Hydrogen Fuel Quality

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Project ID: SCS007

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Overview

Timeline

Project start date: 10/1/2006
Project end date: 9/30/2014*
Percent complete: 75%

* Dependent on standards development cycle and DOE target levels

Barriers

2012 MYRD&D barriers addressed

F: Enabling national and international markets requires consistent RCS

G: Insufficient Technical Data to Revise Standards

Budget

- Total project funding: $2,350K
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY11: $450K
- Funding for FY12: $400K

Partners/Collaborators

WG-12 representatives from governments, national labs, universities, and companies, including:

- US (details on Collaborators slide)
- Canada
- European Commission/JRC
- Japan
- Korea
- Germany
- France

Objectives:

To determine the allowable levels of hydrogen fuel contaminants in support of the development of **science-based** international standards for hydrogen fuel quality (ISO TC197 WG-12).

To validate the ASTM test method for determining low levels of non-hydrogen constituents.

Background:

For the past 6 years, open discussions and/or meetings have been held and are still on-going with OEM, Hydrogen Suppliers, other test facilities from the North America Team and International collaborators regarding experimental results, fuel clean-up cost, modeling, and analytical techniques to help determine levels of constituents for the development of an international standard for hydrogen fuel quality (ISO TC197 WG-12).

Approach – Fuel Quality

- Apply our expertise in ultra-low impurity measurement and analysis capabilities for single cell testing to the development of a science-based international standard for hydrogen fuel quality
- Collaborate with the ISO TC197 WG-12 international team on methodologies for data collection and analysis in support of the development of consensus standards for fuel quality
- Provide technical feedback and guidance to collaborators on selection of materials, calibration techniques, and data analysis

Impurities Testing

Defining "Tolerance"

- *…the ability to electro-oxidize H_2 in the presence of an impurity at an acceptable polarization loss…quantified at some current density in terms the maximum concentration which can be tolerated, as defined by some nominal polarization loss at the anode (typically 20 – 100 mV)…*

  [ref with respect to CO: Bellows et. al., Ind. Eng. Res., 1996, 35, 1235-1242]

- *'Zero' performance losses due to impurities after recovery…*
  [FreedomCAR Tech Team Mtg, 2010] currently called the USCAR/DOE *Driving Research and Innovation for Vehicle efficiency and Energy sustainability* (U.S. Drive) Fuel Cell Technology Team

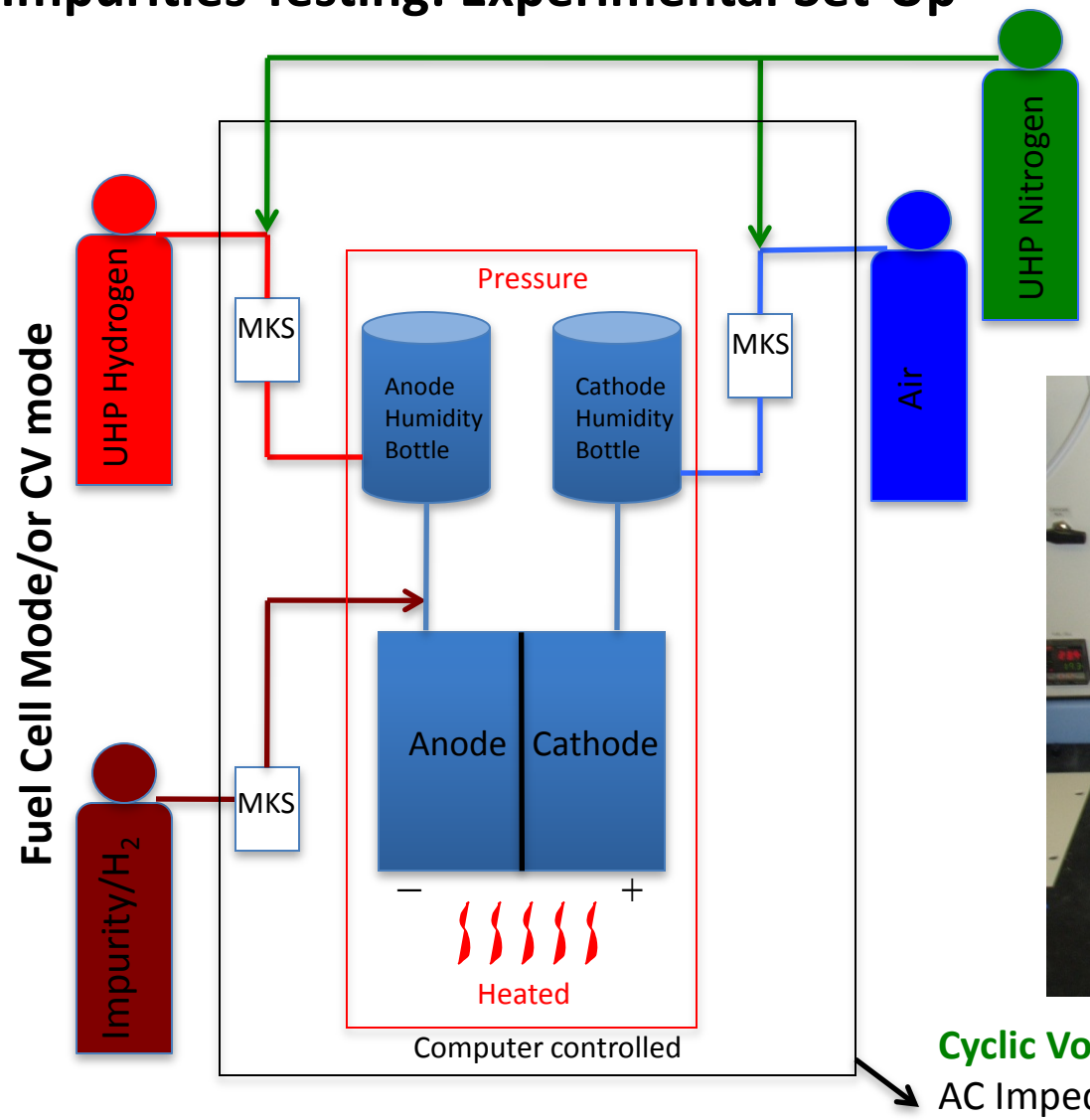
Strategies:

- Air Bleeding induces *durability issues* (i.e. high voltages at the H_2/O_2 interface leads to carbon corrosion)
- Higher Pt loading makes reaching technical targets very challenging (an *expensive approach*)

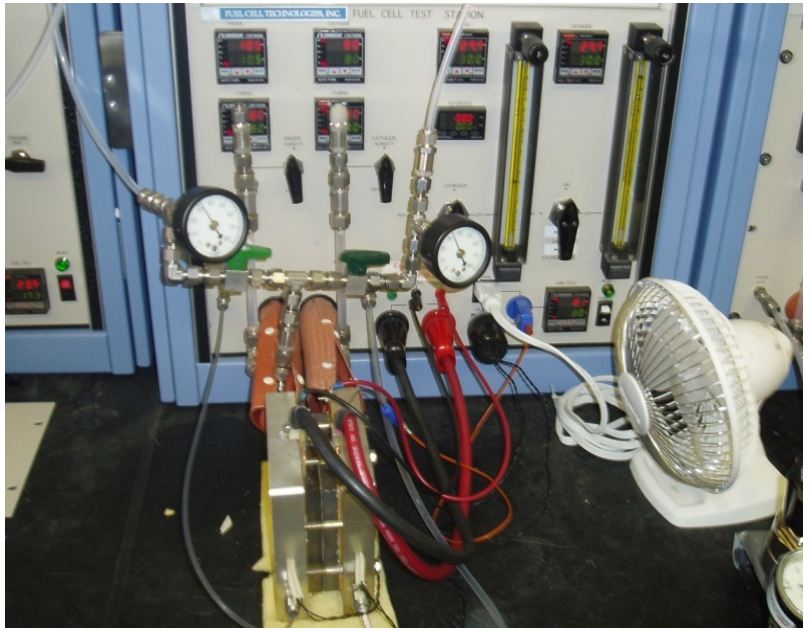
What is the maximum concentration that an operating fuel cell can tolerate without implementing risky mitigating strategies?

Accomplishments

Impurities Testing: Experimental Set-Up



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

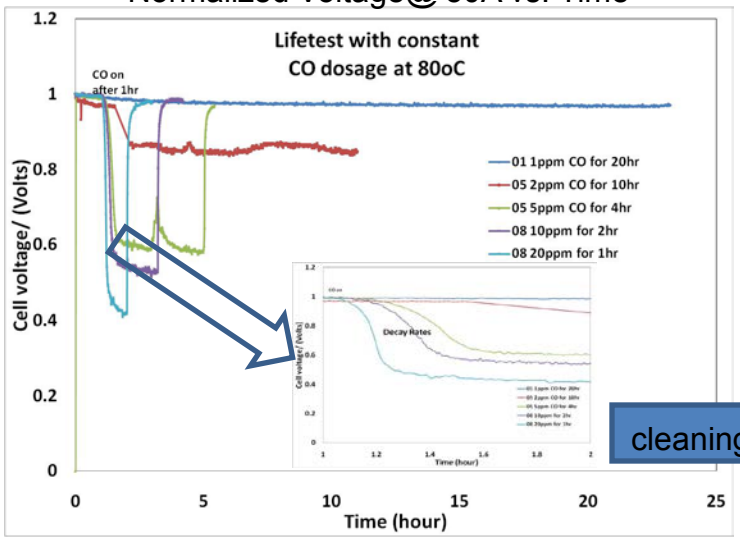


Cyclic Voltammetry
AC Impedance
VIR Curves
Endurance Test

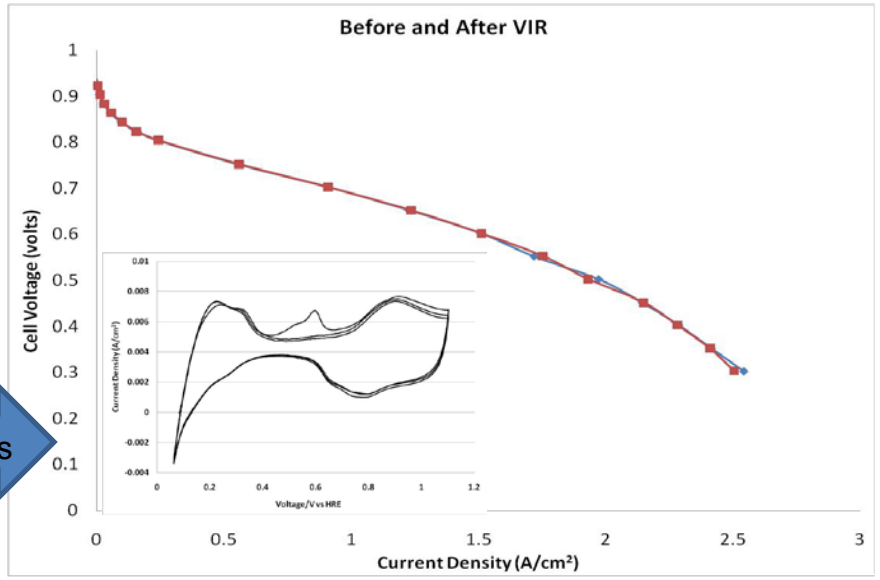
Fuel Cell Testing Results

REMINDER: FY11 Fuel Cell Testing Results - Carbon Monoxide @ 0.1 mg Pt/cm²

Normalized Voltage@ 50A vs. Time



cleaning between expt's

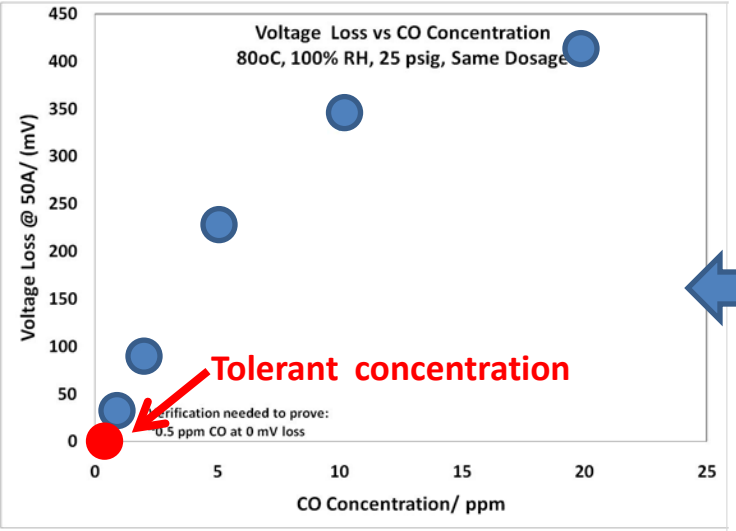


The same dosages were introduced but clearly **the rate and extent of poisoning** increases with the [CO].

CV Conditions: 20 min purge with 400 sccm H_2 (CE/Ref) and N_2 (W)
P: 28.7/28.7 psig, At exp't Temp & RH
Sweep rate: 0.06 – 1.1 V at 20mV/s for 3 cycles

VI conditions: H_2/Air: 1.2/2.0 stoic
P: 28.7/28.7 psig, 80°C,100% RH

Voltage loss vs. [CO]



Results indicate the 'Common MEA' should be able to **tolerate approximately 0.5 ppm CO** for at least **40 hrs**.
This concentration is 2.5 times the amount in the specification.

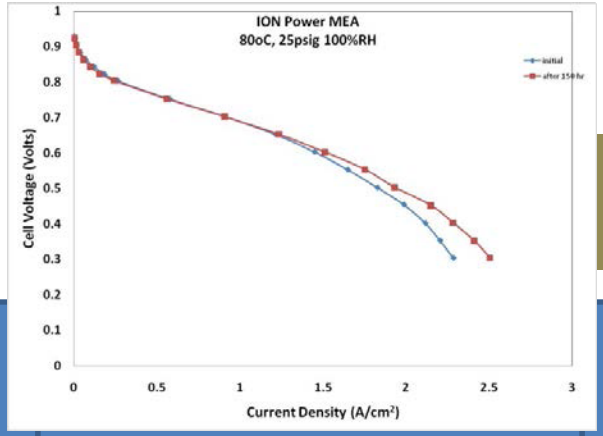
However, the DOE target for anode loading is 0.05 mg Pt/cm².

FY12 Results

Accomplishments

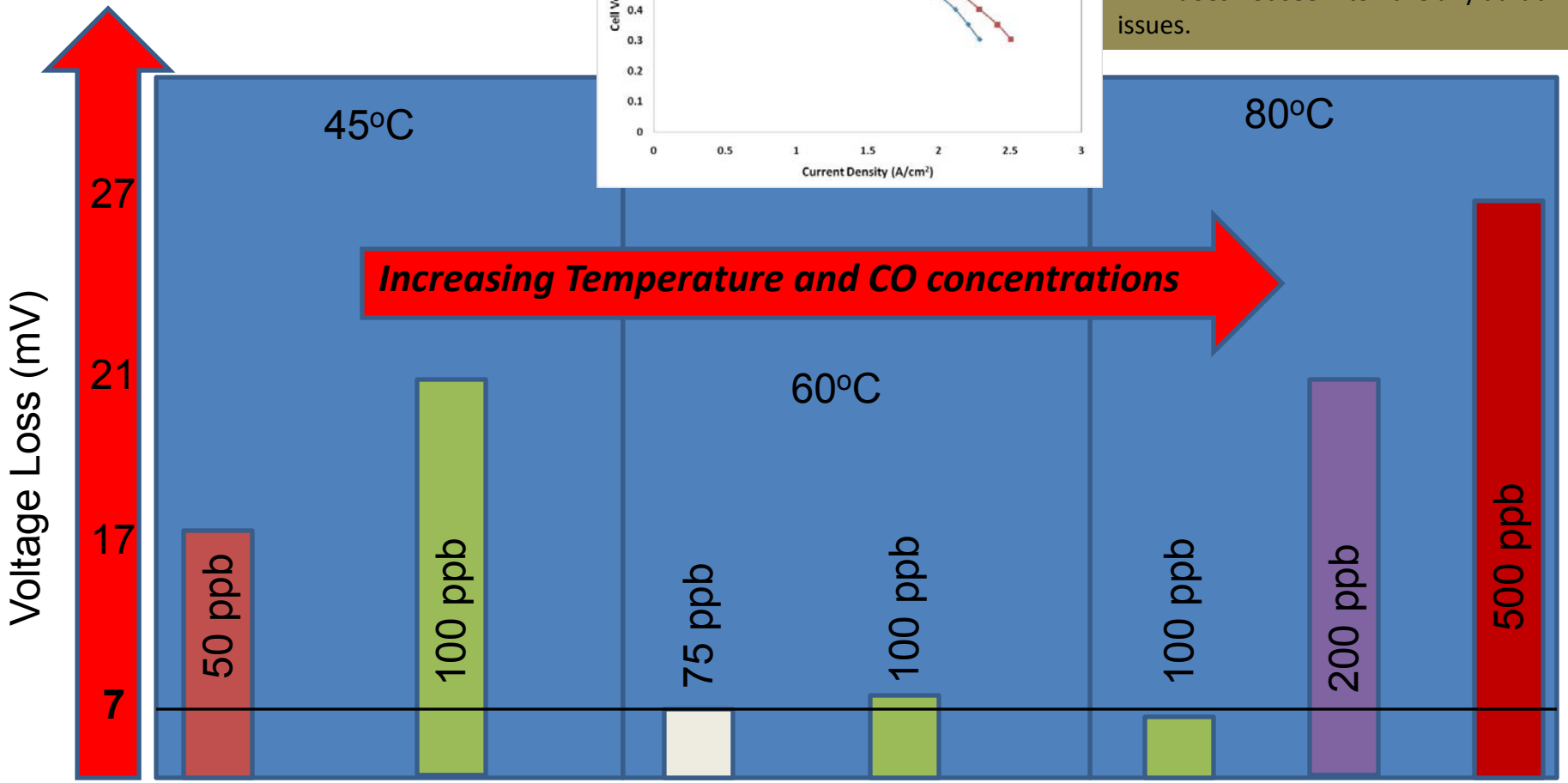
CO Tolerance

ION Power supplied DOE 2010 and 2015 targeted loadings: A @ 0.05 Pt mg/cm^2



New results

Initial results comparable to common MEA, MEA does not seem to have any durability issues.



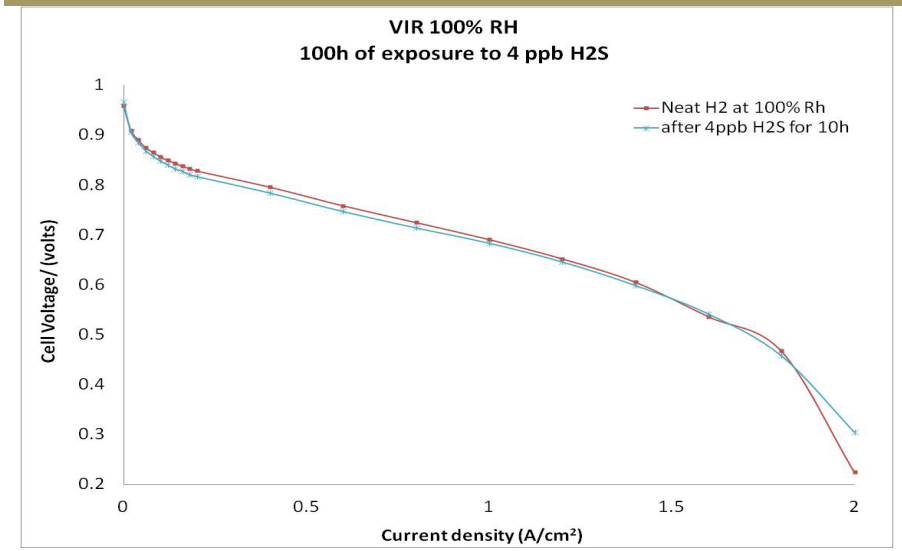
Test sequence similar to the 'Common MEA'. CO tolerant if the V-loss was less than 1% of initial voltage. The cell operated at ~700 mV (at 50A). i.e. Voltage losses < 7 mV satisfied this condition.

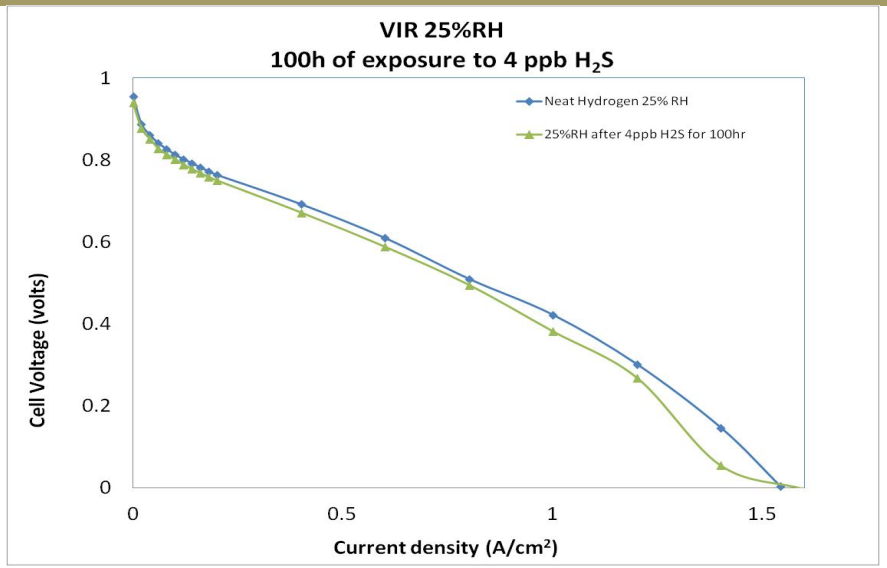
Accomplishments

H_2S Testing (Anode: 0.05 mg Pt/cm²)

New results

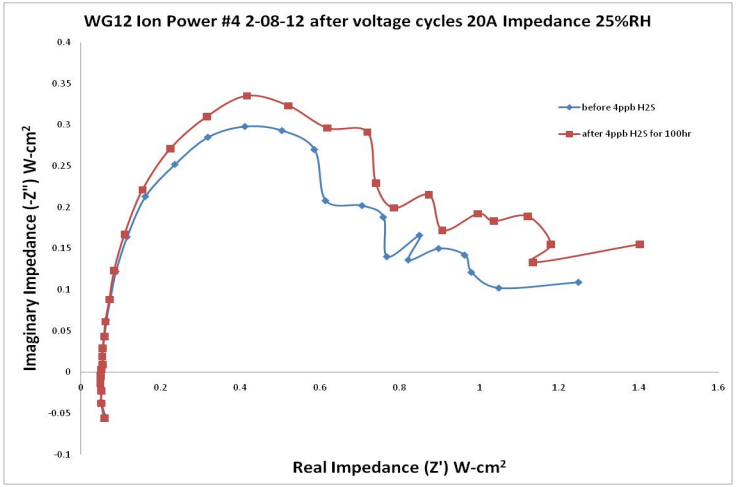
Common MEA tolerated 4 ppb for short term (~100 h), but Losses become more evident at exposure times. CVs show a larger coverage for the higher concentration. Also, we observed an expected increase in CTR as illustrated in the impedance spectra. (**Findings from FY11 Results**)





After 100 h of 4 ppb H_2S:

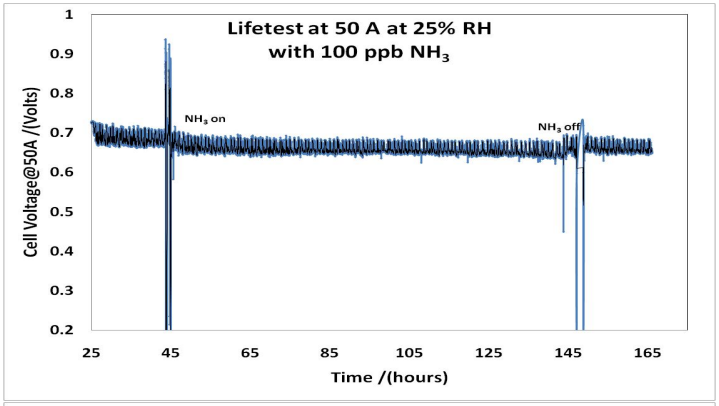
- At 100% RH there is~**11mV** decay, while 25% RH reduces **20mV (clearly more sensitive than common MEA)**
- Losses increase as the RH decrease
- Charge Transfer Resistance increase as Pt surface attain more S coverage

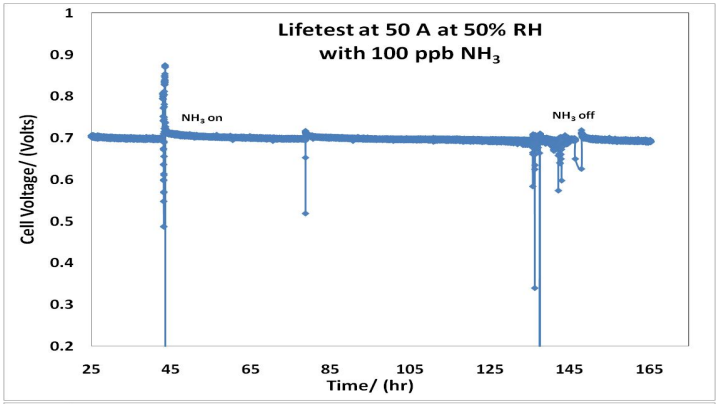


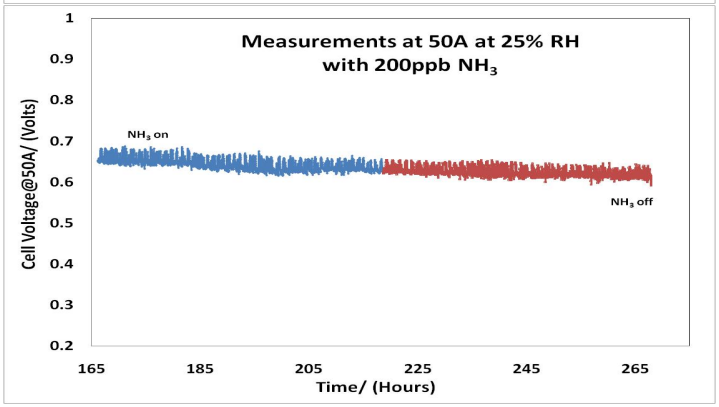
REMINDER: FY11 Fuel Cell Testing Results with Common MEA for NH_3

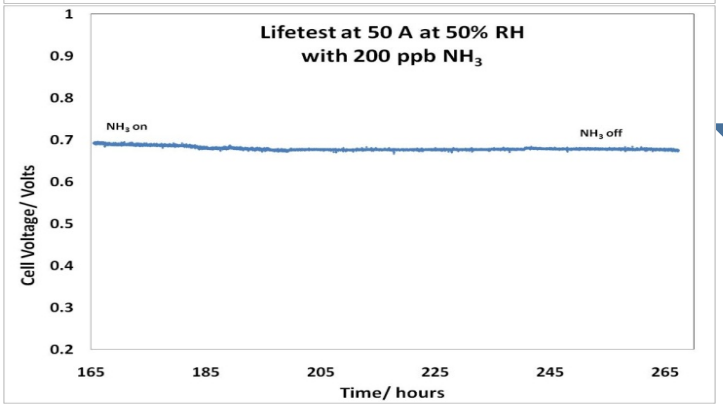
Results shown reflect the impact of NH_3 as a function of RH and concentrations in the anode feed for 100 h.

Increasing RH → **Decreases losses**









Increasing Concentration → **Increases losses**

Test at 25% RH showed the losses for 100 and 200 ppb were 24 and 36 mV, while 50% RH were 8 and 17 mV. At 500 ppb NH_3 performance dropped 33mV in 50h (not shown).

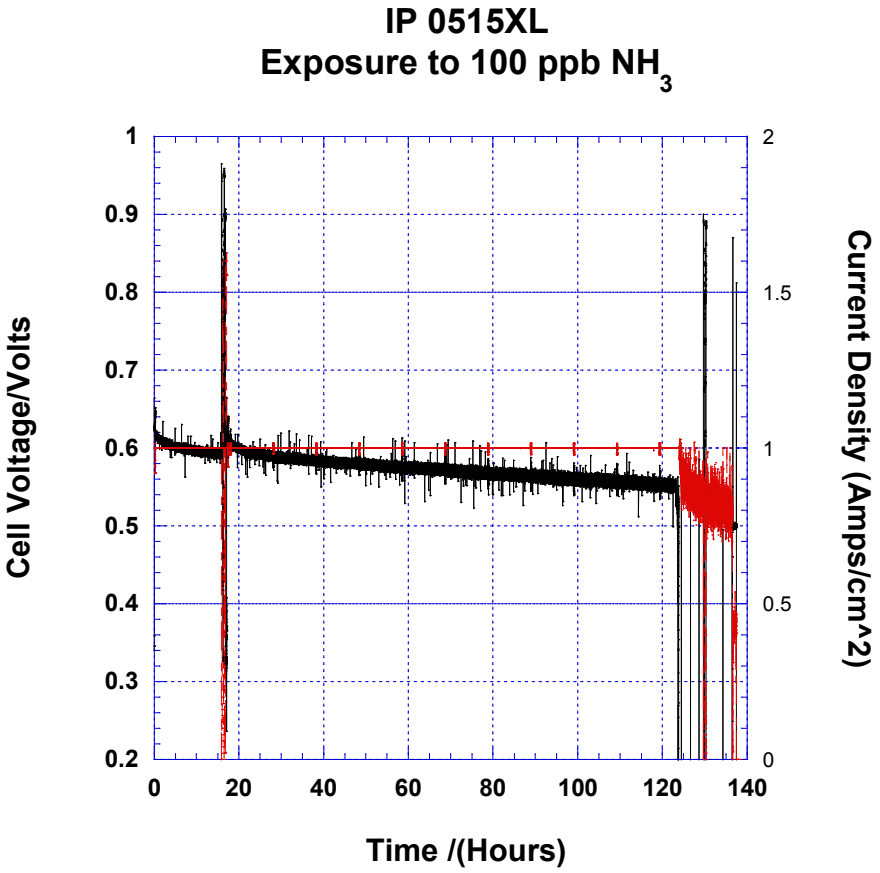
- CTR account for initial losses, local ionomer impacted may be reversible.
- HFR increase indicative of NH_4^+ build-up in the membrane, typically irreversible under normal FC operation
- MTR: unchanged with increasing ammonia

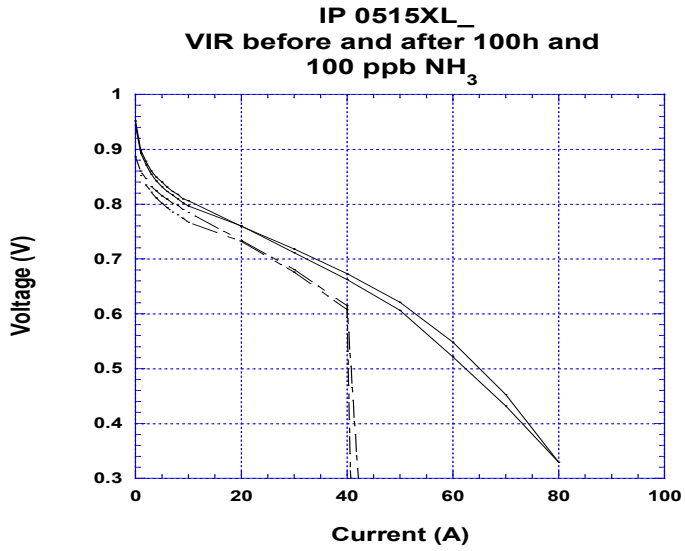
100ppb NH_3 at 100% RH sustainable with Common MEA for 100h.

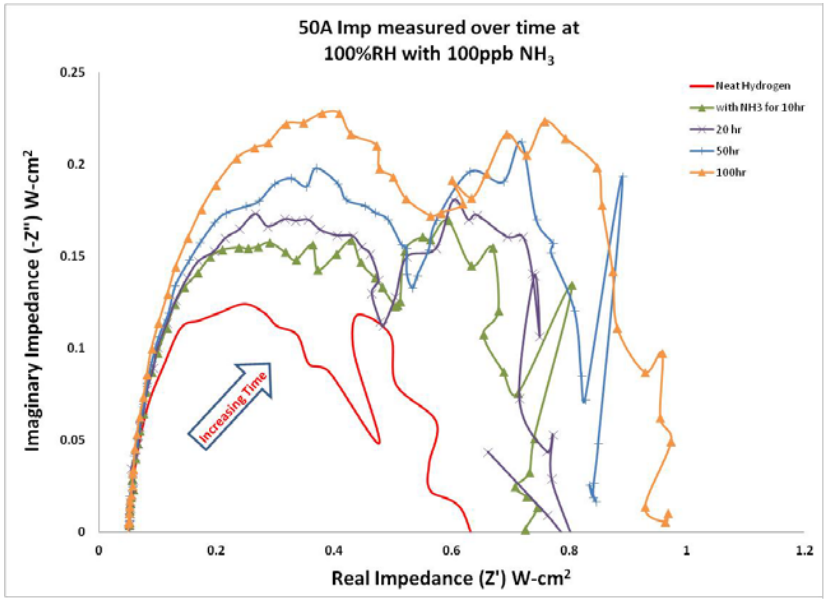
Accomplishments

NH_3 (Anode: 0.05 mg Pt/cm^2)

New results







Typically when the Pt loading is reduced, so is the ionomer content within the catalyst layer. This inherently impacts the NH_3 tolerance. Exposure to 100ppb NH_3 for 100h at 100% RH led to a significant voltage drop. The VIR indicates similar findings and the Impedance suggests the ionomer is mostly responsible.

Approach – ASTM Test Method Validation

ASTM Test Method: *Determination of Trace Gaseous Contaminants in Hydrogen Fuel by Fourier Transform Infrared (FTIR) Spectroscopy, D7653-10*

What useful information can FTIR provide?

Because no two molecular structures have the same IR spectra, this technique can:

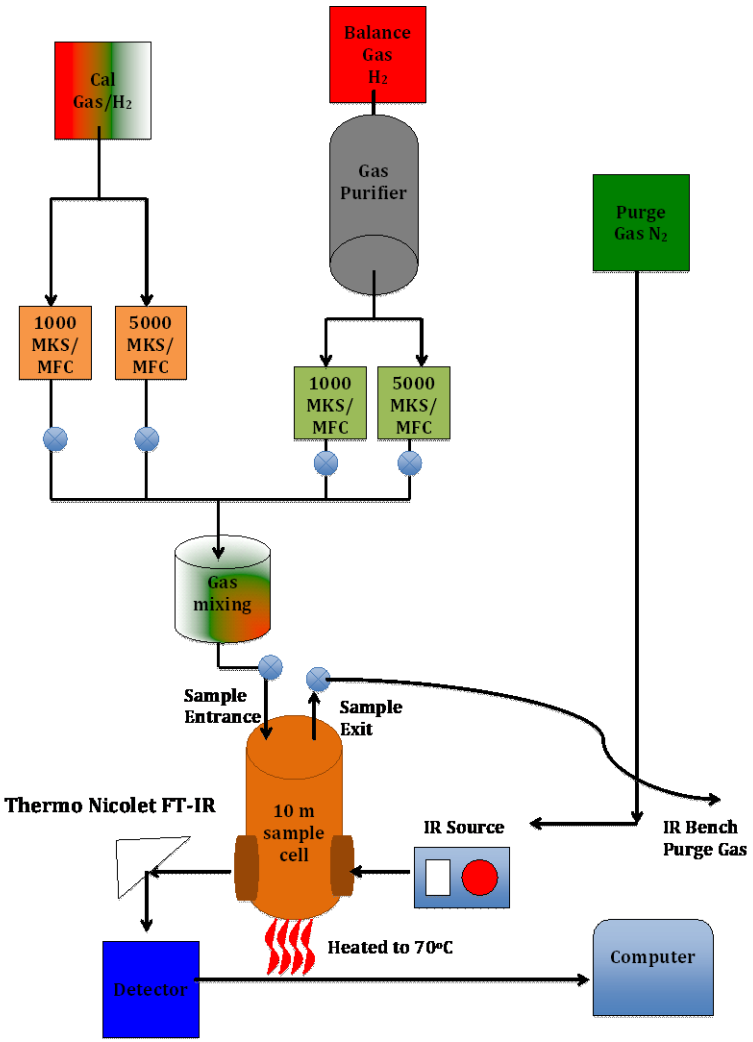
- Identify **unknown** materials
- Determine the **quality or consistency** of a sample
- **Quantify the components** in a mixture

How is it relevant to Hydrogen Fuel Quality?

- Powerful tool to quantify multiple gaseous species and there is no need for chromatography to separate.
- Hydrogen is not IR active so there is no interference when probing other constituents
- The method is precise and sensitivity can be increased by running multiple scans.
- Measurements are taken very quickly
- Instrument calibration is unnecessary (self-calibrating)
- Field measurements

Accomplishments

FTIR Experimental Set-Up



Description of materials/components

- Certified Gases from *Linde*®
- 10m gas cell was used to increase sensitivity as well as a MCT (mercury, cadmium, telluride) liquid nitrogen cooled detector
- FT-IR purged continuously with nitrogen to decrease interference from ambient water vapor and carbon dioxide.
- The gas cell was heated to 70°C to drive off water
- A background is taken followed by a blank or reference spectrum is taken to make sure impurities are not introduced in other ways

Procedure:

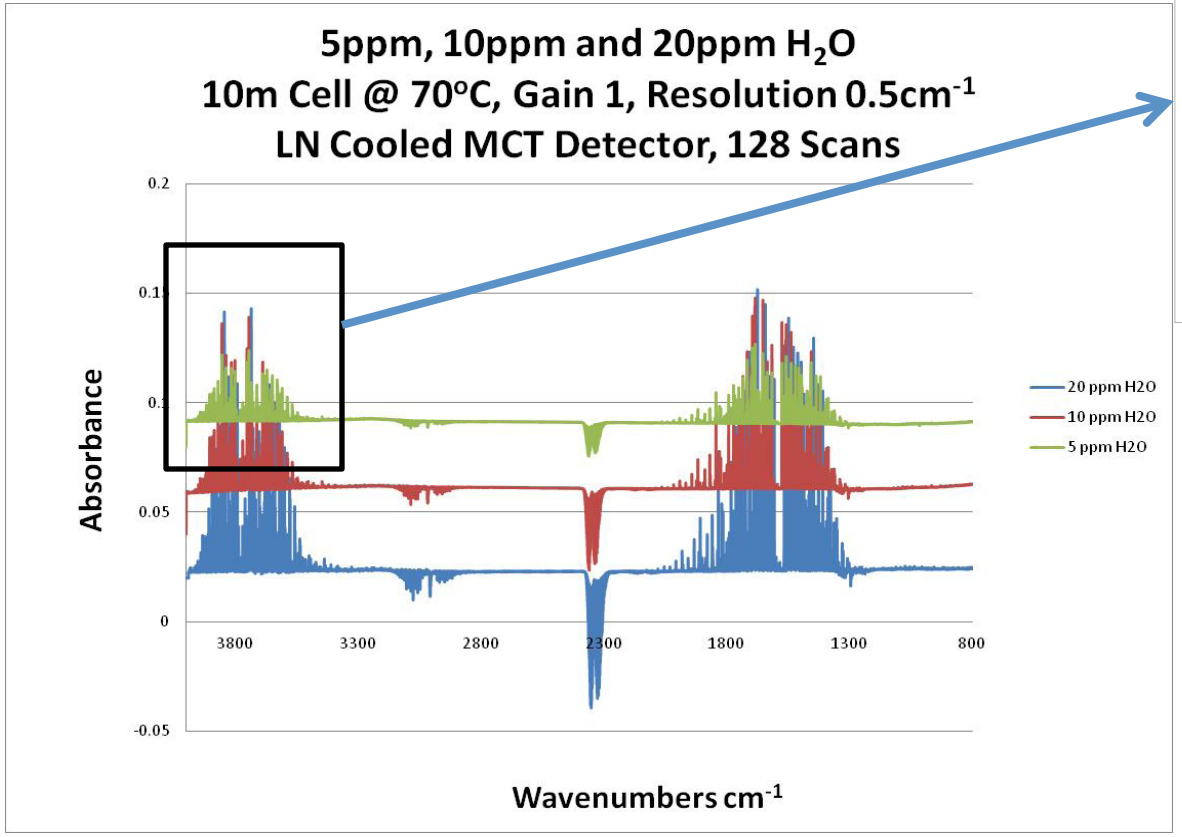
Take several spectra at each concentration. Use these spectra to build the calibration curve

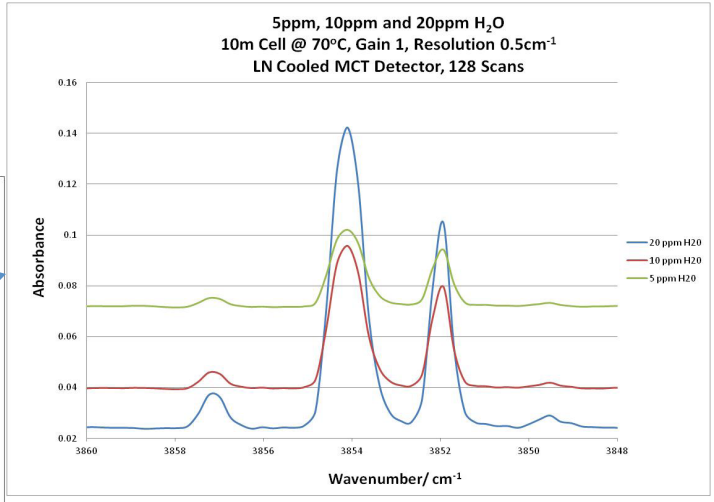
A calibration curve can be built by using a known contaminant standard and diluting it down using the same balance gas.

Accomplishments

ASTM H_20 FTIR results

New results





There is a correlation between the area and [H_20].

The larger the absorbance peak, the higher the concentration.

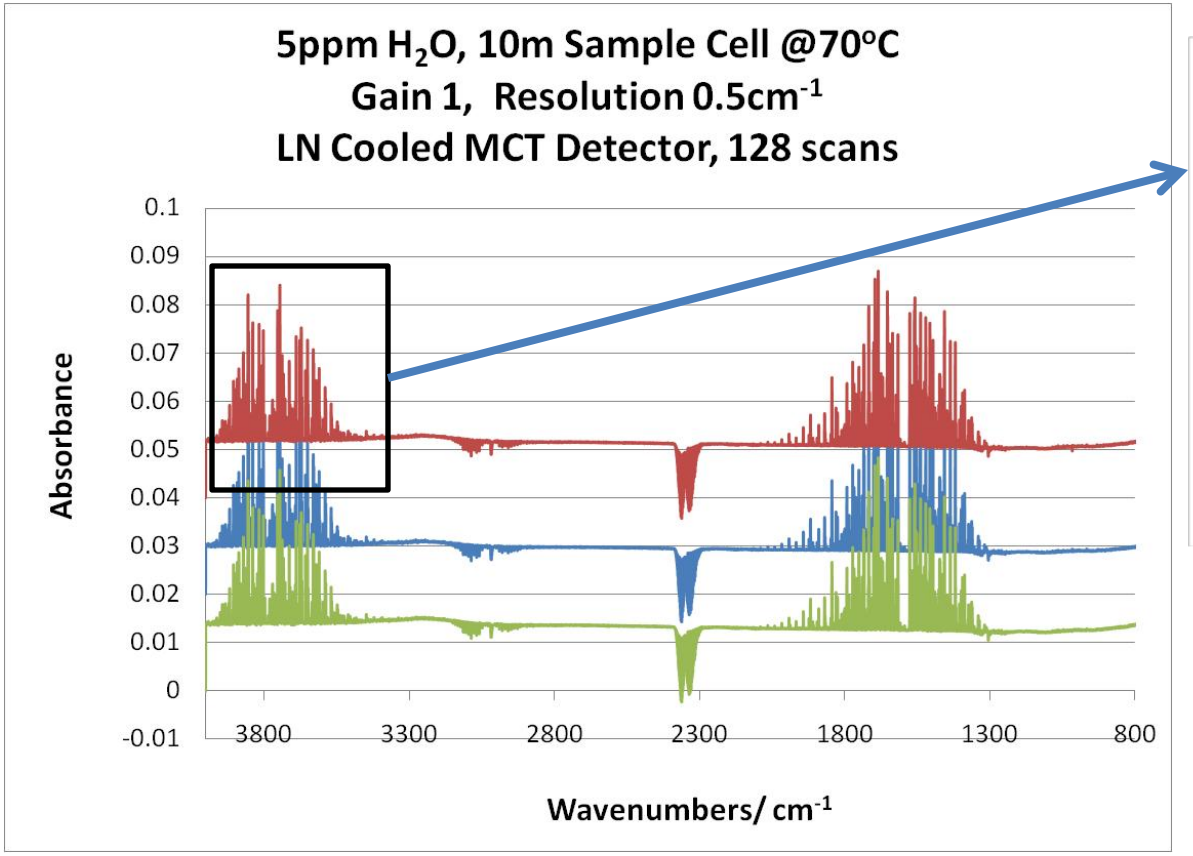
NIST Standard identifies H_20 peak at 3854 cm^{-1}

Different concentrations were run by diluting the calibration gas

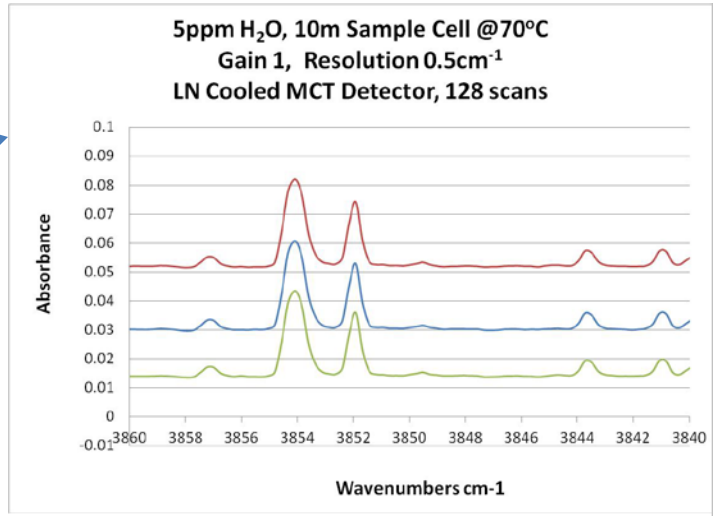
Accomplishments

FTIR results

Several identical spectra 5 ppm H_20



New results



Close-up View

- A stacked view of the results show multiple spectra taken to improve sensitivity
- Overlapping the Spectra and zooming in on the wavelength shows reproducibility
- Each concentration was measured multiple times
- The area measured for each spectra was averaged

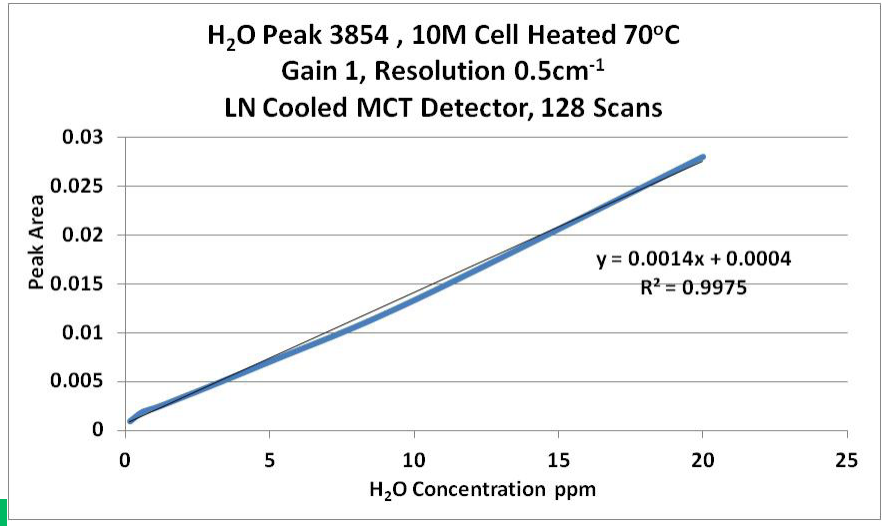
Accomplishments

FTIR H_20 Results

New results

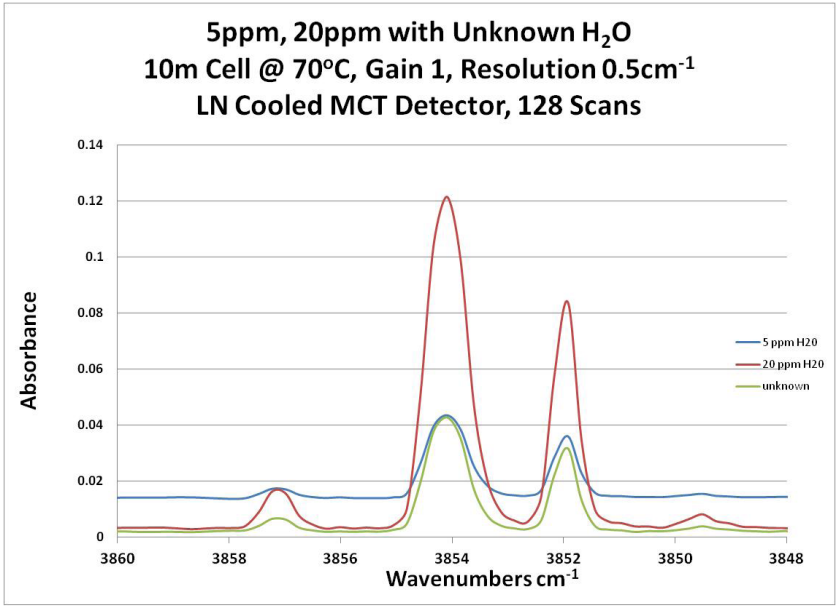
Peak areas taken from the average of each Spectra were used to produce calibration chart

$[H_2O]$	peak area
0.156	0.00088
0.6	0.00186
1.25	0.0025
5	0.007
10	0.0133
20	0.028



An unknown concentration of contaminant gas was introduced into sample cell; used calibration curve to determine the concentration

Calculating % error in measurement

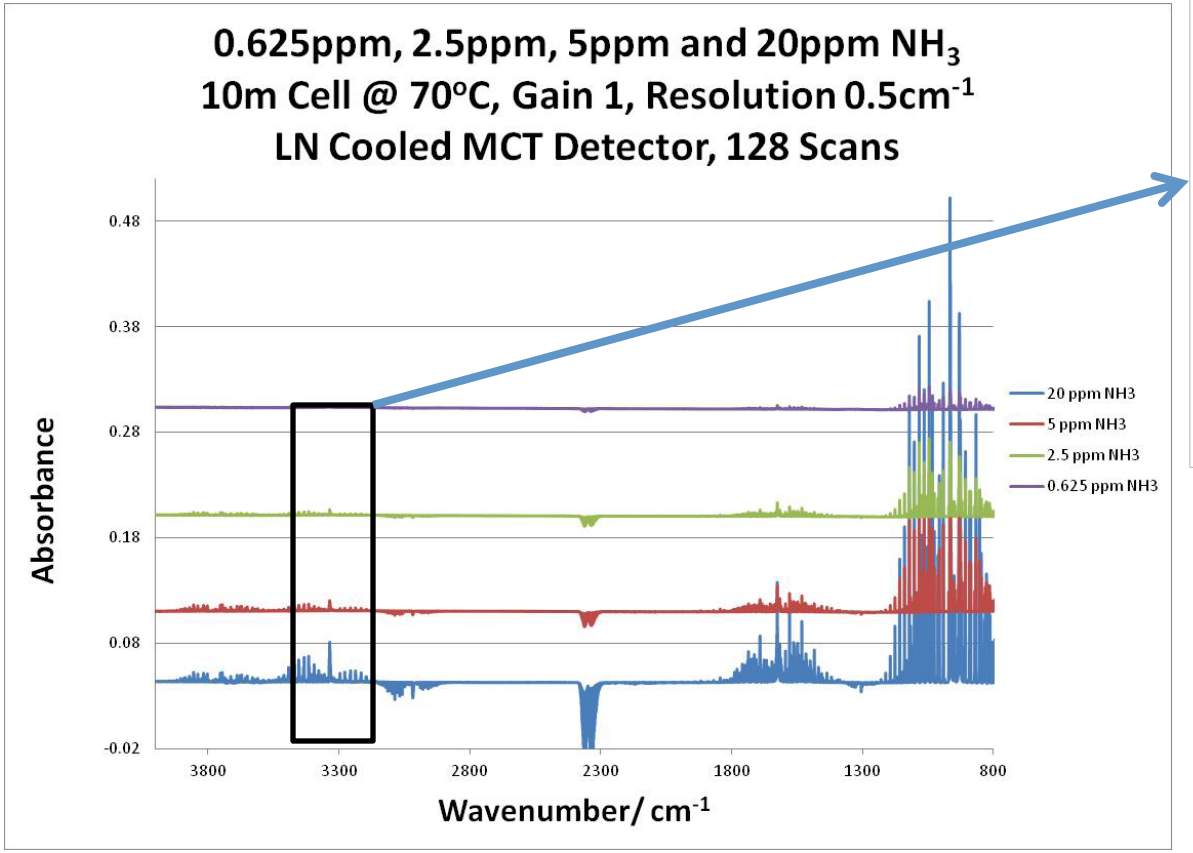


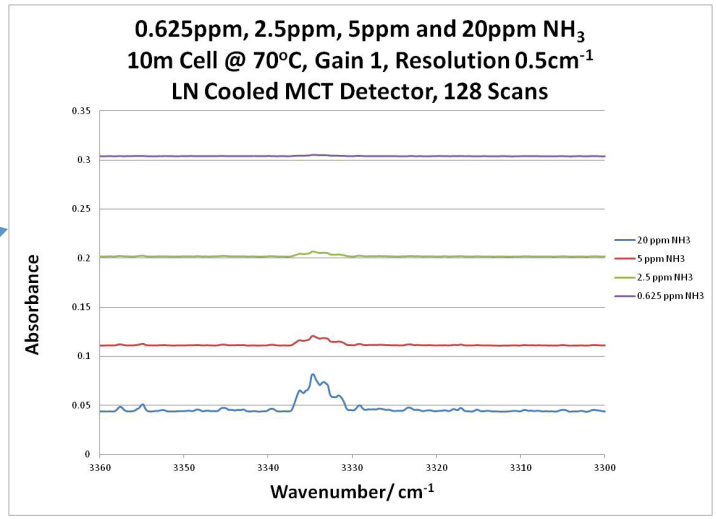
The unknown concentration introduced was 6.993ppm and we measured 6.643ppm, therefore the error calculated was 5%.

Accomplishments

FTIR NH_3 Results

New results





Close-up View

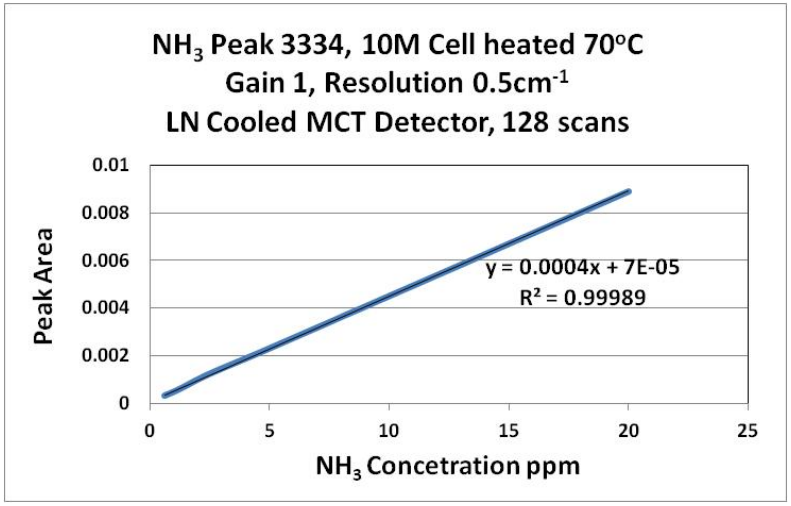
- NIST Standard identifies NH_3 peaks at 3334 and 1625 cm^{-1}
- Although not shown, multiple spectra were also taken at each [NH_3] to improve sensitivity
- A close-up view also shows the link between area and concentration
- A calibration curve was also produced.

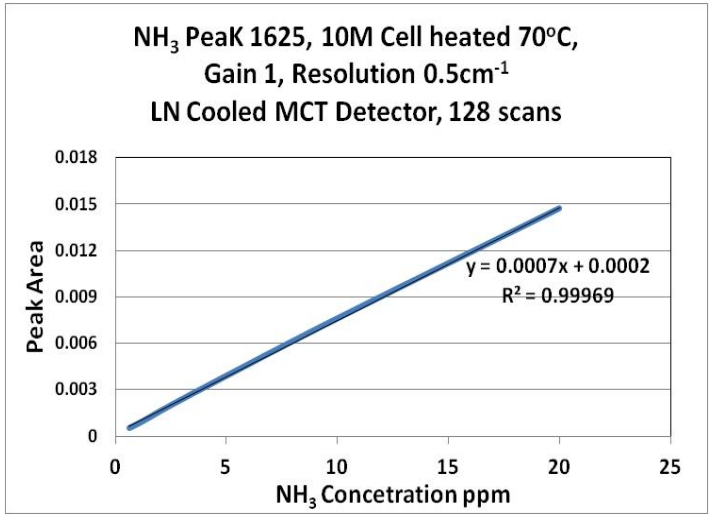
Accomplishments

FTIR NH_3 Results

New results

Calibration curves of successive measurements of different concentrations





$[NH_3]$	Peak Area
0.3	0
0.625	0.00031
1.25	0.00059
2.5	0.00123
5	0.0023
10	0.0045
20	0.0089

$[NH_3]$	Peak Area
0.625	0.00053
1.25	0.00099
2.5	0.002
5	0.0039
10	0.0076
20	0.0147

Calibration curves also allow detection limits to be determined and verified.

Collaborations

- WG -12 Members from USA
  - University of Connecticut
  - University of South Carolina
  - Clemson University
  - SRNL
  - NIST
  - NREL
  - ANL
- ASTM Round Robin Testing
  - CAFCP
  - Conscicorp
  - ASTM
  - Air Products
  - Linde
  - Atlantic Analytical
  - MKS
- Review article - Single Cell Testing Section (LANL lead) with co-authors
  - Guido Bender, NREL
  - Mike Angelo, HNEI
  - John Van Zee, Univ So. Carolina
  - Trent Molter, UConn
  - Hector Colon-Mercado and Scott Greenway, SRNL
  - Gerald Voecks , consultant
  - Rajesh Ahluwalia, ANL

Proposed Future Work

- Additional fuel quality tests will be performed using
  - Combinations of impurities
  - Aged materials (ASTs)
  - Varying testing conditions
- Complete review article
- Continue to participate in test method validations

Summary

Fuel Quality: measured tolerance at 0.05 mg Pt/cm^2 anode:

CO: 45^{o}C: could not tolerate 50 ppb CO

60^{o}C: tolerant to at least 75 ppb CO

80^{o}C: tolerant > 100 ppb CO (Common MEA~500ppb CO)

H_2S and NH_3 become more challenging as the Pt loading is lower. And even small amounts can cause losses. (Common MEA could tolerate 4 ppb H_2S and 100 ppb NH_3 for 100h)

ASTM FTIR test completed using NH_3 and H_20

Acknowledgements

LANL gratefully acknowledges:

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Program Manager: ***Antonio Ruiz***

ISO TC197 Working Group 12 Members

& Thank You - the AUDIENCE.

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