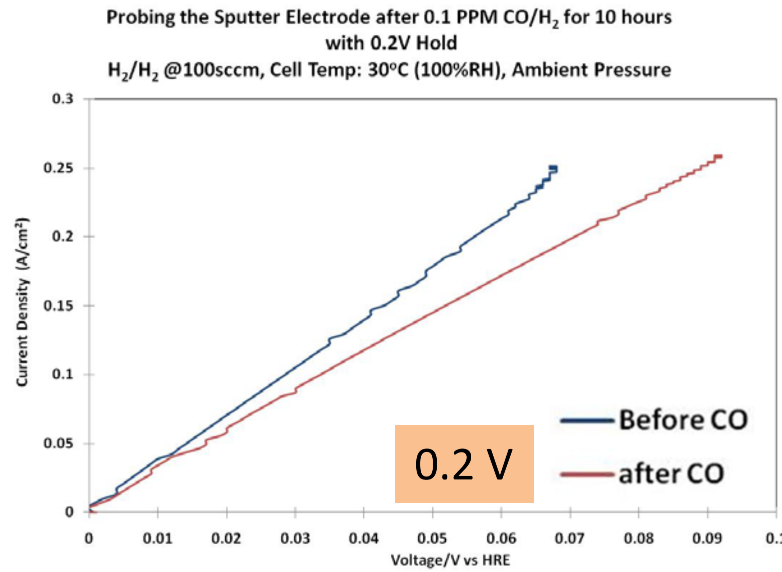
- Hydrogen pumping exp'ts show responses to different CO dosages
- Sputtered electrode more responsive as CO concentration increases.
- The current density is lower for the higher CO.
- Dosage monitoring feasible with sputtered electrode
- Cyclic voltammetry indicates CO oxidation peak. (not shown here)
- Losses become more evident as CO builds on the sputtered electrode surface over time.

Los Alamos
NATIONAL LABORATORY
EST.1943

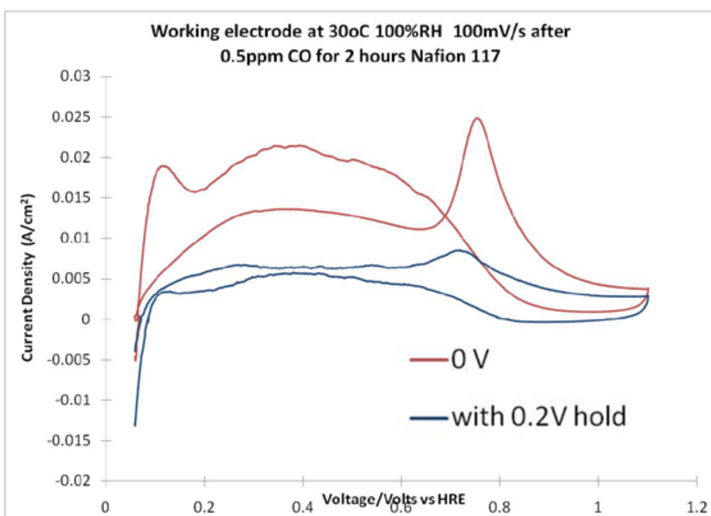
2. Impact of CO on the Sputtered Electrode : Voltage

FY13 Results





- Electrode can be cleaned with applied potential
- Dosage monitoring can be reset at a preset dosage level with a clean up step.
- Continuous monitoring of CO demonstrated



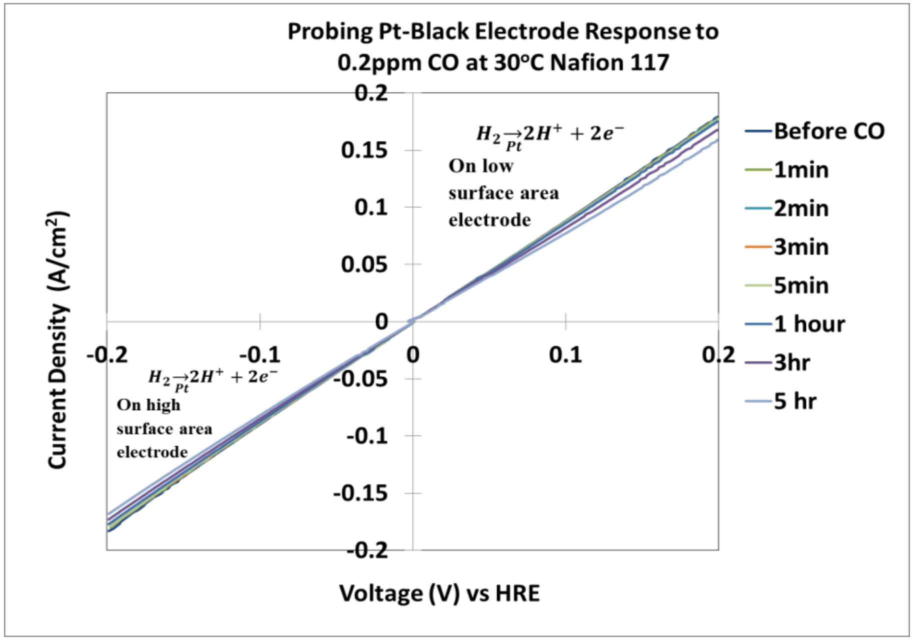
CV shows the decrease in CO coverage and thus in sensitivity when a bias voltage is applied.

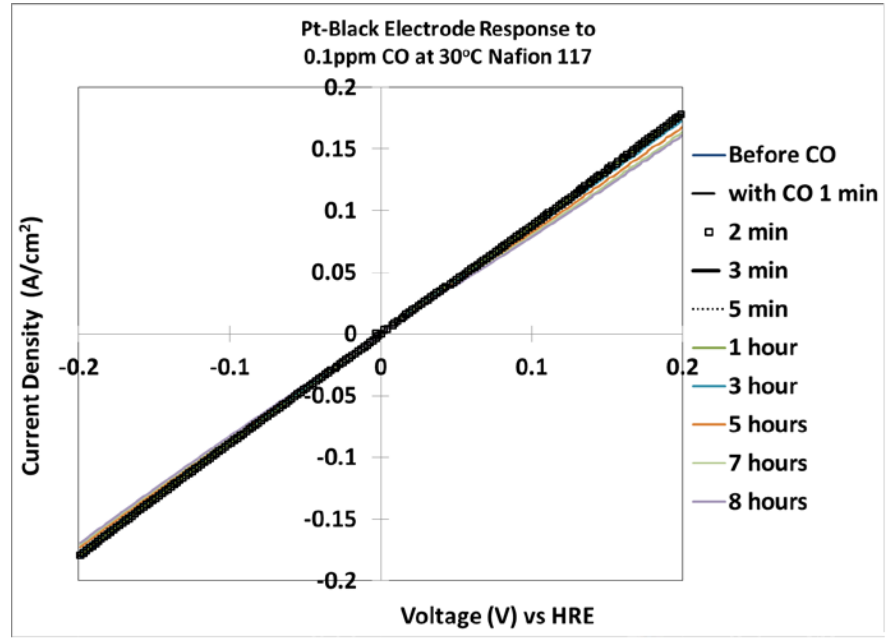
Los Alamos NATIONAL LABORATORY EST. 1943

Accomplishments:

2. Impact of CO on Pt-Black electrode: Concentration

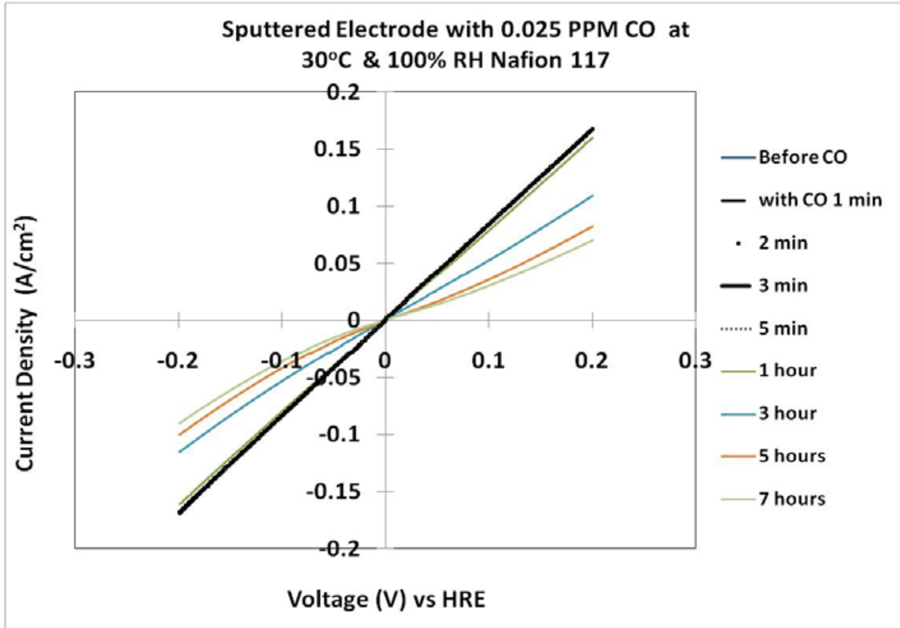
New Results

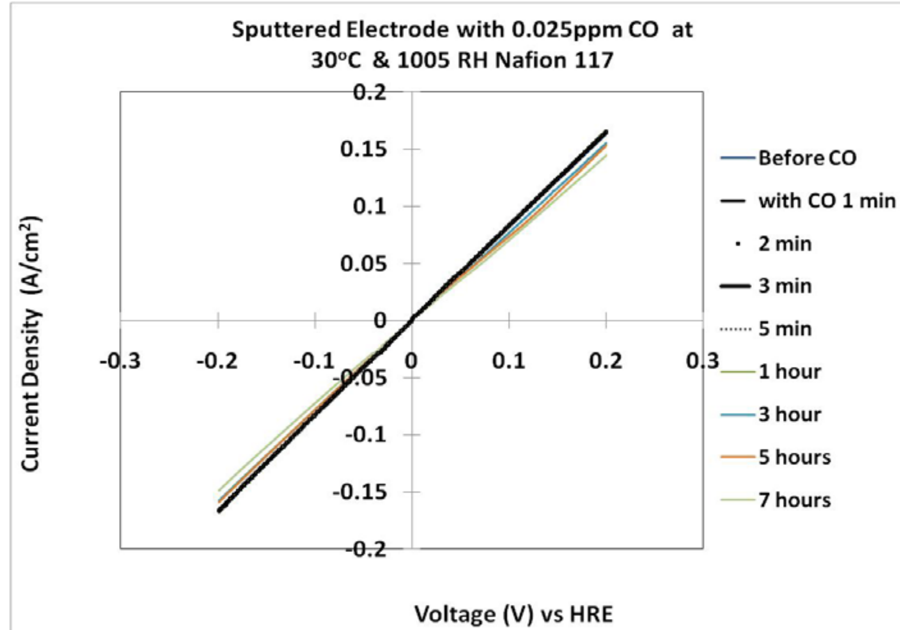




- Similar H_2 Pumping experiments were conducted on a Pt-black electrode (0.2, 0.1, 0.05, and 0.025 ppm CO)
- Responded to 200 ppb CO (1hr < t < 3 hrs)
- The Pt-black electrode responded to as little as 100 ppb CO, time < 5 hr (no response to 50 ppb CO)
- At 0.1 mg Pt/cm^2, our response threshold lies between 50 and 100 ppb CO.

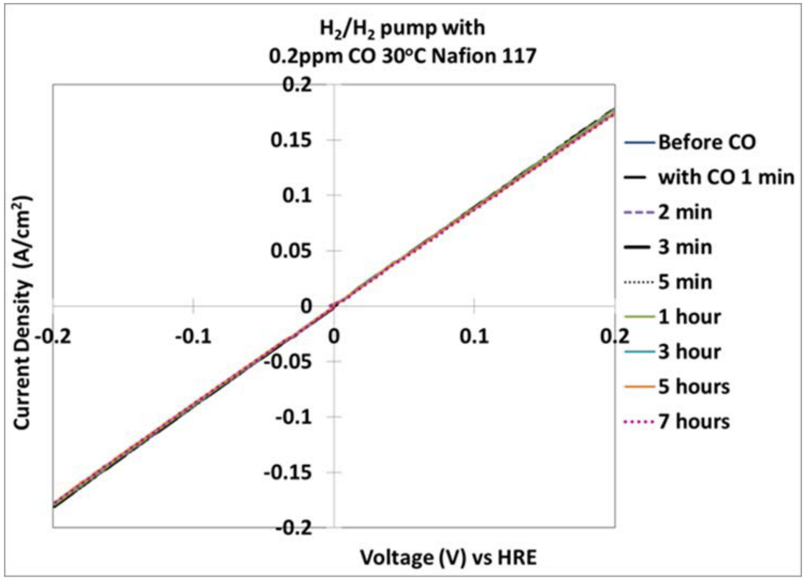
Accomplishments: 2. Impact of CO on Sputtered Electrode: Concentration New Results

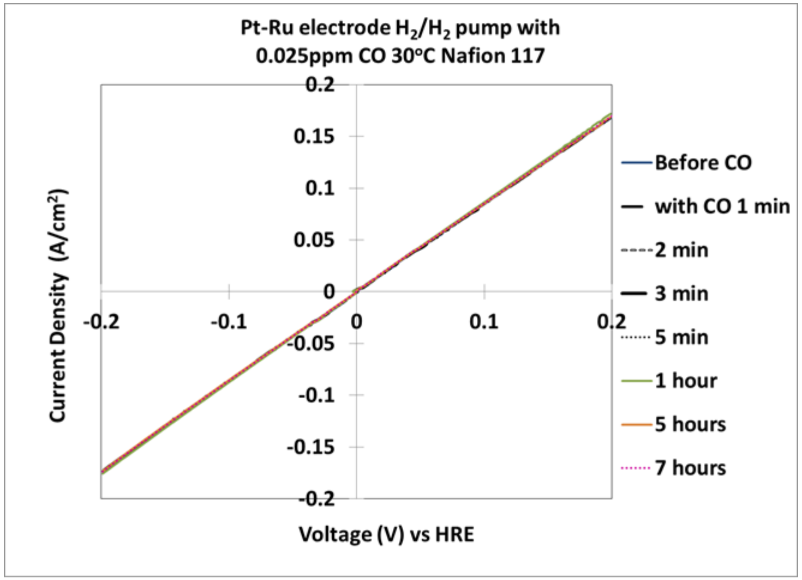




- Similar H_2 Pumping experiments were conducted on the sputtered electrode (0.2, 0.1, 0.05, and 0.025 ppm CO)
- Responded to 100 ppb CO, time < 1 hr
- Responded to as little as 25 ppb CO, time < 3 hr
- More sensitive than Pt-black (particle size larger= lower surface area)
- Response time improved from 5hrs to 1 hr at 100 ppb CO.

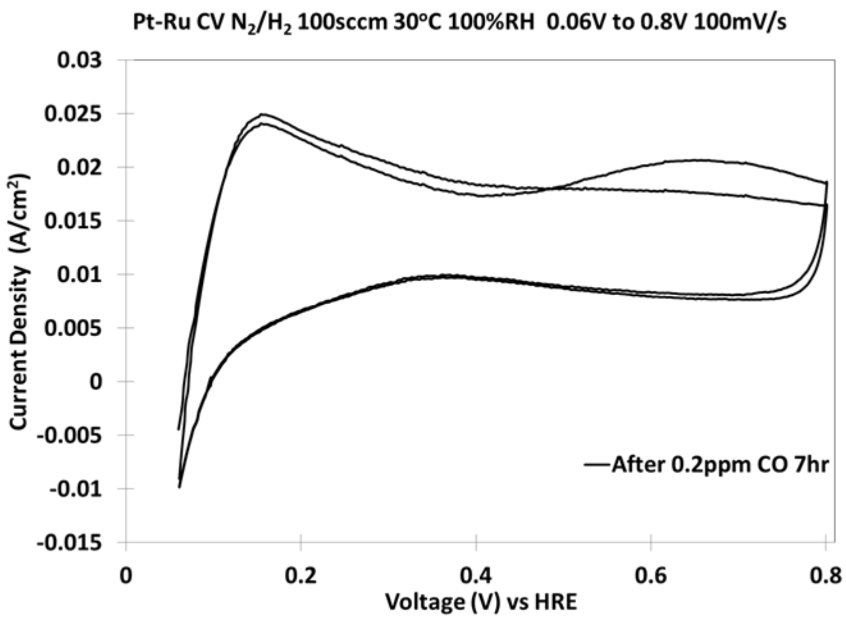
Accomplishments: 2.Impact of CO on Pt-Ru electrode: Concentration **New Results**

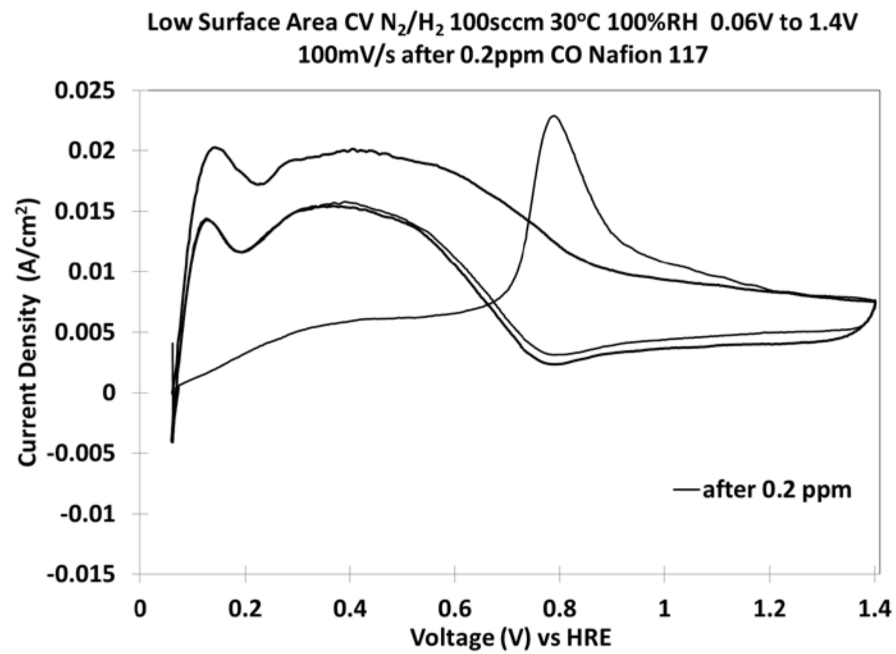


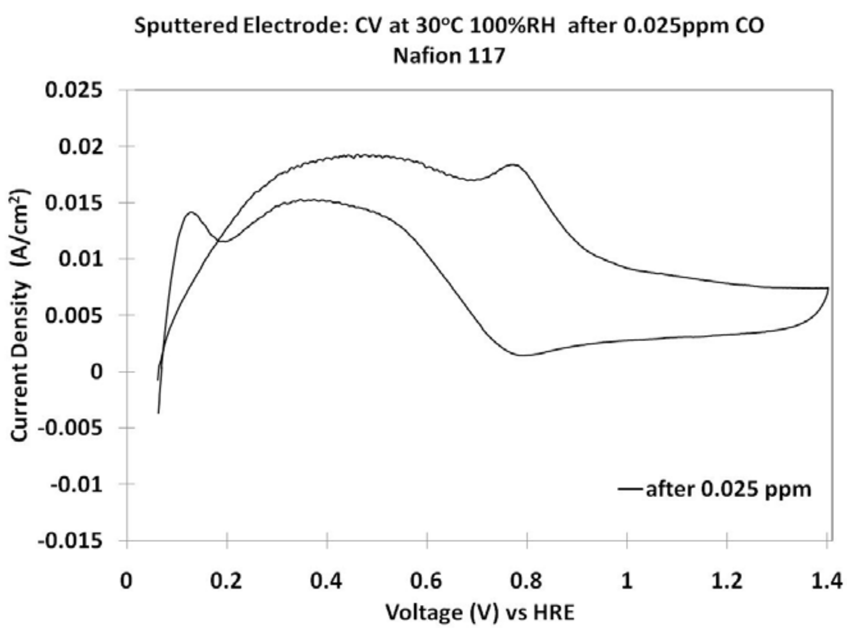


- Pt-Ru has been shown to tolerate ppm levels of CO
- Similar H_2 Pumping experiments were conducted on a Pt-Ru electrode (0.2, 0.1, 0.05, and 0.025 ppm CO)
- The Pt-Ru electrode did not respond to the sub-ppm levels of CO
- This may prove effective in analyzing multiple contaminants

2. In-Line Analyzer: CO adsorption



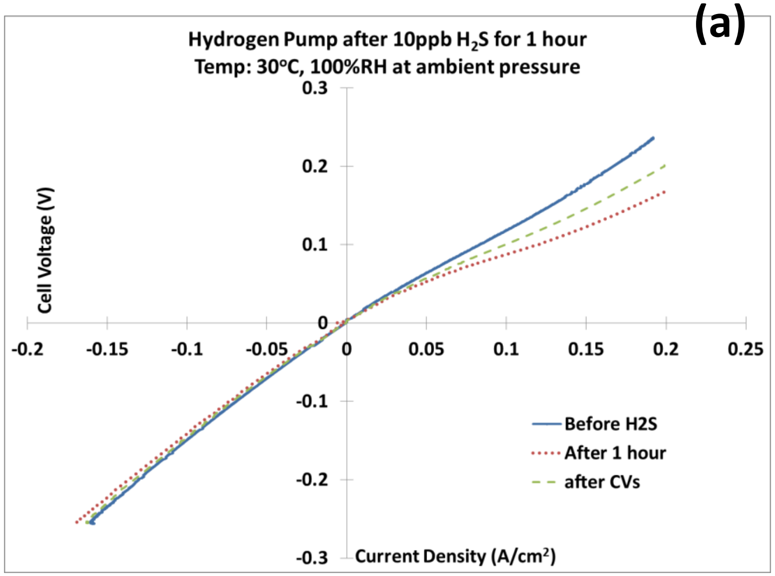




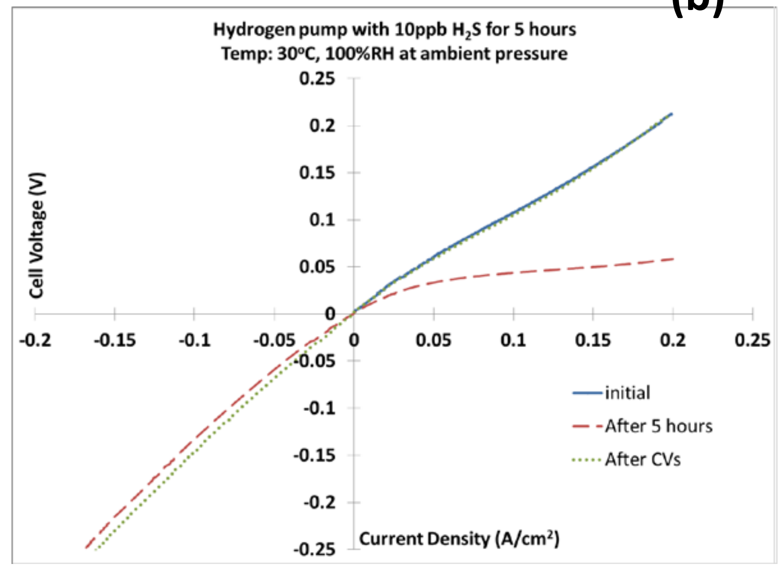
- Stripping voltammetry indicates CO oxidation peak
- CO peaks observed on Pt-Black and sputtered electrodes upon exposure but not on Pt-Ru electrode

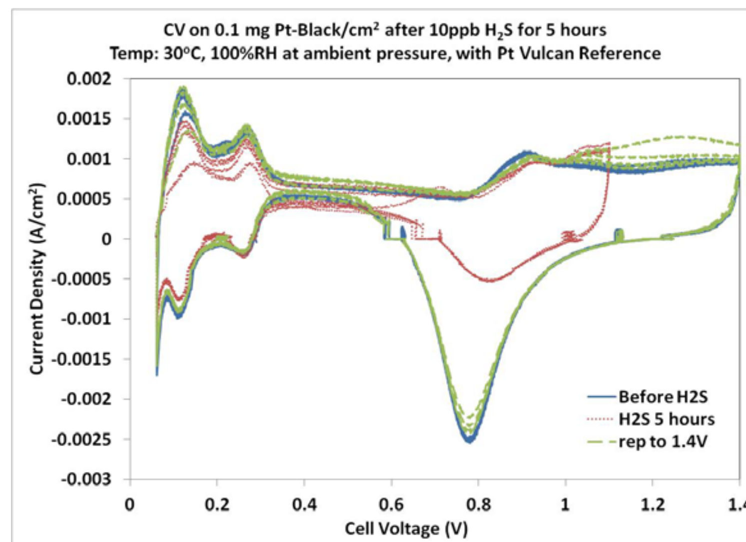
Figures (a) and (b) show the response before and after exposure to **10 ppb H_2S**; and after CVs.

(a)



(b)

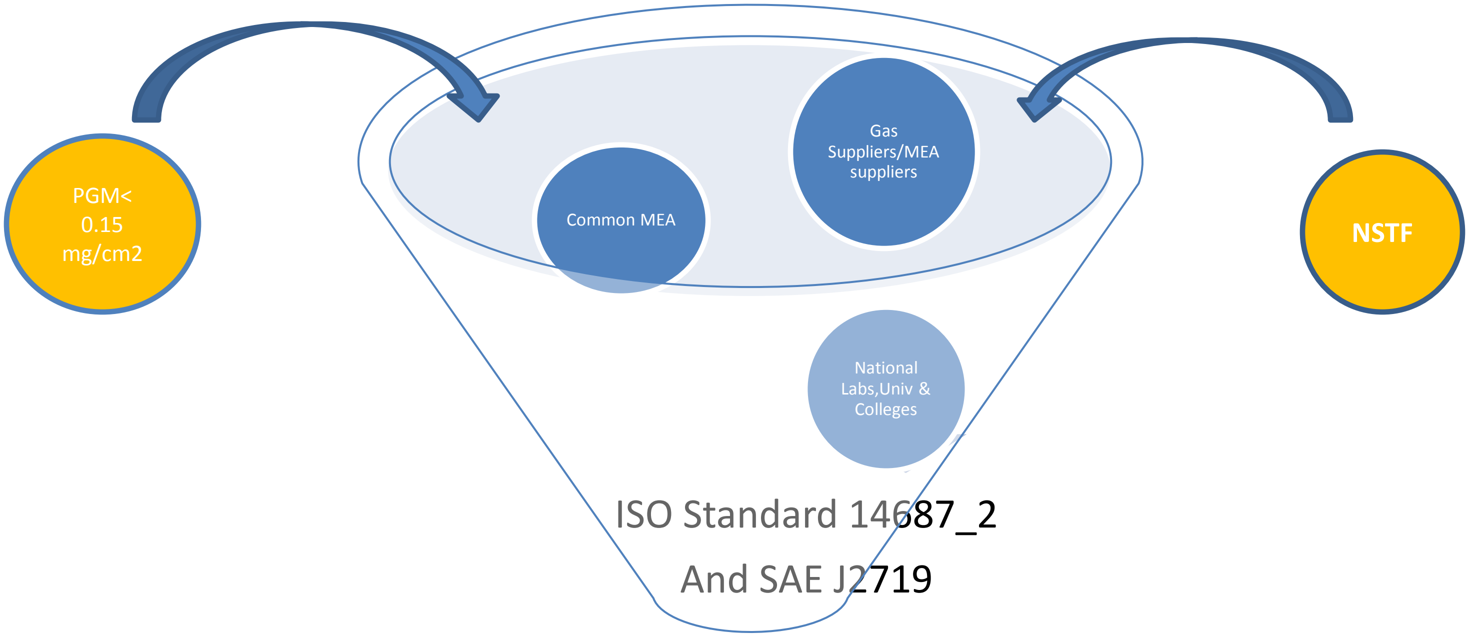




- Clear response observed after 1 hr of exposure
- Partial recovery after CVs were run up to 1.1V
- Losses were amplified as exposure time increased
- CVs show 1.1V not enough to fully clean surface;
- 1.4 V need and multiple cycles to reset analyzer

MILESTONE COMPLETED

3. Relevance (Hydrogen Fuel Quality)



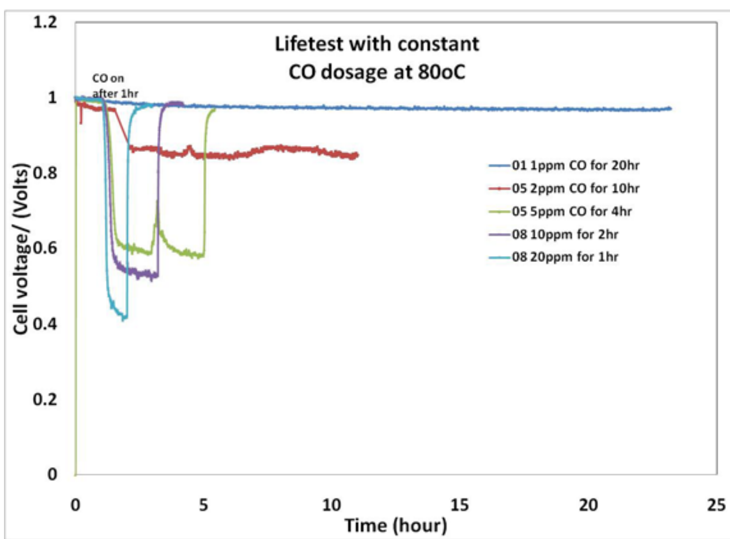
Collectively, through the efforts of WG-12 members, an ISO standard fuel standard for hydrogen fuel quality was developed. But since then, fuel cell materials have made significant Advances and the DOE PGM targets have steadily decreased. And, the performance and durability of these materials remains unclear using these ISO specs.

Approach:

3. Experimental Set-Up for Impurities

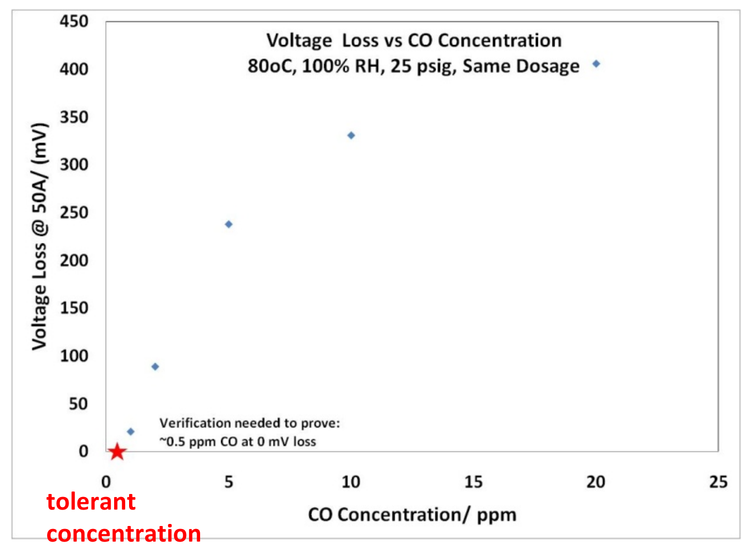
- Fuel Cell: 5 and 50 cm^2 Active Area
- Gas Diffusion Media: SGL 24 & 25 BC
- Calibrated MKS flow controllers
- Certified Impurities (Scott Specialty Gases)
- Ultra Pure H_2/Air(oiless-compressor)
- *Focus Impurity: carbon monoxide, ammonia and hydrogen sulfide*

Normalized Voltage@ 50A vs Time



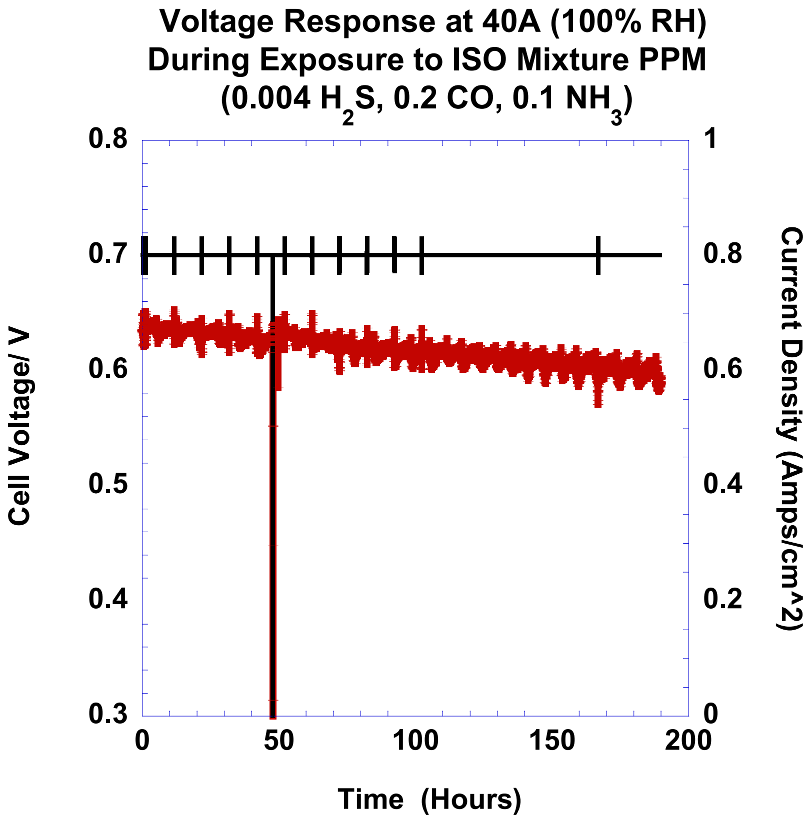
The same dosages were introduced but clearly **the rate and extent of poisoning** increases with the [CO].

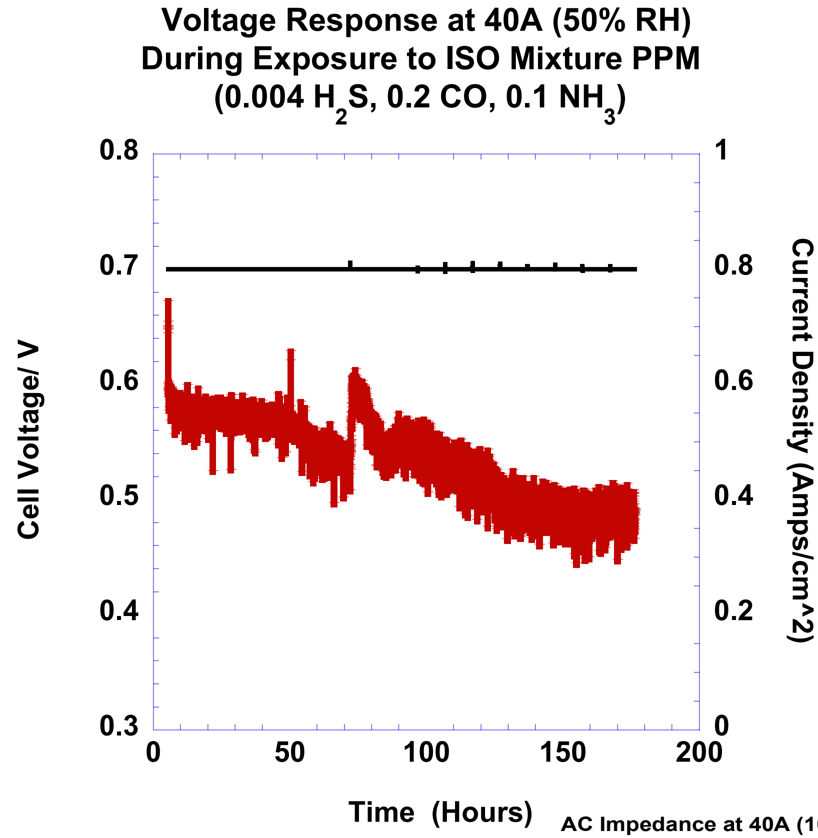
Voltage loss vs. [CO]



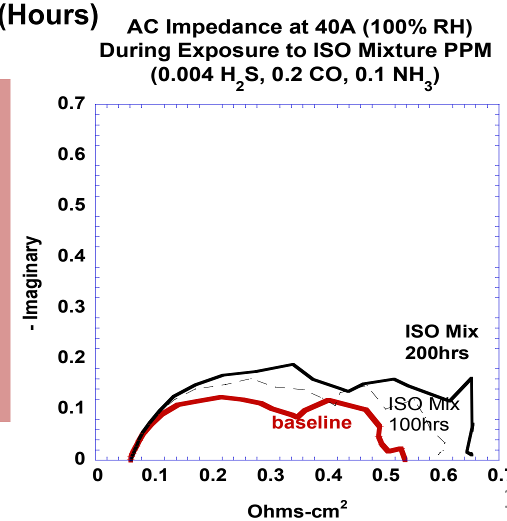
'Common MEA' **tolerates ~0.5 ppm CO** for at least **40 hrs**.
This concentration is 2.5 times the amount in the specification.

Accomplishments: Mixture(Anode: 0.03 /Cathode: 0.125 mg Pt/cm^2) **New Results**





- ~ 200h Tests with 2017 DOE Target loadings:
- Test indicates ~56mV losses at 100% RH
- Test indicates ~120mV losses at 50% RH
- Impedance at 40A was measured periodically.
- HFR did not increase, CTR and MTR increased

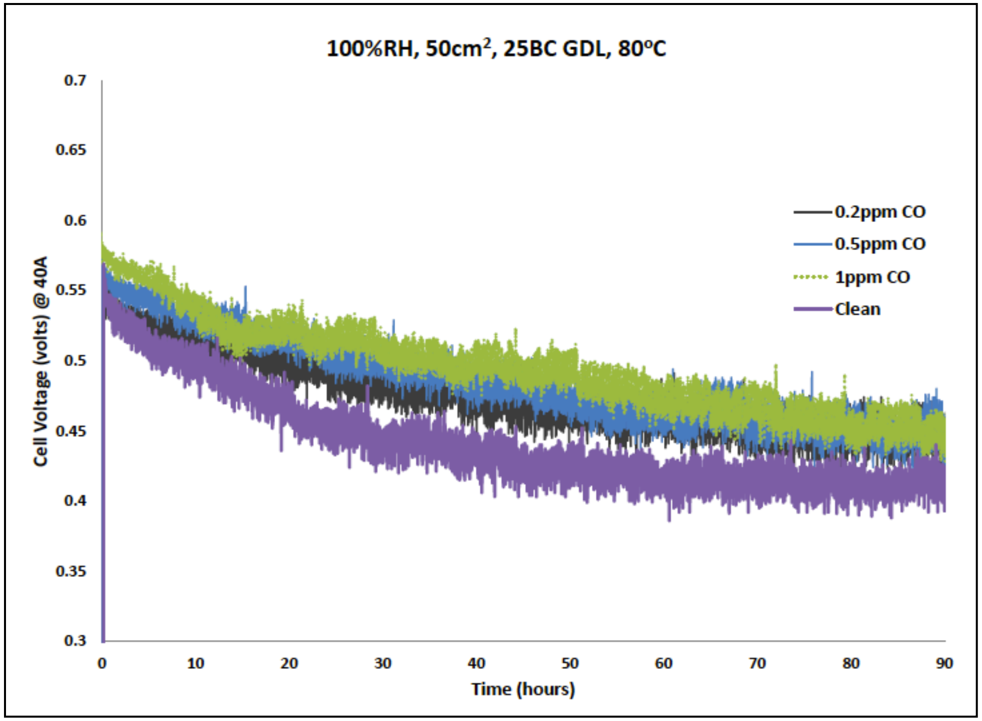


Los Alamos NATIONAL LABORATORY EST.1943

Accomplishments:

CO Tolerance: 0.03 and 0.125 mg Pt/cm²

New Results



- Three different concentrations (0.2ppm, 0.5ppm and 1ppm) of CO in H_2 were tested.
- Voltage decay was independent of the CO concentration (CO tolerance of these low loaded MEAs is > 1 ppm)
- Baseline cell did show a significant decay in voltage of 1.5mV/hour.
- The decay is under investigation and needs to be resolved in order to establish the CO tolerance limit without ambiguity.
- CVs after poisoning showed an increase in both the anode and cathode CO coverage with increasing CO concentration.
- CO present in the clean cell maybe responsible for the increased voltage decay shown in the baseline cell.
- This issue will be examined in the next quarter.

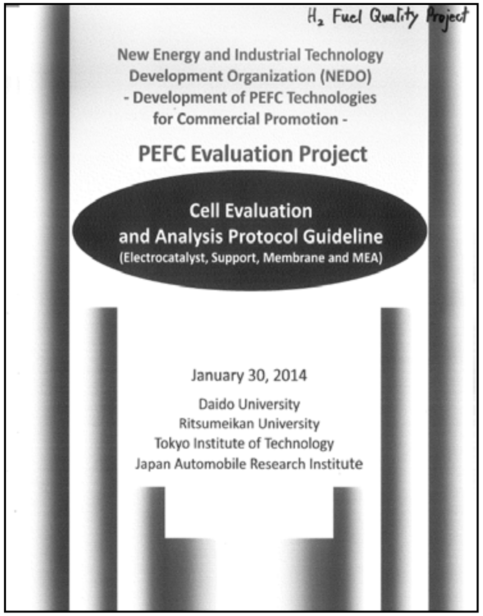
3. US DOE-LANL/JARI Collaboration Underway

Collaboration Areas:

- **CO tolerance** at lower anode loadings, in particular at **the DOE Targets: total PGM ≤ 0.15 mg Pt/cm^2**
- **Exchange of materials** (MEAs) between LANL and JARI
- LANL will send JARI the US FCTT Durability Protocol for discussion of applicability to impurity testing.
- **LANL and JARI will agree on a joint test protocol to evaluate fuel quality effects on MEAs** subjected to more realistic drive cycle testing.

JARI:

- Sent LANL MEAs
  - 0.05/0.10 mg Pt/cm^2
  - 0.30/0.30 mg Pt/cm^2
- Provided detailed testing protocols
- MEA Baseline testing
- JARI scientists scheduled to visit and perform fuel cell testing at LANL


H_2 Fuel Quality Project

New Energy and Industrial Technology Development Organization (NEDO)
- Development of PEFC Technologies for Commercial Promotion -

PEFC Evaluation Project

Cell Evaluation and Analysis Protocol Guideline
(Electrocatalyst, Support, Membrane and MEA)

January 30, 2014

Daido University
Ritsumeikan University
Tokyo Institute of Technology
Japan Automobile Research Institute

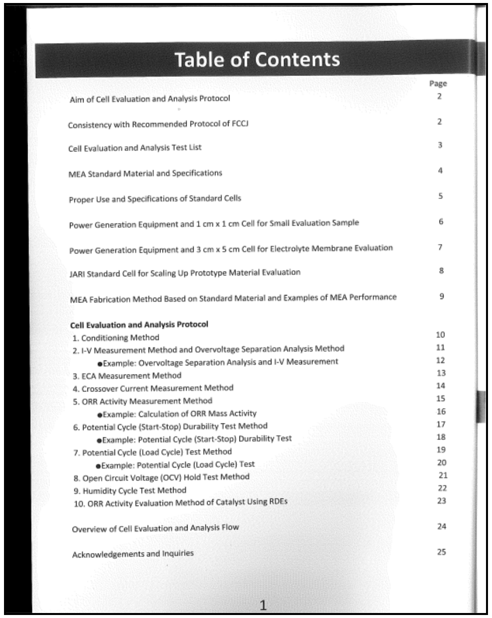


Table of Contents

1

Protocols provided by JARI

Los Alamos NATIONAL LABORATORY EST. 1943

3. US DOE-LANL/JARI Collaboration Underway

Los Alamos
NATIONAL LABORATORY
EST.1943

Protocol

MEA Conditioning:

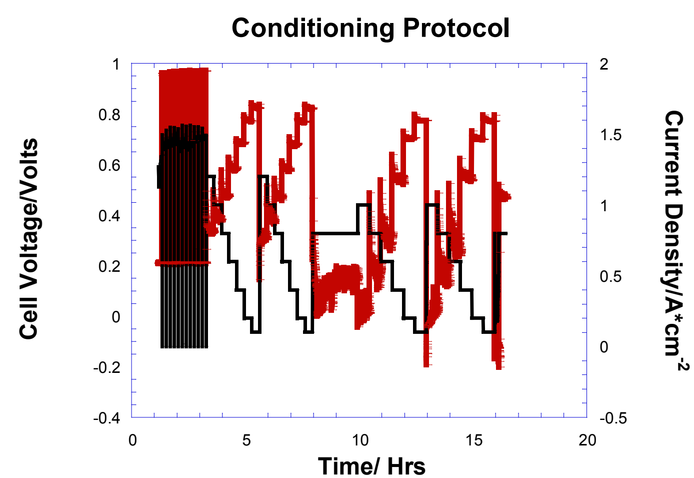
1. **Initial Start-up- Heat-up & Humidification**
2. **Pre-conditioning Cycling Step Repeat 12 times**
3. Simple VI curves
4. VI Performance Qualification

Time (min)	**Voltage** (mV)	I_d (mA/cm²)	**Temp** (◦C)	**Pressure** (kPa)	**Stoich**	
					H2	Air
As needed	0	0	65◦C	0		
10	200	gas flow 2λ@1500 mA/cm²	85	170		
0.5	1000					
20/point	---------	*	85	170		
30/point	---------	1400, *	65	0		

* VI current set points(mA): 1200, 1000, 800, 600, 400, 200, 100

LANL:

- Agreed upon testing materials
- Procured 24 MEAs identical to JARI's MEA composition
- Received test articles from JARI
- Began testing both Protocols
- Scheduled a visit to test at JARI facilities



3. US DOE-LANL/EU Collaboration

Los Alamos NATIONAL LABORATORY EST. 1943

Agenda: US-EU Collaboration on Hydrogen Fuel Quality
December 16, 2013
MPA-11 Conference Room
9:30 – 2:00 pm

I. **9: 00 - 9:30 am**
Dr. Jari's Badge Pick-up at the Otowi..Tommy Rockward, LANL

II. **9:30-9:35 am**
Welcome to LANL..Andrew Dattelbaum, Group Leader

III. **9: 35 -10: 05 am**
Fuel Cell Program Overview..Rod Borup, Program Manager

IV. **10: 05 - 10: 35 am**
Safety, Codes and Standards Overview ....Mukundan, Project Manager (PI)

V. **10: 35 – 10: 45 am**
Break

VI. **10:45 – 11: 15 am**
US Hydrogen Fuel Quality Efforts...Tommy Rockward, LANL

VII. **11:15 – 12: 00 pm**
EU Hydrogen Fuel Quality Efforts..Dr. Ihonen Jari, EU

VIII. **Lunch**

IX. **1: 15- 1:30 pm**
Lab Tour..Mukundan and Tommy

X. **1:30 – 2: 00 pm**
Discussions on Areas for Potential Collaborations..................All

Accomplished:

✓Hosted Dr Jari Ihonen, EU- HyCoRA Project
✓Detailed possible collaboration area
✓Adopted EU's fuel recirculation system for testing fuel impurities
✓Identified and Procured parts to implement recirculation system

Possible Collaboration Areas:

1. Compare results from single cell impurity testing:
   a) **HyCoRA**: VTT: **Testing with Anode Recirculation**
   b) LANL: Potential Segmented Cell testing and standard open anode testing
2. Anode loadings of Interest
   a) **US**: total: 0.15 mg Pt/cm^2
   b) **JARI** total: 0.6 mg Pt/cm^2
   c) **EU** total: 0.35-0.40 mg Pt/cm^2
3. Short term Impurity tests:
   a) Typical vehicle operation time < 8 hrs
   b) Drive cycle
   c) Start/Stop FC operation
4. Test fresh and aged (ASTs) MEAs
5. **Low cost hydrogen quality monitors for**
   a) On-board
   b) At fuelling station
6. Novel materials (e.g. Pt-Pd anodes, NSTF)
7. **Exchange of Materials/Protocols**
   a) **Agree on common test protocol(s)**
   b) **Baseline Tests**
8. Gas Analysis/ Mass Balance

Summary

1. Contributions to ASTM
   - Sub-committee Chair D03.14
   - Multiple standards developed and/or under development
   - ILS 775 underway
2. In-line Fuel Quality Analyzer
   - In-line analyzer studies with various platinum electrodes
   - Response to H_2S shown.
3. Impurity testing expanded to state of the art MEAs
   - CO tolerance of low loaded MEAs measured
   - ISO Mixture test at different RHs
4. US DOE/JARI Meeting on Fuel Quality and Durability
   - Established collaboration
   - Identified common research areas
   - Materials exchange (MEAs and Protocols).
   - Tests underway

Future Work

- Continue providing leadership to ASTM efforts…
  - Chairing ASTM Bi-Annual Meetings
  - Set-up Symposium on Hydrogen Storage System Cleanliness
- Construct an Electrochemical Analyzer based on the proof of concept demonstrated for the CO and H_2S dosage monitor
  - Test response of analyzer using 4 ppb H_2S
  - Tailor electrode to respond in minutes (≈3 mins) for re-fueling and hours (< 8 hours) for on-board applications
- Expand inline analyzer proof of concept to include NH_3
- Incorporate a fuel recirculation system for impurity testing
- Determine CO and H_2S tolerance limits of NSTF MEA
- Expand efforts with the DOE-LANL/JARI/EU collaboration
  - Complete baseline tests of MEAs
  - Report on results before contamination testing begins

Los Alamos
NATIONAL LABORATORY
EST. 1943

Reviewer's Excerpts

- …project plan for **moving ASTM standards through ILS…**? …train laboratories and share your expertise…didn't see any **collaboration with laboratories** conducting hydrogen quality sampling in the real world: Atlanta Analytical, **Smart Chemistry**… ***ASTM's ILS 775 is on-going with Smart Chemistry, Air Liquide,*** **Advanced Biofuels, *and Shimadzu***
- The **emerging relationship with JARI** is very encouraging. As I mentioned above, I would like to see this activity **also team with those other international entities who are working on (or will be working on fuel quality issues on stacks)**… The lack of feedback to the SAE J2719 team… ***Collaboration with JARI began and established with the European Union. Discussions with SAE leadership regarding the significance of LANL's efforts as it pertains to hydrogen quality.***
- Add the development of a commercial in-line gas analyzer to the project scope to help target both the round robin test method validation and the in-line gas analyzer efforts toward a S.M.A.R.T. project goal. Investigate the cost effectiveness of the in-line analyzer. It needs to be on track for a low cost, effective device. An industrial partner to accelerate the commercialization of the in-line analyzer needs to be found. ***The in-line gas analyzer work has increasingly become a larger component of this project.The in-line analyzer is not ready for commercialization.***

Acknowledgements

LANL gratefully acknowledges the Fuel Cell and Vehicle Technologies Program/Safety, Codes & Standards *Technology Development Manager:* **Will James**

ISO TC197 Working Group 12 Members

SAE Leadership

ASTM staff manager: Carolyn Booker and Alyson Fick

& Thank You- the AUDIENCE.

Los Alamos
NATIONAL LABORATORY
EST.1943