Project ID:
SCS007

Hydrogen Fuel Quality

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Los Alamos National Laboratory

2013 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

May 14, 2013
Arlington,VA

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Overview

Timeline

- Project start date: 10/1/06
- Project end date: TBD
- Percent complete: 80 %

Barriers

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

Budget

- Total project funding: $2,425K
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY12: $475K
- Expected Funding for FY13: $475K

Partners/Collaborators

- WG -12 Members
- Japanese Automotive Research Institute
- ASTM
- Air Liquide
- CAFP
- CONSCI

OUTLINE

- **Relevance**: Background and Milestone
- **Approach** and **Technical Accomplishments:**
  1. Contributions to ASTM
     - ❖ Sub-committee Chair D03.14
     - ❖ Hydrogen and Fuel Cells Update
  2. In-line Fuel Quality Analyzer
     - ❖ Rationale
     - ❖ Approach
     - ❖ Preliminary Results
  3. a). Testing Results/Findings: (H_2S and CO)
     - ❖ Common MEA vs DOE Target Loadings

     b). US DOE/JARI Meeting on Fuel Quality and Durability
     - ❖ Highlights
     - ❖ Concerns and Potential Collaborations
- **Future Work**

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Objective:

- **To carry out the duties of ASTM sub-committee chair for D03.14 gaseous hydrogen fuel efforts.**
- **To help determine levels of impurity constituents for the development of an international standard for hydrogen fuel quality (ISO TC197 WG12).**
- **To demonstrate proof-of-concept of an electrochemical analyzer to detect low levels of impurities in hydrogen fuel.**

Milestone Accomplished:

The North America Team with OEM, Hydrogen Suppliers and International collaborators help to develop an international standard for hydrogen fuel quality (ISO14687/ TC197/WG12)

ISO 14687-2, *Hydrogen Fuel – Product Specification, Part 2: PEM fuel cell applications for road vehicles*

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1. ASTM D03.14 Hydrogen and Fuel Cells Update

Work Item	Title	Constituents (DL)	Update
Published	Standard Test Method for Determination of Trace Carbon Dioxide, Argon, Nitrogen, Oxygen and Water in Hydrogen Fuel by Jet Pulse Injection and Gas Chromatography/Mass Spectrometer Analysis	CO2 (0.5 ppm), nitrogen (5 ppm), argon (1 ppm), oxygen (2 ppm), and water (1 ppm)	*Published official item: D7649-10* Awaiting test samples
Published	Standard Practice for Sampling of High Pressure Hydrogen and Related Fuel Cell Feed Gases	Gaseous sampling	*Published official item: D7606-11*
Published	Standard Test Method for Determination of Ammonium, Alkali and Alkaline Earth Metals in Hydrogen and Other Cell Feed Gases by Ion Chromatography	Formic Acid (low ppb to ppm)	*Published official item: D7550-09*
Published	Standard Test Method for Sampling of Particulate Matter in High Pressure Hydrogen used as a Gaseous Fuel with an In Stream Filter	Particulate sampling	*Published official item: D7650-10* Addressed
Published	Standard Test Method for Determination of Trace Gaseous Contaminants in Hydrogen Fuel by Fourier Transform Infrared (FTIR) Spectroscopy	Ammonia,CO2, CO, formaldehyde, formic acid, and water (defined by EPA 40 CFR part 136 Appendix A "meet detection limits of SAE TIR J2719")	*Published official item: D7653-10* ILS complete, collecting data on going
21162	Standard Test Method for the Characterization of Particles from Hydrogen Fuel Streams by Scanning Electron Microscope	Particulates	N/A
Published	Standard Test Method for Visualizing Particulate Sizes and Morphology of Particles Contained in Hydrogen Fuel by Microscopy	Particulates	*Published official item: D7634-10*
Published	Standard Test Method for Gravimetric Measurement of Particulate Concentration of Hydrogen Fuel	Particulates	*Published official item: D7651-10*
Published	Standard Test Method for Test Method for the Determination of Total Hydrocarbons in Hydrogen by FID Based Total Hydrocarbon (THC) Analyzer	Total hydrocarbons (0.1 ppm)	*Published official item: D7675-11* Editorial changes
23815	Determination of Total Halocarbons contained in Hydrogen and other gaseous fuels	Total halogenated compounds ("halocarbon determination requirements contained in SAE J2719" 0.1 ppb)	Editorial changes address, negatives need resolution(D.Bartel)
Published	Standard Test Method for Determination of Trace Hydrogen Sulfide, Carbonyl Sulfide, Methyl Mercaptan, Carbon Disulfide and Total Sulfur in Hydrogen Fuel by Gas Chromatography and Sulfur Chemiluminescence Detection	Total sulfur (0.02 ppb)	*Published official item: D7652-11*
34574	Standard Test Method for Determination of Trace Hydrogen Bromide, Hydrogen Chloride, Chlorine and organic halides in Hydrogen Fuel by Gas Chromatography with Electrolytic Conductivity Detector and Mass Spectrometer	Trace Hydrogen Bromide, Hydrogen Chloride, Chlorine and organic halides	Ballot closed Dec 12, New Standard

ASTM sub-committee chair: D03.14

Scope: 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.

Ref: http://www.astm.org/COMMIT/D03SUBSCOPES.pdf

2. Approach: Inline Fuel Quality Analyzer

Rationale

- 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.
- Studies have shown that ***minimal amounts (as low as parts per billion) of impurities*** such as **CO, NH_3 and H_2S** are ***detrimental to performance and durability*** of PEM fuel cells.
- There is a need for an **inline *hydrogen analyzer to continously monitor*** these impurities and alert the user to any fuel quality issues.
- Our focus is to ***optimize electrode materials/configuration*** for a dispersed platinum-type membrane electrode assembly (MEA) to be employed ***as a stripping voltammetry analyzer.***
- 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.

2. Approach: Inline Fuel Quality Analyzer

Materials Selection/Testing

- Material Selectivity/Sample Preparation:
  - Low surface area, resistant to voltage cycling and sensitive to contaminants
  - Testing with sputtered 0.1 Pt/cm^2 on ELAT pressed onto Nafion® 212 with 0.2 Pt/cm^2 electrode
  - Repeat with N117
- Various tests:
  - H_2/H_2 Experiments 0~0.1V
    - 5cm^2, 30^oC and 60^oC, 0 psig, 100% RH
  - Sensitivity Test: Utilize external power supply (VI) with and with out varied CO concentrations
  - Probing the surface: H_2/N_2 CV 0-1.1 or 1.4 before and after CO
  - Durability Results: 3000 CV cycles on sputtered side 0.06-1.4V

2. Sample Preparation

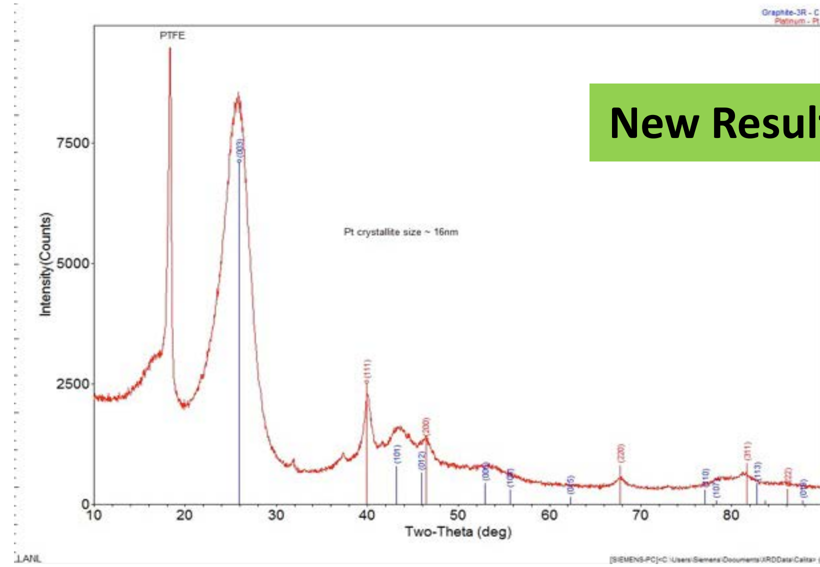
Principle:

- Membrane electrode assembly (MEA) similar to a fuel cell. Operating as an electrochemical hydrogen pump.

The Approach:

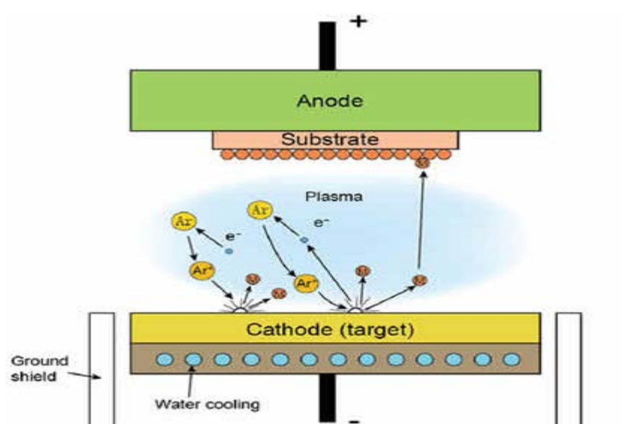
- Sputtered electrode provides stable Pt particle sizes and the low loadings desired in an analyzer.

New Results



XRD pattern of carbon cloth with sputtered Pt verifies carbon, PTFE and Pt at ~ 16nm

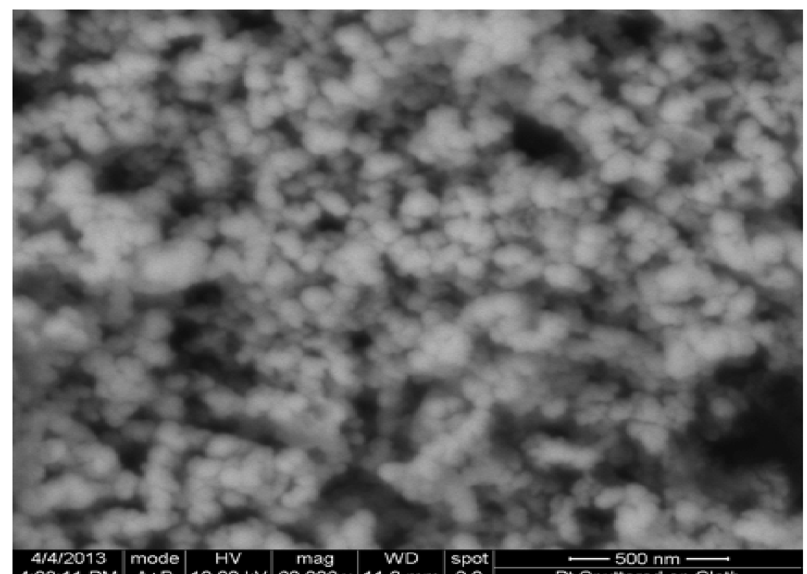
Example of Sputtering System



In a DC diode sputtering system, Argon is ionized by a strong potential difference, and these ions are accelerated to a target. After impact, target atoms are released and travel to the substrate, where they form layers of atoms in the thin-film

www.directvacuum.com/sputter.asp

SEM images after sputter onto gas diffusion media



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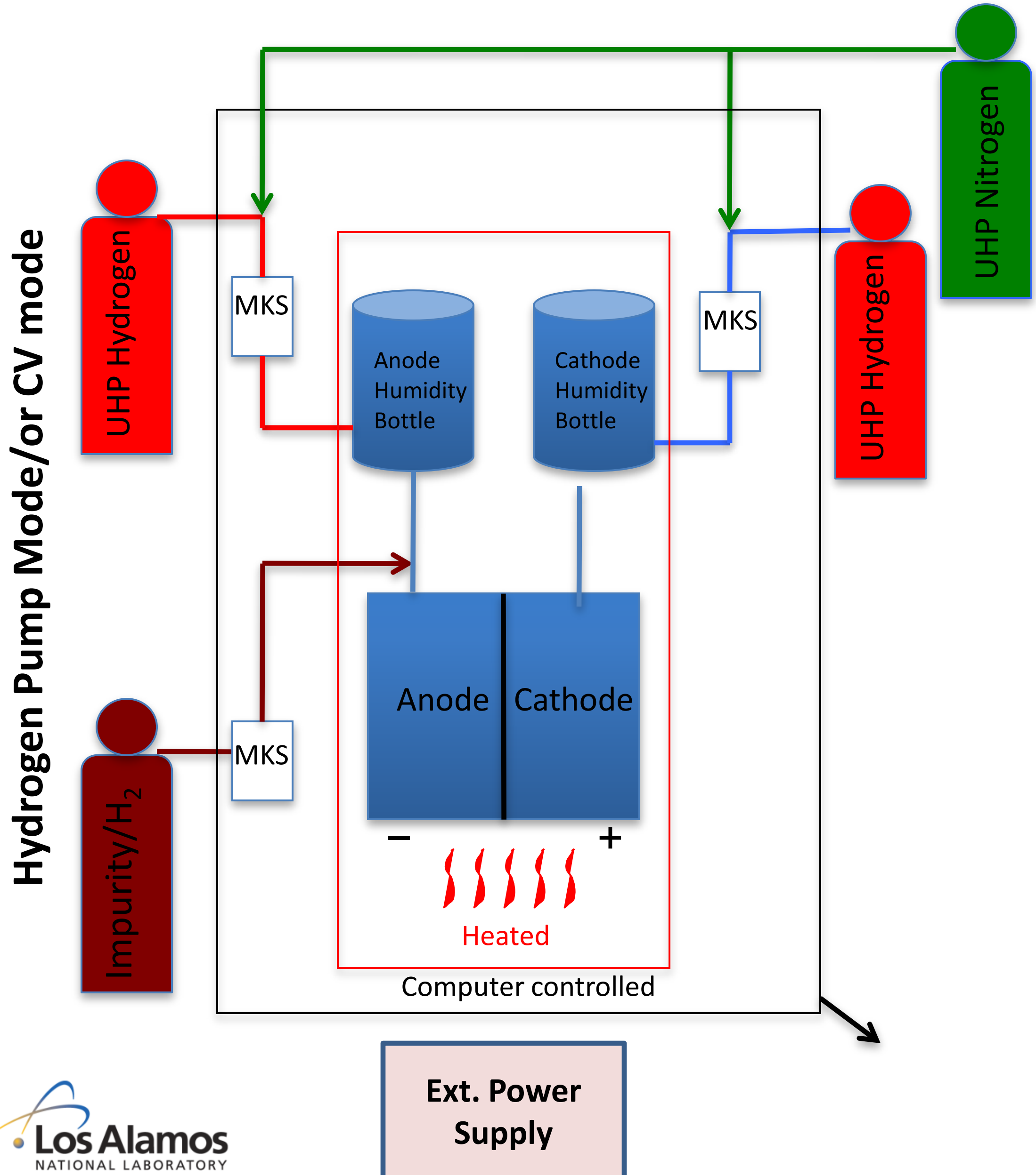
2. Experimental Set-Up



- Fuel Cell: 5 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*
- *Future : H_2S, NH_3*

Pump Mode: H_2/H_2
Cyclic Voltammetry: H_2/N_2
Durability-VIR Curves

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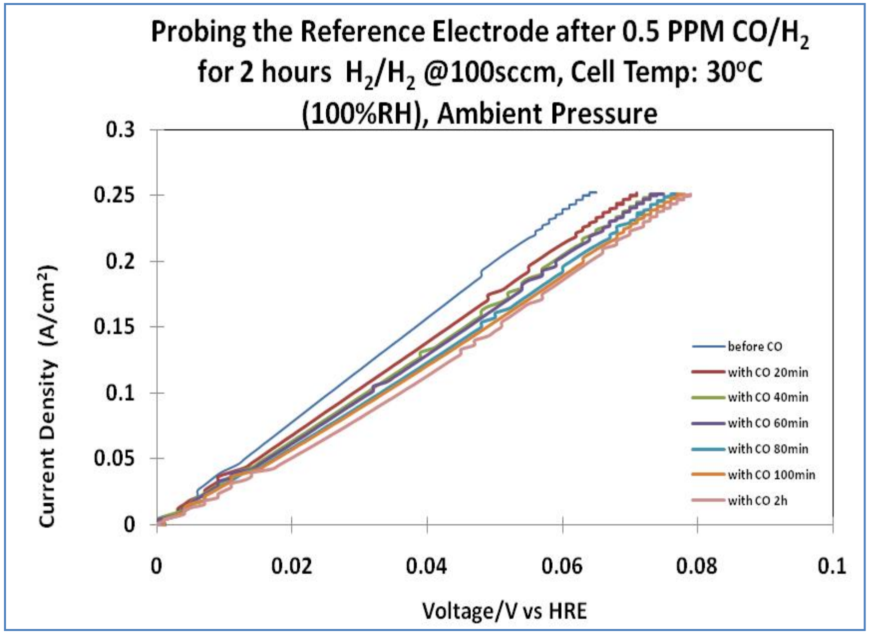
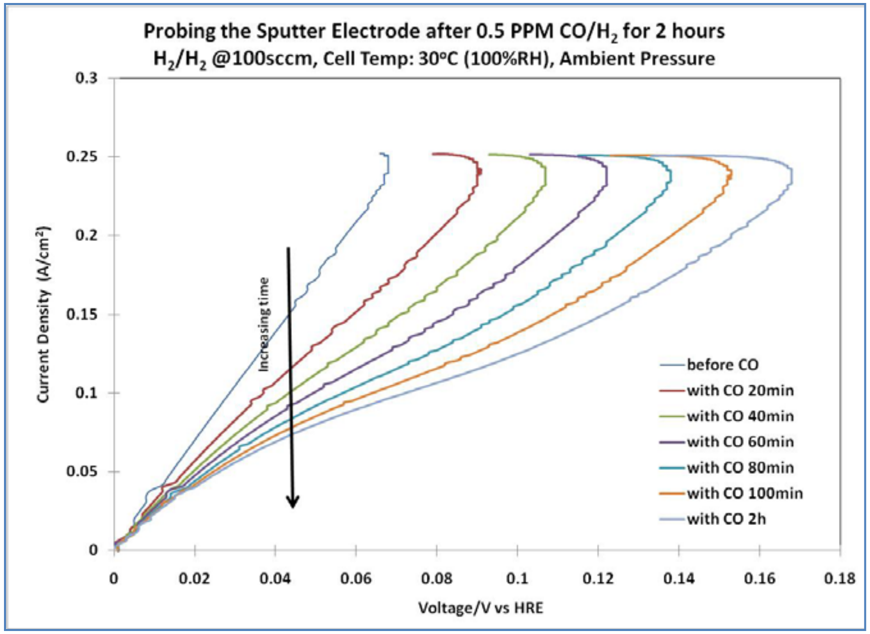
Results

2. Comparison between Reference Electrode vs Sputtered: Sensitivity

New Results





- Sensitivity improved by utilizing low surface area platinum.

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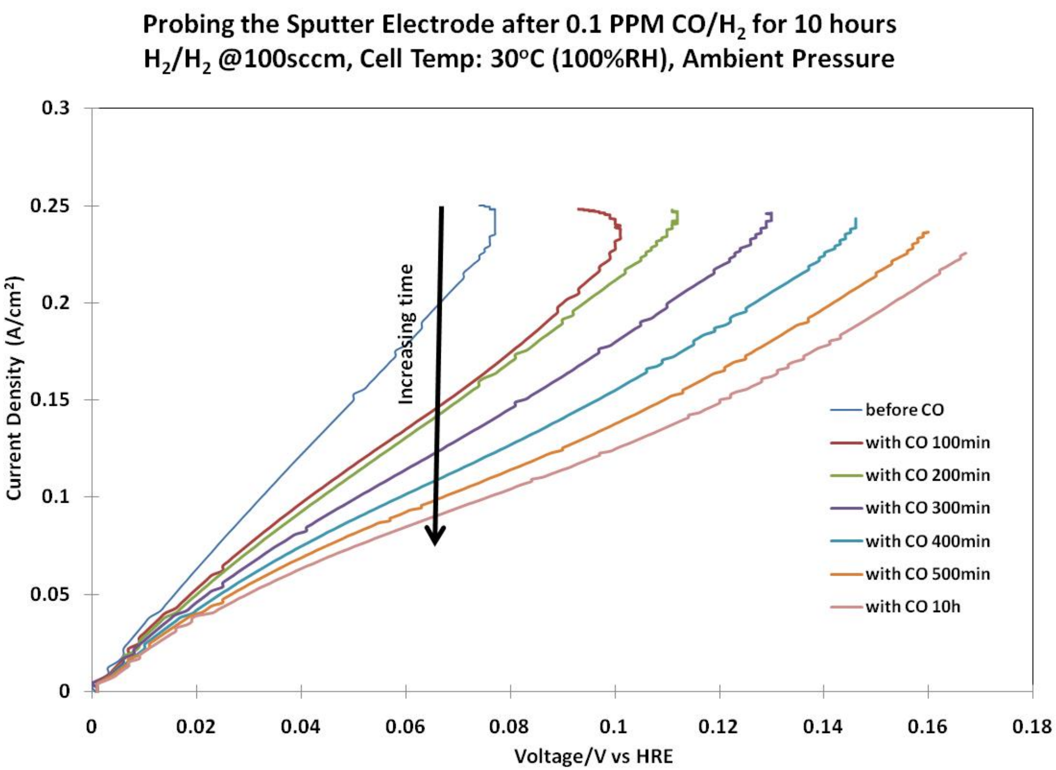
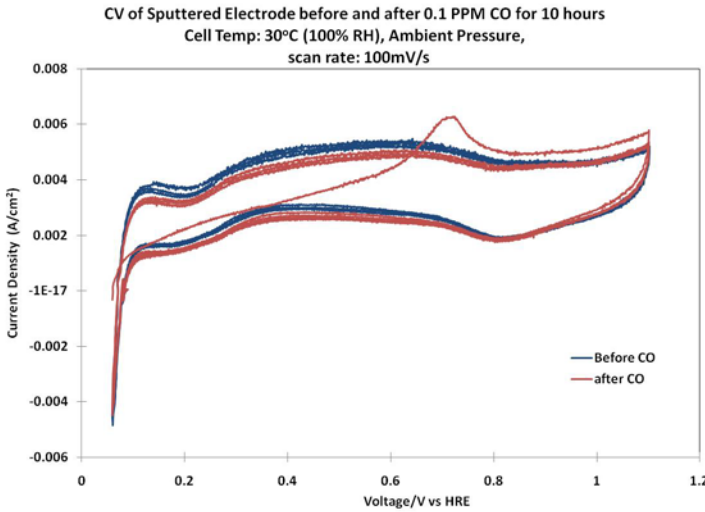
2. Impact of CO on the Sputtered Electrode : Time

New Results

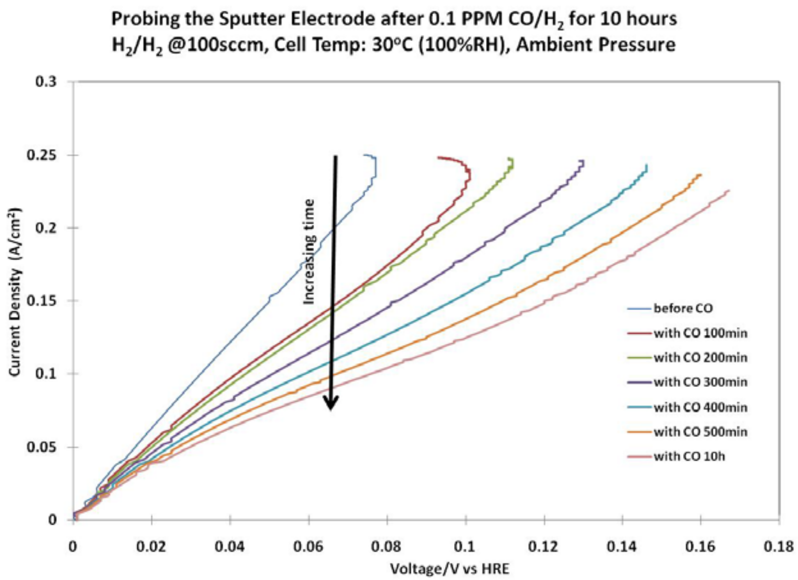


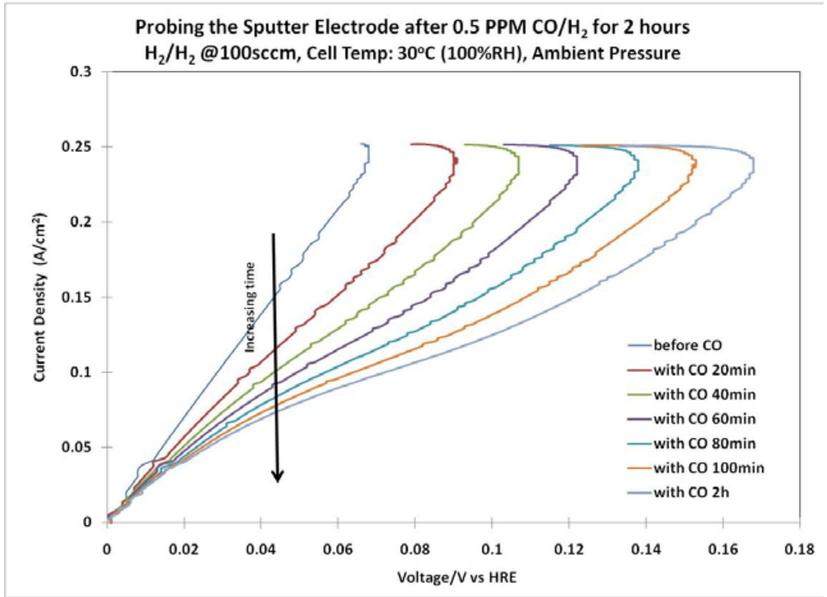


- Hydrogen pumping experiments show responses to different CO dosages
- Cyclic voltammetry indicates CO oxidation peak.
- Losses become more evident as CO builds on the sputtered electrode surface over time.

2. Impact of CO on the Sputtered Electrode : Concentration

New Results



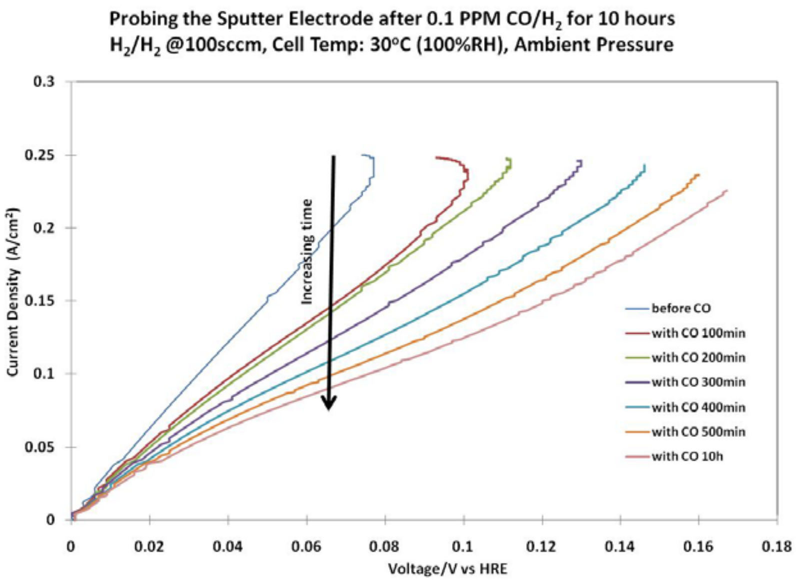


- The sputtered electrode becomes more responsive as the CO concentration increases.
- The current density is lower for the higher CO (i.e. 0.5 ppm CO).

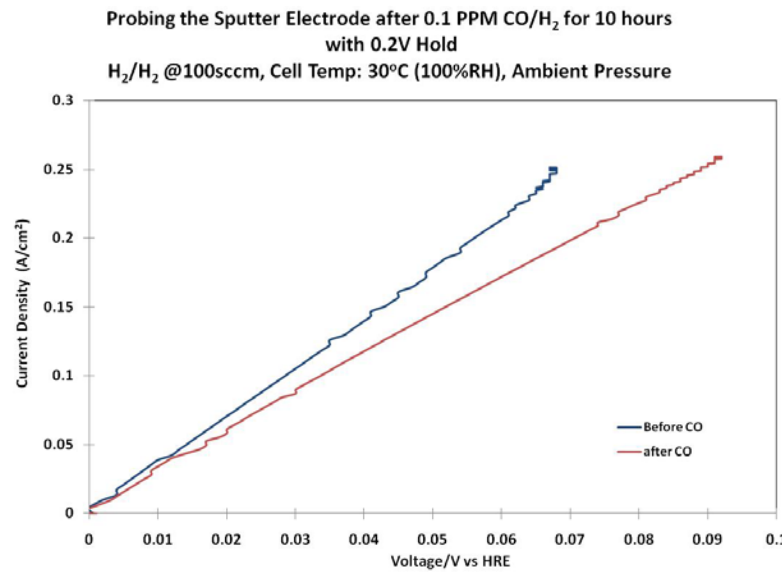
- Dosage monitoring feasible with sputtered electrode

2. Impact of CO on the Sputtered Electrode : Voltage

New Results



0 V



0.2 V

- 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

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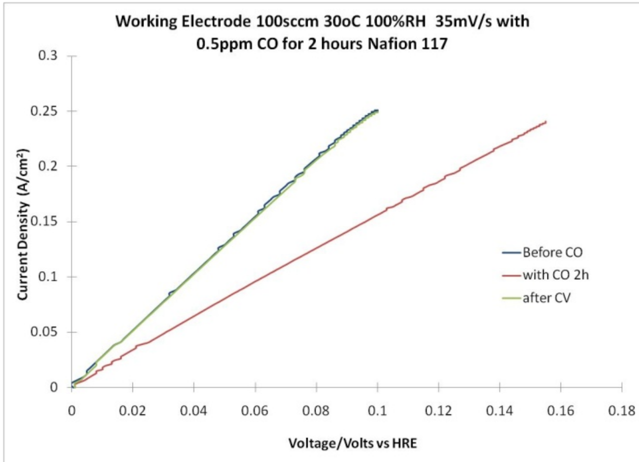
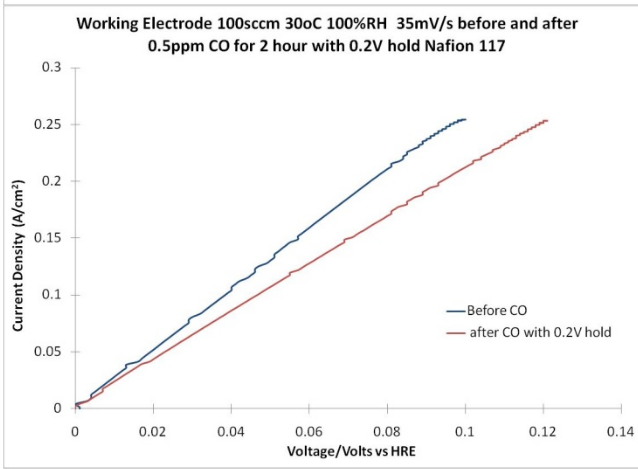
2. Effect of membrane thickness: N117

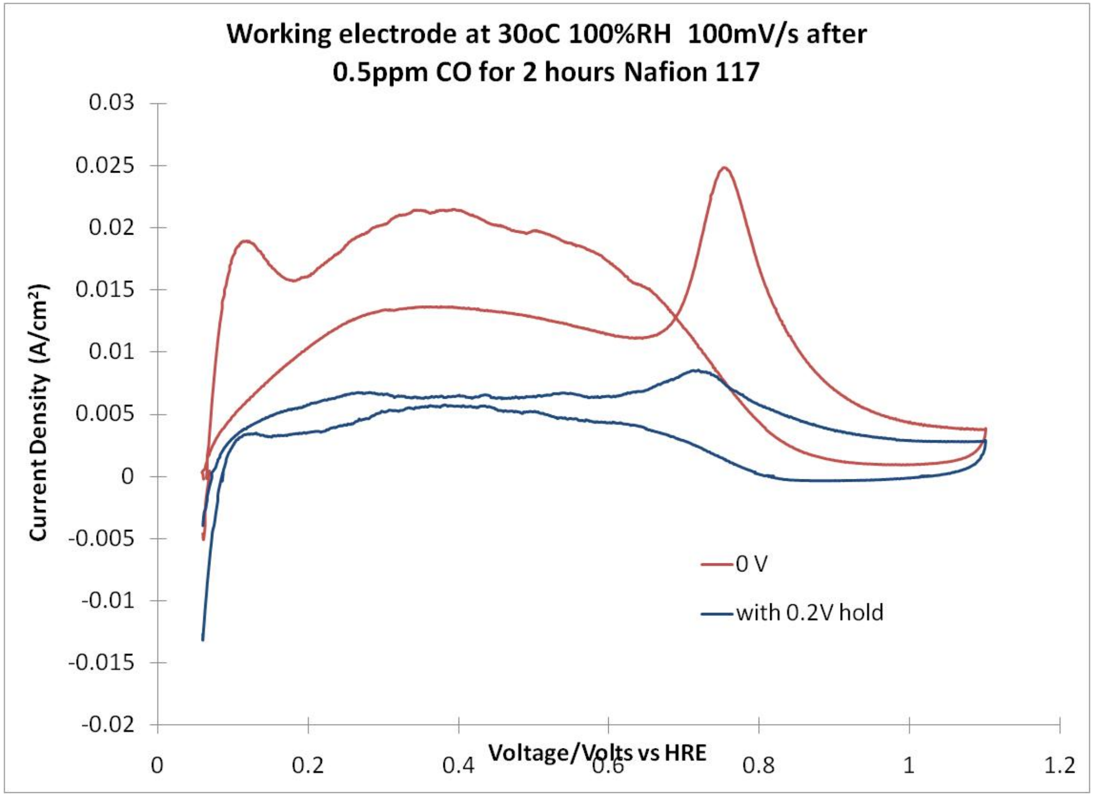
New Results

0 V



0.2 V





- Similar trends were observed for N117 as previously shown for N212.
- CV shows the decrease in CO coverage and thus in sensitivity when a bias voltage is applied.
- Improved durability with little loss in performance
- Potential for improved NH_3 sensitivity

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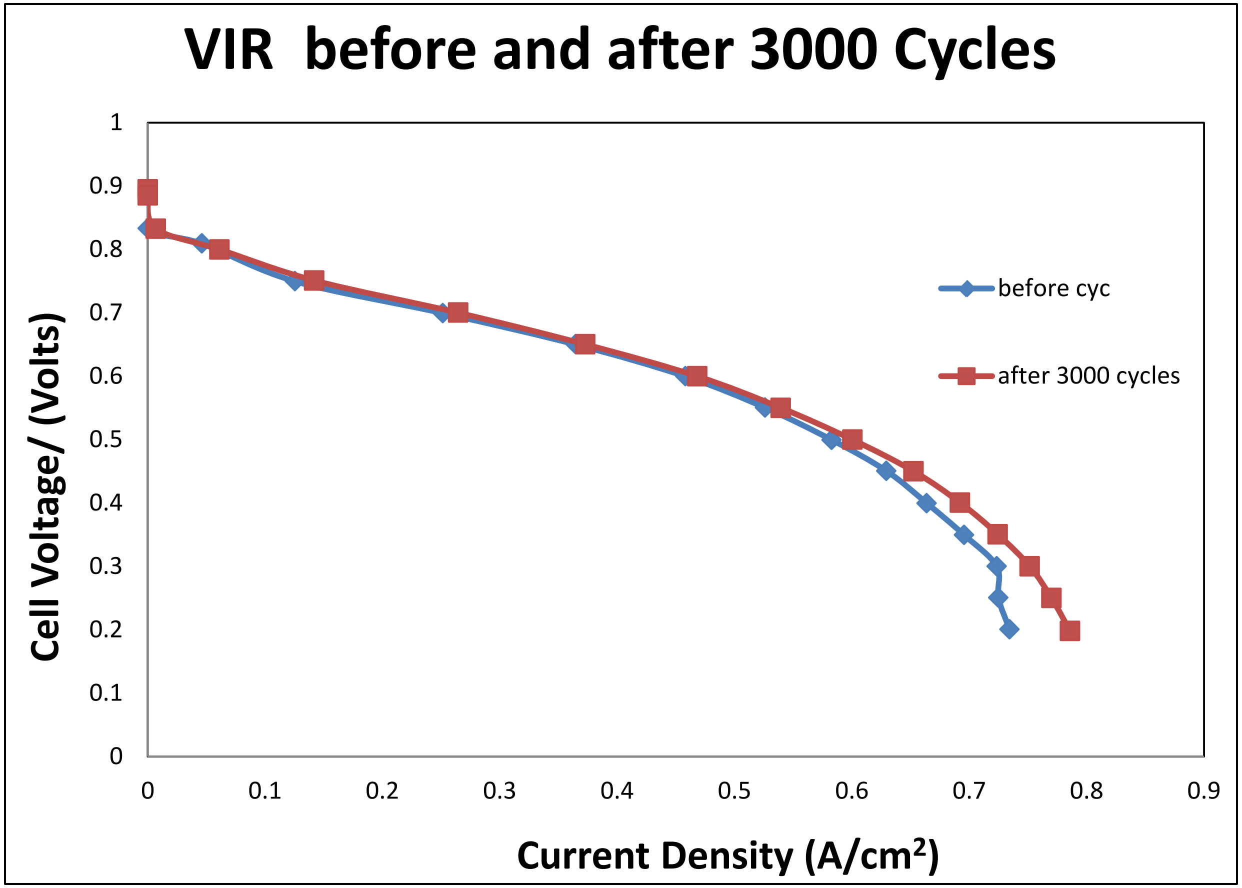
2. Durability

New Results



Testing conditions: 5 cm^2, N212
A: 0.1 mg Pt/cm^2 sputtered ELAT
C: 0.2 mg Pt/cm^2
30^{o}C, Ambient, 100% RH
H_2/air: 160/550sccm
GDL: **25BC**

Results indicate:
Performance increased after cycles and therefore no immediate durability issues…

Improved conditioning protocol required for better stability

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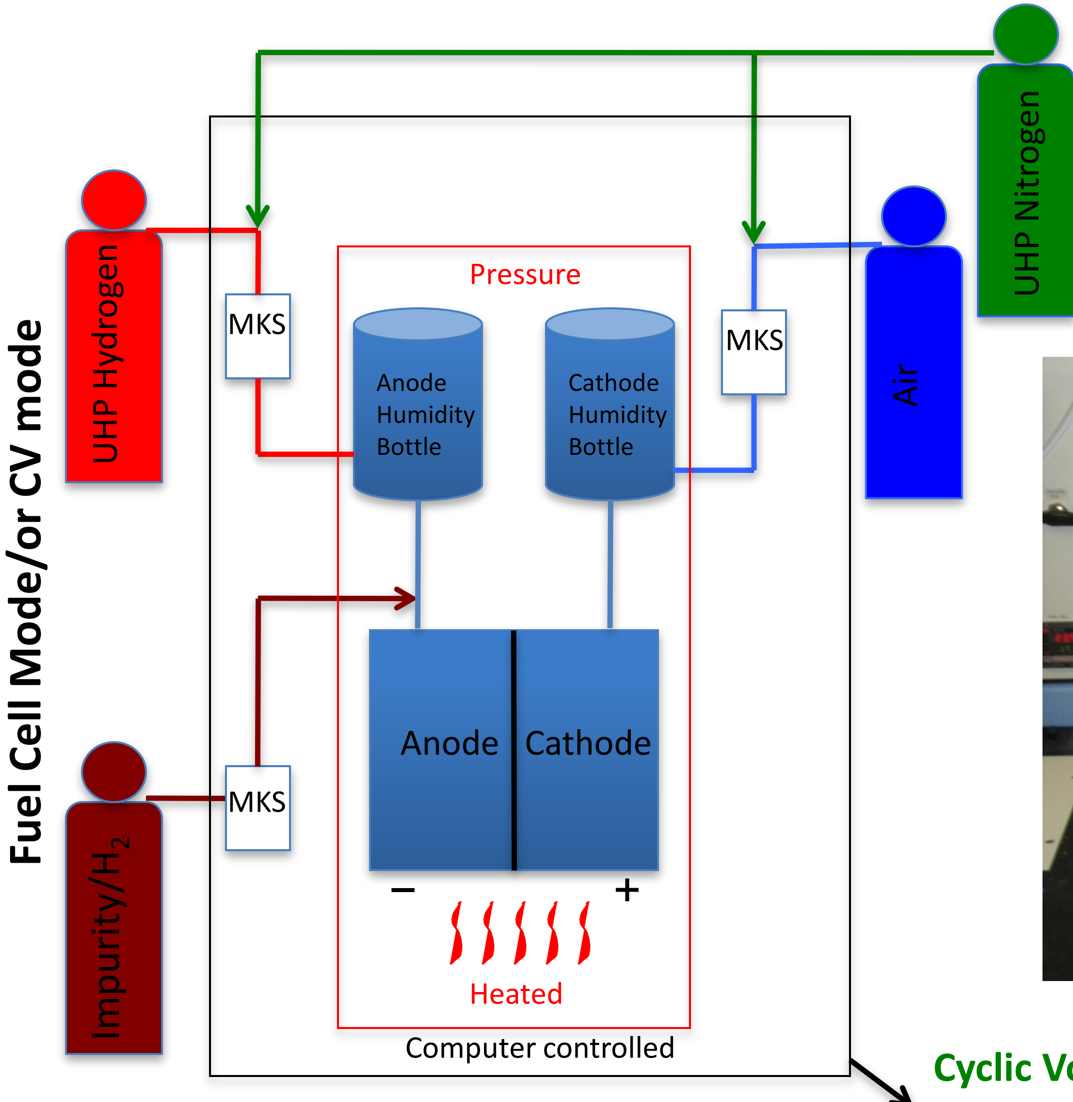
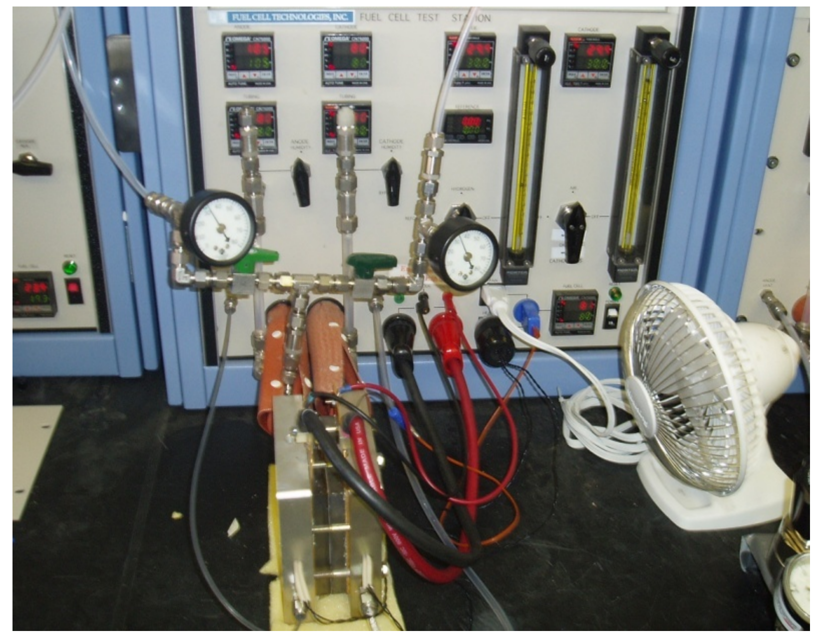
3. Experimental Set-Up for Impurities



- 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 and hydrogen sulfide*



Cyclic Voltammetry
AC Impedance
VIR Curves
Endurance Test

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3. Results with Carbon Monoxide 0.5 and 0.1 mg Pt/cm²

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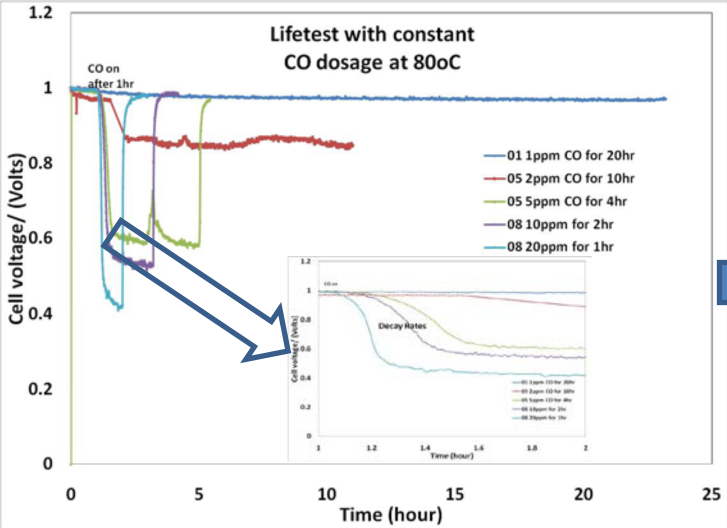
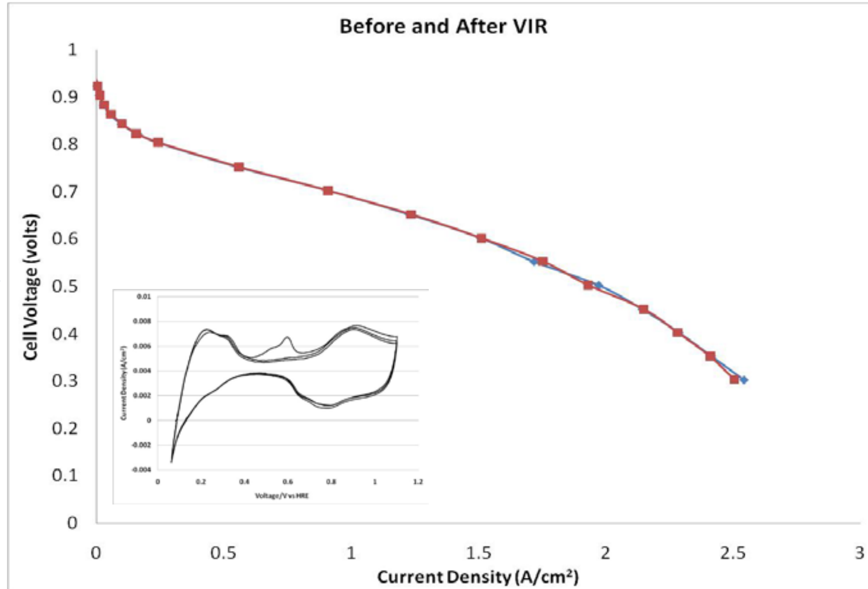
Normalized Voltage@ 50A vs Time



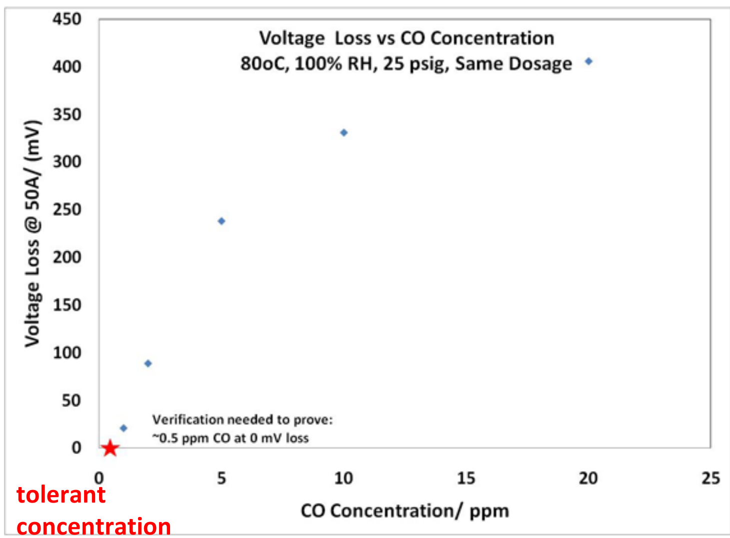
Previous Results

cleaning



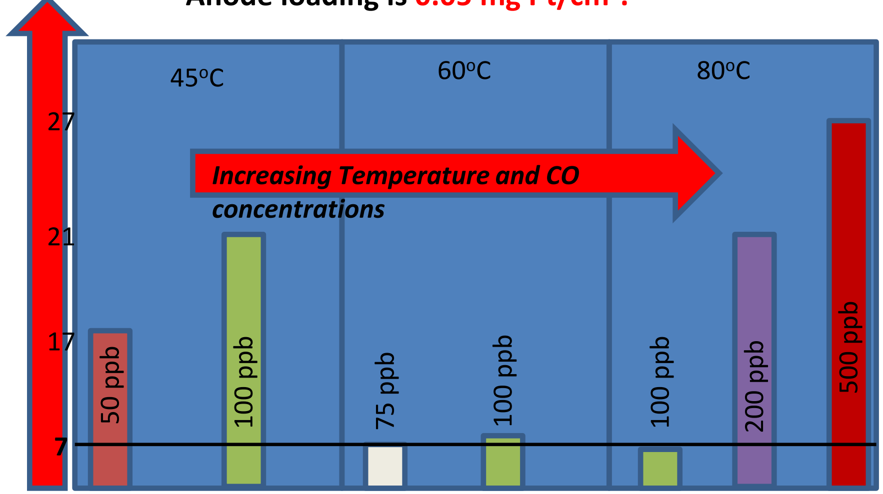
The same dosages were introduced but clearly **the rate and extent of poisoning** increases with the [CO].

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.

Anode loading is 0.05 mg Pt/cm².



Test sequence similar to the ‘Common MEA’. CO tolerant if the V-loss was less than 1% of initial voltage. The cell operated at ~700 mV (at 50A). i.e Voltage losses < 7 mV satisfied this condition.

3. H_2S Testing (Anode: 0.05 and 0.1 mg Pt/cm^2)

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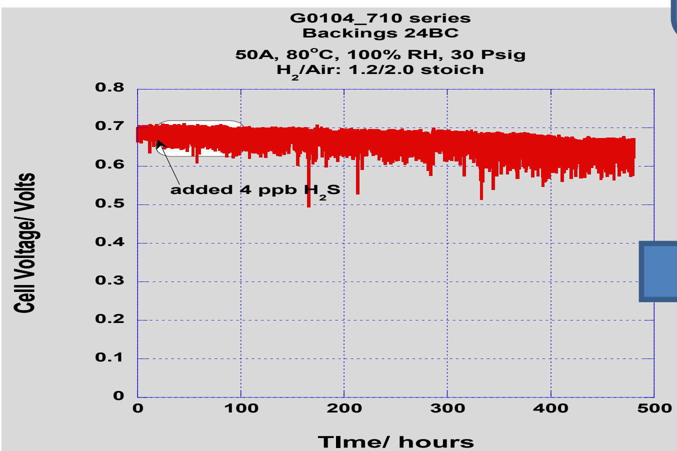
Common MEA tolerated 4 ppb for short term (~100 h), but Losses become more evident at exposure times. Reducing the loading introduces greater in shorter exposure times.

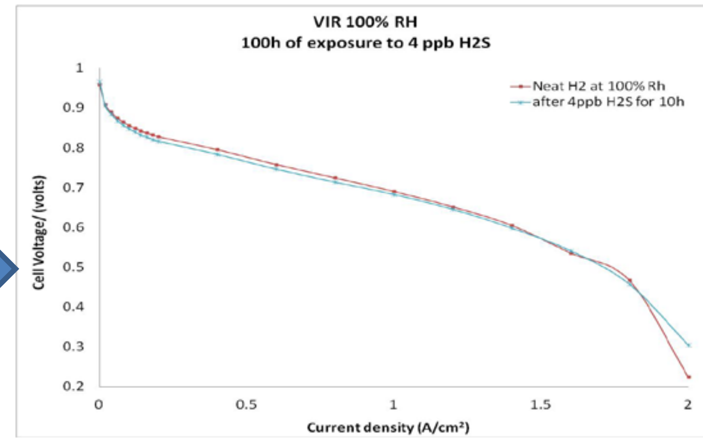
0.1 mg Pt/cm^2

Previous Results

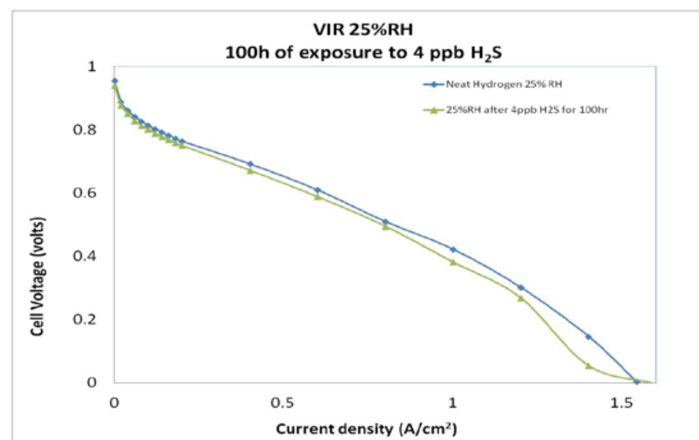


Decreasing loading

0.05 mg Pt/cm^2



Decreasing relative humidity



Common MEA:
Tolerated 4 ppb H2S for at least 100 hrs

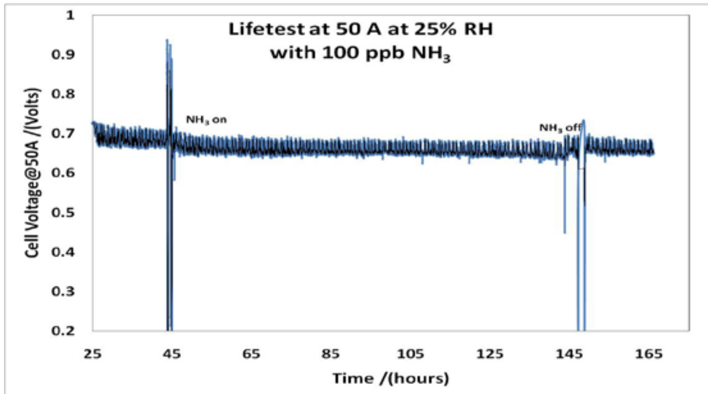
Lower anode loading:
At 100% RH there is~**11mV** decay, while 25% RH reduces **20mV (clearly more sensitive than common MEA)**

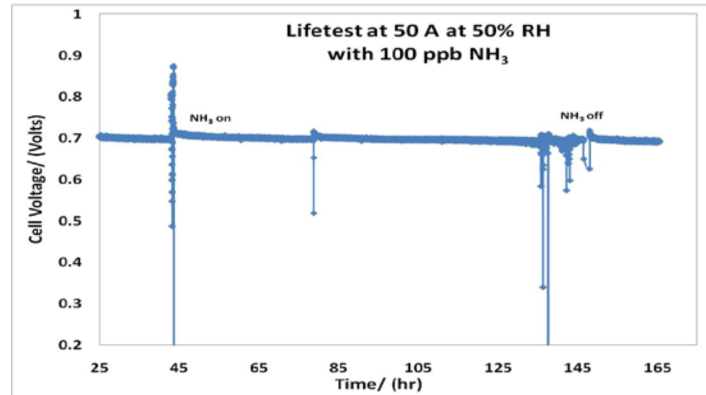
3.Testing NH_3 0.5 and 0.1 mg Pt/cm²

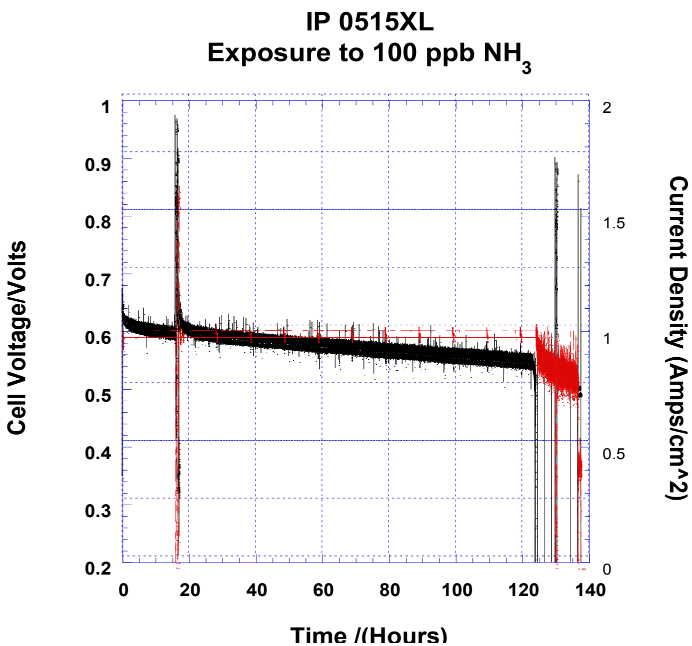
100ppb NH_3 at 100% RH sustainable with Common MEA for 100h.

Increasing RH → Decreases losses

Previous Results







Results shown reflect the impact of NH_3 as a function of RH in the anode feed for 100 h.

Test at 25% RH showed the losses for 100 was 24mV while 50% RH was 8mV. At the lower anode loading the performance dropped >50mV.

3. Approach (Fuel Impurities)

The previous mentioned results partially ***led to the development of an ISO standard for Hydrogen Quality*** (for road vehicles), but…

We tested a **common MEA (0.1/0.4 mg Pt/cm^2)** because obtaining lower Platinum loaded MEAs were difficult. But, the **DOE target** for PGM is lower than 0.5 mg Pt/cm^2, in fact the current target is at **0.15 mg Pt/cm^2 (total).** Fuel cell results reported with these loading as well as state-of-the-art materials are limited…

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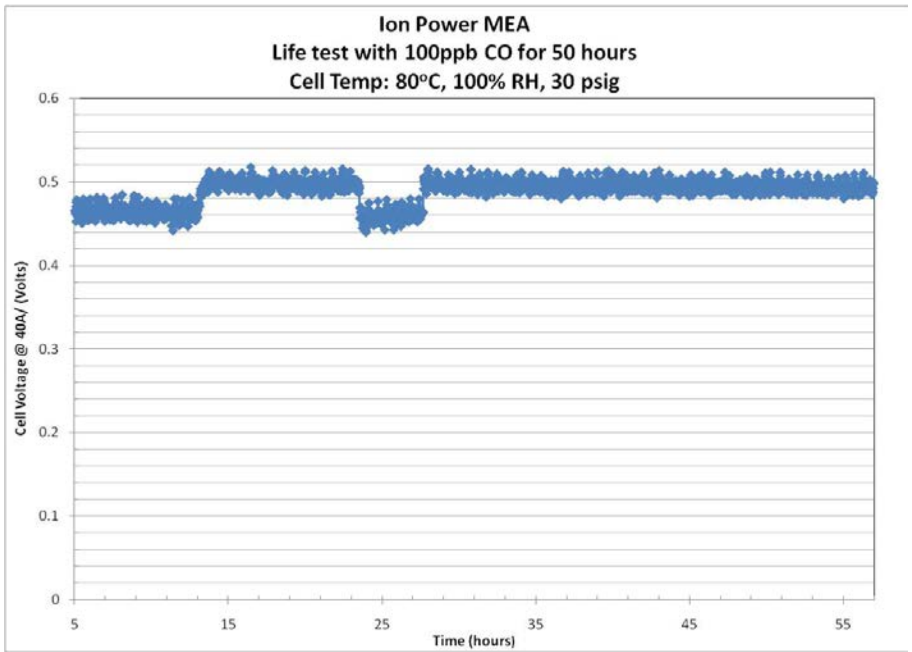
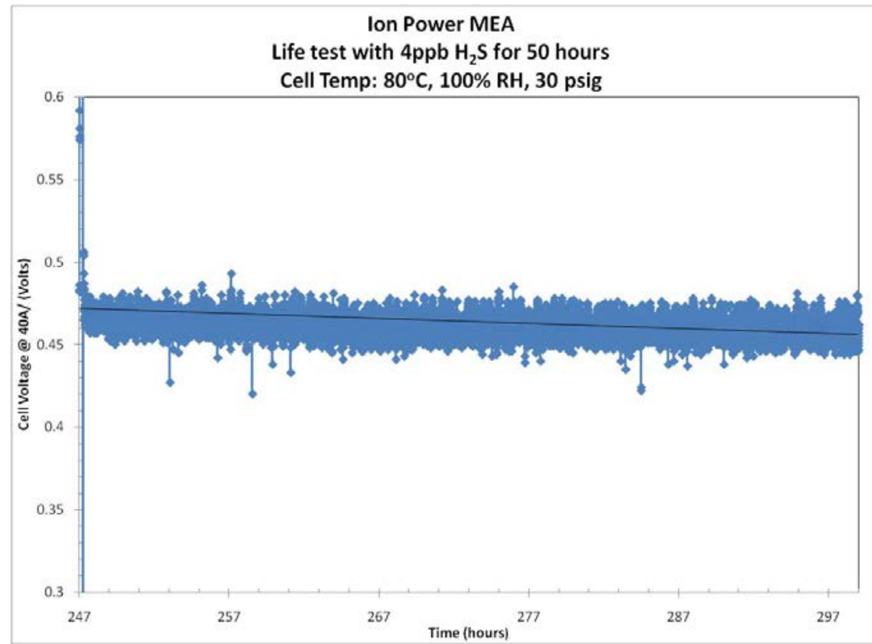
3. Effects of CO and H_2S on Ultra-Low Pt Loadings

100% RH

Anode: 0.03 mg Pt/cm^2 and cathode: 0.12 mg Pt/cm^2

New Results





At 100% RH, the losses for CO alone was at XXX, and when introduced with 4 ppb H2S The losses increased to 19mV.

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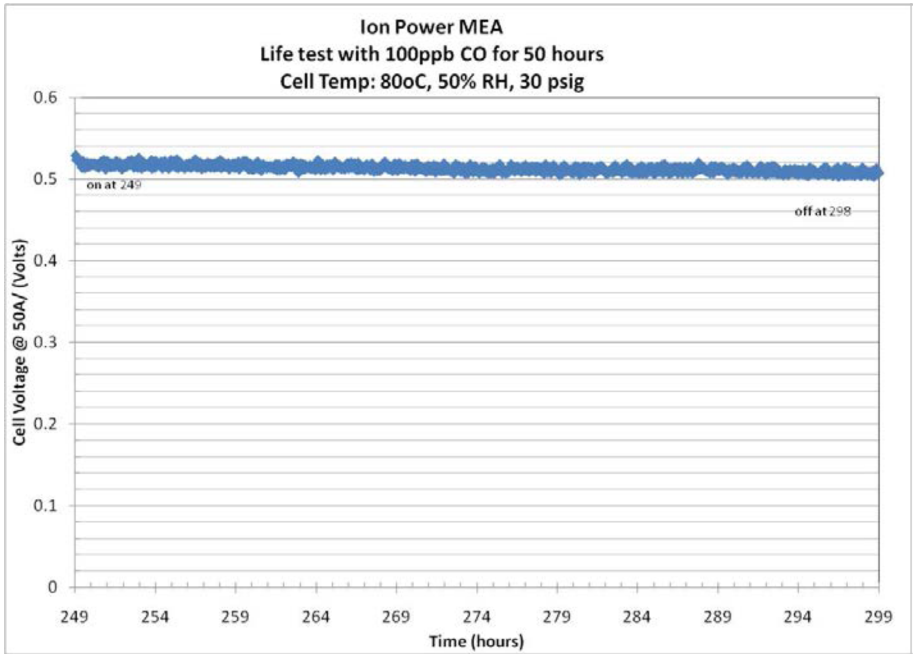
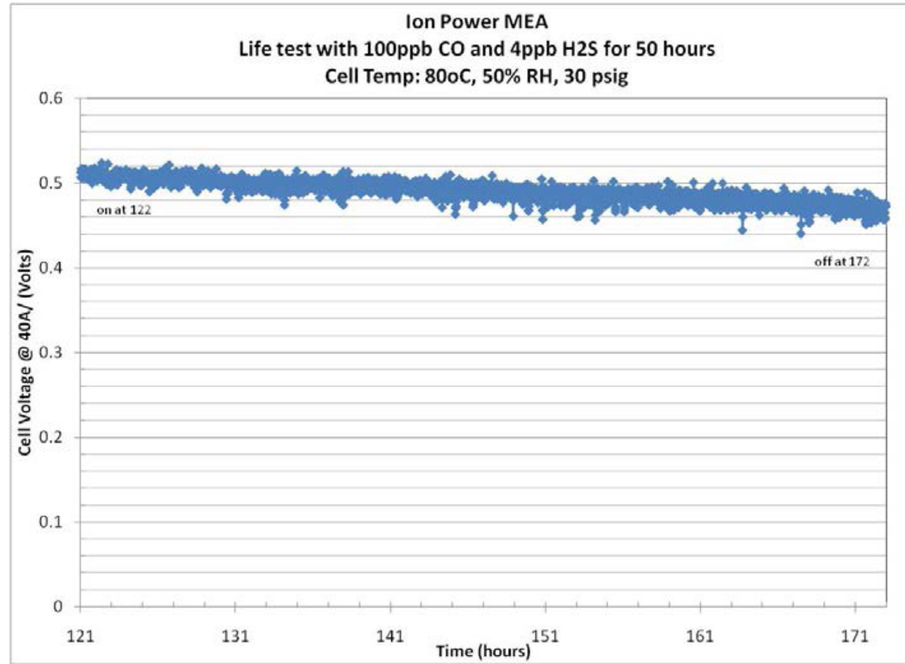
3. Effects of CO and CO/H_2S on Ultra-Low Pt Loadings

50% RH

Anode: 0.03 mg Pt/cm^2 and cathode: 0.12 mg Pt/cm^2

New Results





At 50% RH, the losses for CO alone was at 22mV, and when introduced with 4 ppb H2S Combined losses increased to 45mV. Clearly, unacceptable by the tech team guidance.

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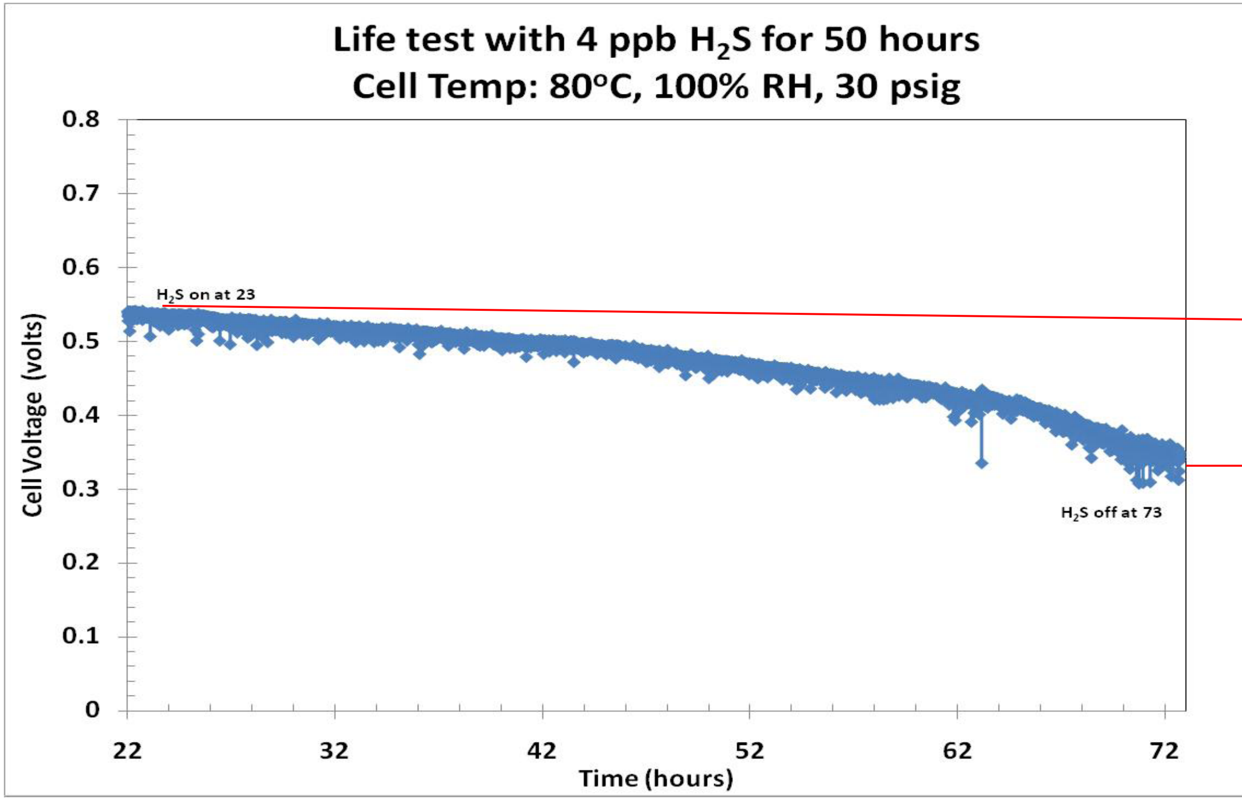
3. State-of-the-art Material NSTF Initial Results

H_2S

New Results

Anode loading: 0.03 mg Pt/cm^2
Cath loading: 0.12 mg Pt/cm2



$V_{loss} = V_{init} - V_{final}$
$= 541mV - 343mV$
$= 198mV$

After 50h, the voltage losses observed at 50A after 4 ppb H_2S was introduce were approximately 200mV. Recovery techniques have not been incorporated.

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3. US DOE/JARI Meeting

JARI highlights/concerns:

- multiple presentations
- placed emphasis on ***system particulates, measuring techniques, particulate size and origination and the use of filters***
- discussed the impact of ***impurities at various operating conditions*** using membrane electrode assemblies with ***0.3/0.3 mg Pt/cm²***.
- ***durability testing protocols*** for catalyst degradation was discussed with emphasis on ***delineating carbon corrosion and Pt agglomeration***

LANL highlights/concerns:

- Fuel Quality work performed at:
  1. highlights included ***the test methods to detect trace contaminants in gaseous*** hydrogen that are being developed through ASTM,
  2. the initial results for a ***hydrogen quality analyzer/monitor***,
  3. ***recent results with lower anode loadings*** and the importance of continued efforts in fuel quality testing
- Accelerated Stress Tests (ASTs) and their correlation to real world data:
  1. ***importance of ASTs* and discussed their drawbacks and applicability**
  2. ***difficulty in separating carbon corrosion and Pt agglomeration effects*** in catalyst ASTs
  3. new ***membrane*** AST the combines the ***mechanical and chemical degradation and has much better correlation*** to real world data was presented
  4. A ***gas diffusion layer- AST*** developed at LANL was also presented

Possible collaborations were discussed:

CO tolerance at lower anode loadings, in particular at **the DOE Targets a total PGM ≤ 0.15 mg Pt/cm²**

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.

Summary

1. Contributions to ASTM
   - Sub-committee Chair D03.14
   - Multiple standards developed and/or under development
2. In-line Fuel Quality Analyzer
   - Proof of concept demonstrated for CO analyzer using sputtered platinum electrode
     - Improved sensitivity
     - Improved durability
   - CO dosage monitoring possible. Analyzer under construction.
3. a). Impurity testing expanded to state of the art MEAs
   - Hydrogen fuel standard developed based on common MEA
   - Lower loading results in significantly higher performance loss
   - State of the art NSTF MEAs also exhibit significantly higher losses than common MEA

   b). US DOE/JARI Meeting on Fuel Quality and Durability
   - Potential collaborations identified: Drive cycle testing. Exchange of MEAs

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Future Work

- Continue providing leadership to ASTM efforts…
- Construct an Electrochemical Analyzer based on the proof of concept demonstrated for the CO dosage monitor
- Expand inline analyzer proof of concept to H_2S and NH_3
- Perform tests with ultra low platinum loading and state-of the art materials using the ISO concentration levels
- Understand recovery mechanisms in state of the art MEAs
- Explore DOE/JARI/LANL collaboration that incorporates durability and drive cycle tests in the presence of impurities.

Acknowledgements

LANL gratefully acknowledges the Fuel Cell and Vehicle Technologies Program/Safety, Codes & Standards

Technology Development Managers: ***Antonio Ruiz Nha Nguyen and Will James***

ISO TC197 Working Group 12 Members

Former D03.14 chair: Jackie Button

ASTM staff manager: Alyson Fick

& Thank You- the AUDIENCE.

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