Hydrogen Fuel Quality

Focus: Analytical Methods Development & Hydrogen Fuel Quality Results

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Overview

Timeline

- Project start date: 10/1/06
- Project end date: 9/30/11
- Percent complete: 45%

Barriers

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

Budget

- Total project funding: $1,950K
  - DOE share: 100%
  - Contractor share: 0%
- Funding received in FY08: $850K
- Funding for FY09: $850K

Partners/Collaborators

- University of Hawaii/HNEI
- University of Connecticut
- University of South Carolina
- Clemson University
- SRNL
- NIST
- NREL
- ANL

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Milestones & Deliverables

Month/Year	Milestone or Deliverable
Dec 08	Milestone: Evaluate cross interference and sensitivity of sulfur-specific ion analysis methods to the presence of other impurities. Completed
June 09	Deliverable: Report on ammonia analytical methods development. In progress, ahead of schedule
Sept 09	Milestone: Evaluate cross interference of ammonia ion-specific analysis methods to the presence of other impurities. In progress, ahead of schedule

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Overall LANL Program

Sensor Development

In-Line Analyzer

Analytical Methods Development

Fuel Quality Specification

Testing and Validation

H_2S, CO, NH_3
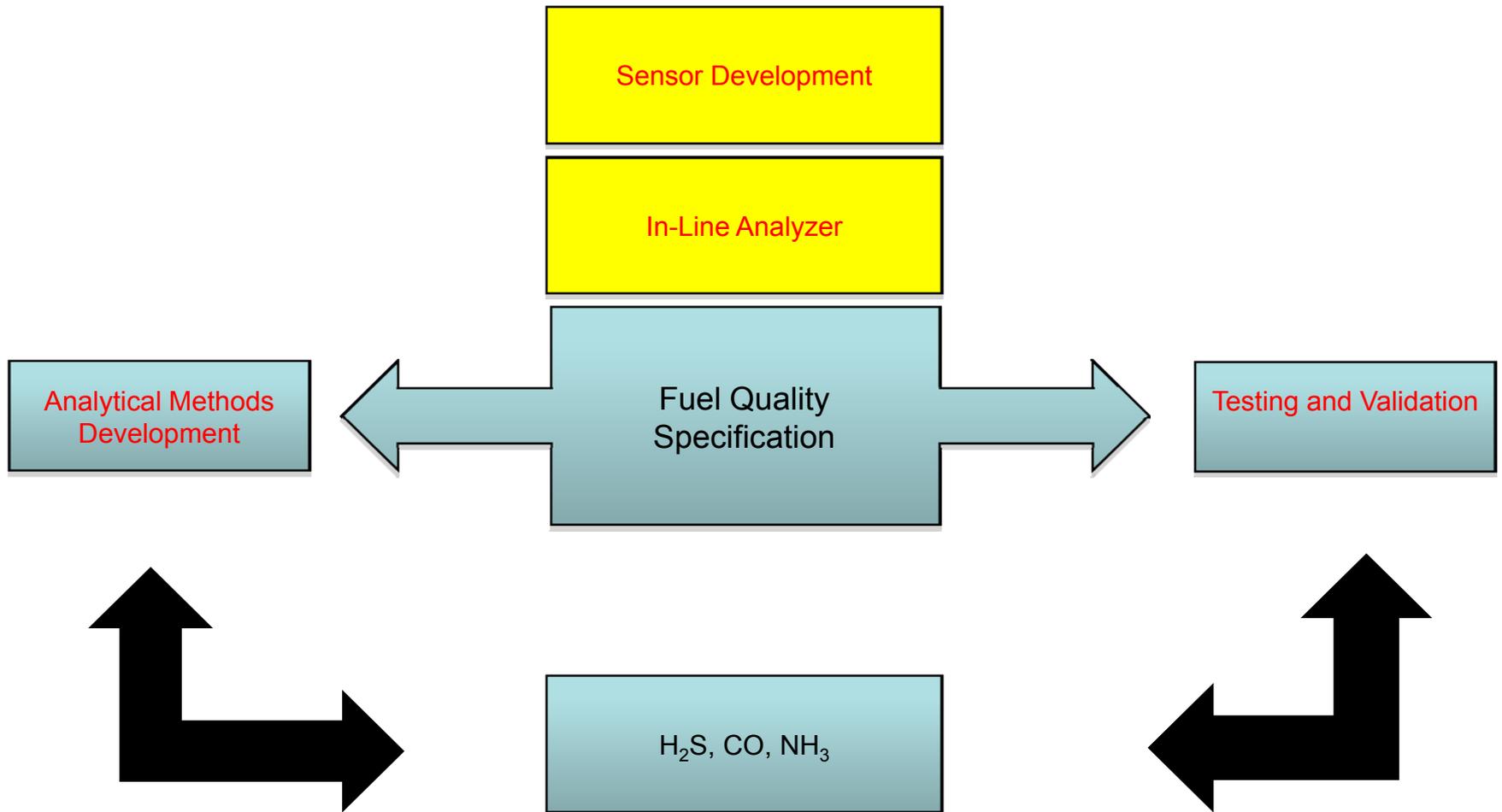
Technical Approach

- Analytical Development: Employ, modify and/or create novel techniques that allow reproducible trace levels of contaminants to be measured.
  - Specifically: CO, Sulfur and Ammonia
- Test the critical constituents (CO, H_2S, and NH_3) and provide data sets to FC modelers to establish predictive mechanistic models.
  - Tested at various conditions (Temperature, Rel. humidity, Concentrations)

Technical Approach:
Gravimetry for CO Surface Adsorption PEMFC Catalysts Study

- Netzsch STA-449 high precision, simultaneous TGA/DSC was relocated for surface coverage measurements
  - CO work required enhanced safety precautions - alarms, etc.
  - H_2S use requires greater safeguards
- Unique Instrument Specifications
  - Rated vacuum tight at 10^{-4} torr operation (required for work with toxic gases)
  - Unique thermostatic controlled balance unit
    - Lab room is subject to large temperature swings through 24hr period
    - Exceptional stability despite variations in ambient T
- Exceptional performance
  - 5 g maximum sample wt. held by special, large capacity "buckets" with use of TGA sample carrier
  - 0.1 µg resolution
  - Instrument rated at <1 µg/hr drift (best possible)
- Energetics of desorption may be studied with DSC

Technical Approach:
Gravimetry Procedure

- Two TG runs required for Analysis
  - 1st : used to clean surface of sample to prep it for CO absorption
  - 2nd : CO (1.1%)/Ar mixture is applied to sample and mass change is recorded
    - [CO] verified by GC analysis

Procedure #1

```
Load balance
with sample
      |
Record weight
under flowing
   UHP Ar
      |
Heat to 85°C
      |
Switch to O₂
      |
Switch to         →    Switch to
UHP Ar                 6%H₂/Ar
                           |
                       Switch to
                       UHP Ar
                           |
                       Cool to RT
                       and record
                       final weight
```

→

Procedure #2

```
Record weight of
cleaned sample
under flowing
    UHP Ar
       |
 Heat to 30°C
       |
Isotherm and
wait for baseline
to stabilize
       |
 Switch to         →    Wait for weight
 1.1% CO/Ar             to stabilize
                             |
                        Switch to
                        UHP Ar
                             |
                     Wait for weight to
                     stabilize and
                     record final
                     reading
```

* No buoyancy corrections since experiments are isothermal.

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Technical Approach: Experimental Details

- Catalyst samples examined in first series of experiments
  - Pt Black - Alfa HiSpec™ 1000
  - Pt/Al_2O_3 - Alfa 5 wt% Pt on gamma alumina
  - Pt/XC-72 - ETEK 20 wt% Pt on carbon XC-72
- Samples were taken from manufacturers bottle and placed into a 3.4ml, high- volume, alumina TG crucible
  - Sample weight kept to around 100mg for each sample
- TG crucible placed onto TGA sample carrier and furnace closed and purged with UHP Ar
  - TGA previously tared and gas flowrates fixed for duration of experiment
  - VERY important that rotameter settings are not changed during the exp.

Technical Accomplishments
Procedure 1: Typical Cleaning Curve

Returning to UHP Ar removes buoyancy effect and mass change Final weight is used for the CO uptake measurement.

Initial weight loss is due to weakly bound adsorbates. E.g. H_2O CO_2 on carbon, etc.

Oxygen step used to oxidize any species that may easily be removed at this T.

H_2 removes the greatest amount of adsorbed species.

Final mass: 128.522mg
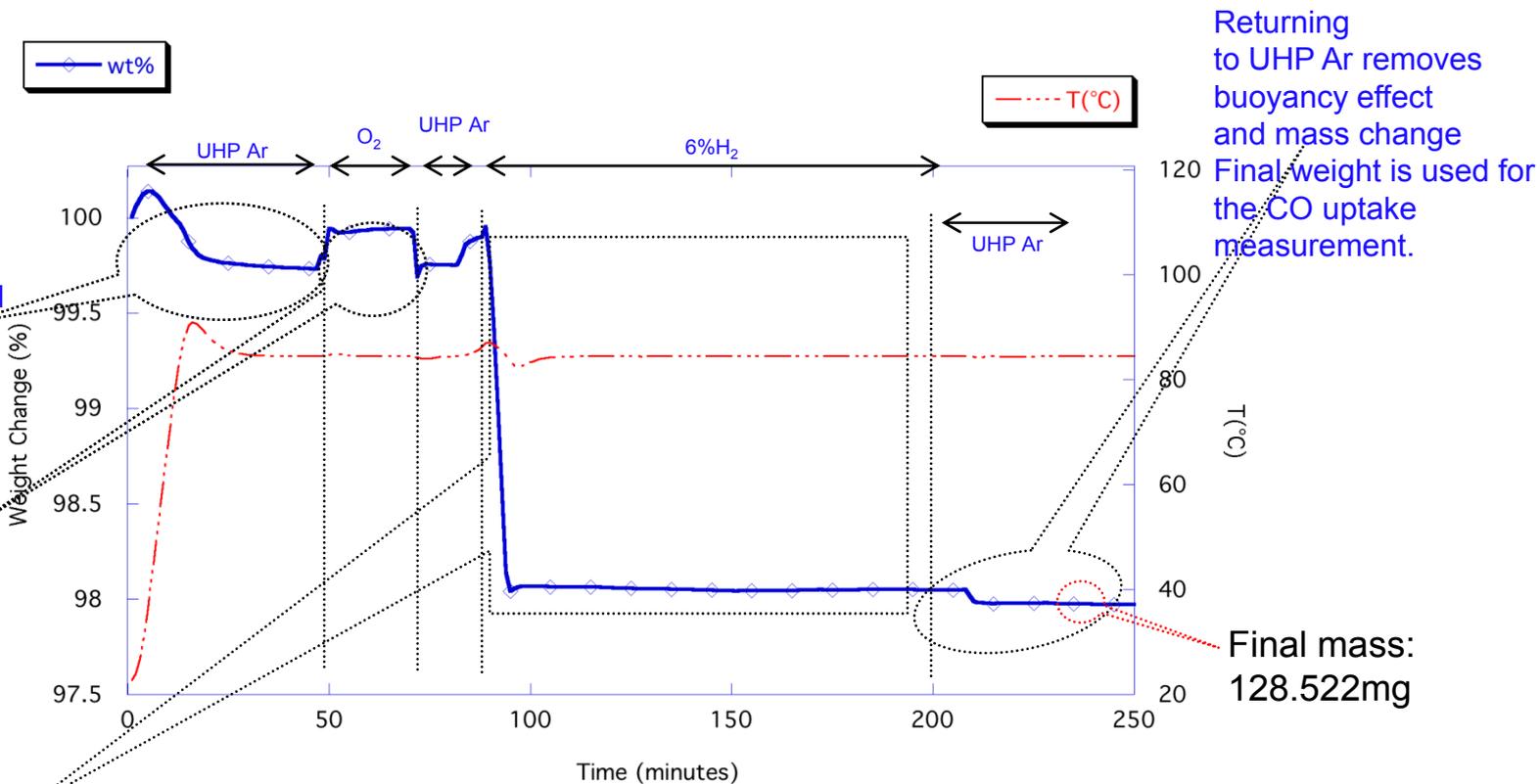
HiSpec™ 1000; Pt black; 131.371mg

25°C, 5K/min to 85°C; isothermal

Technical Accomplishments–
CO adsorption/Pt Black
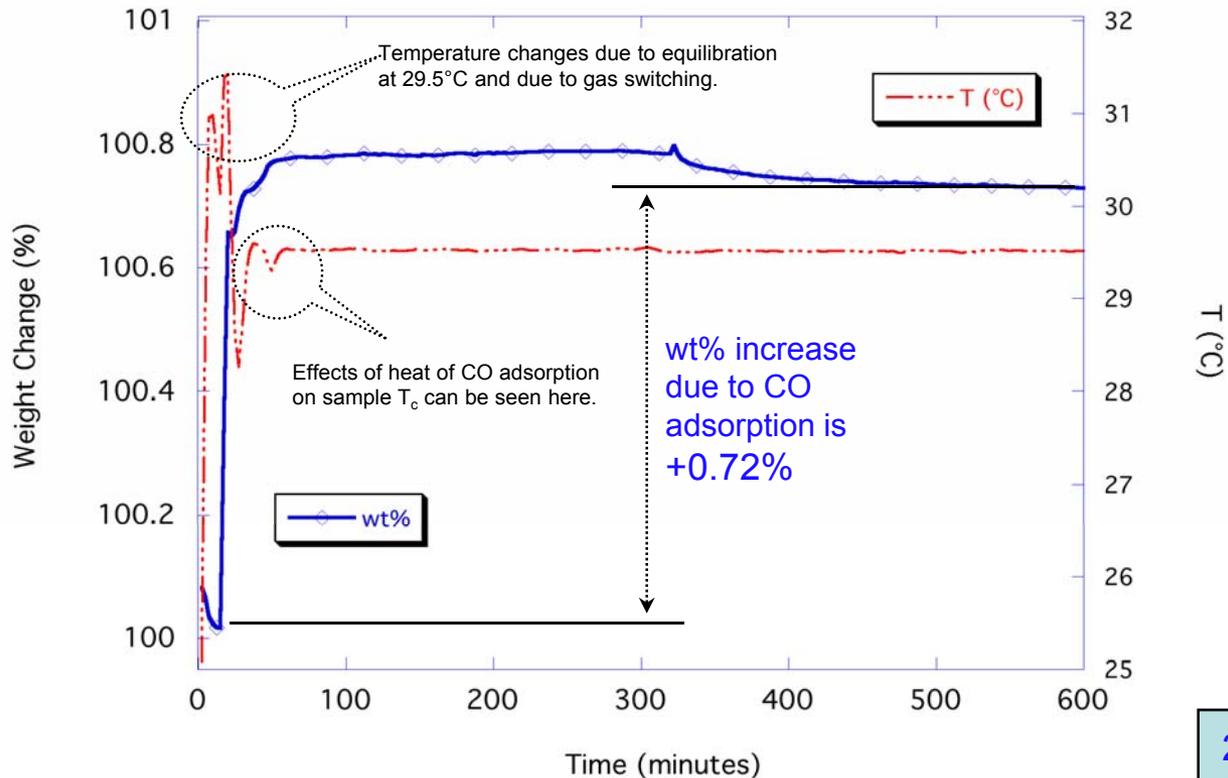
HiSpec™ 1000; Pt black cleaned; 128.522mg

25°C, 5K/min to 30°C; isothermal

Technical Accomplishments–
Pt (5wt%)/Al$_2$O$_3$

Repeat experiments show loss is real, constant and well outside any mass Changes that may be attributed to instrument errors or gas flow Variations (by almost a factor of 3).
• Tightly bound H$_2$O?

wt% increase due to CO adsorption is +0.30%
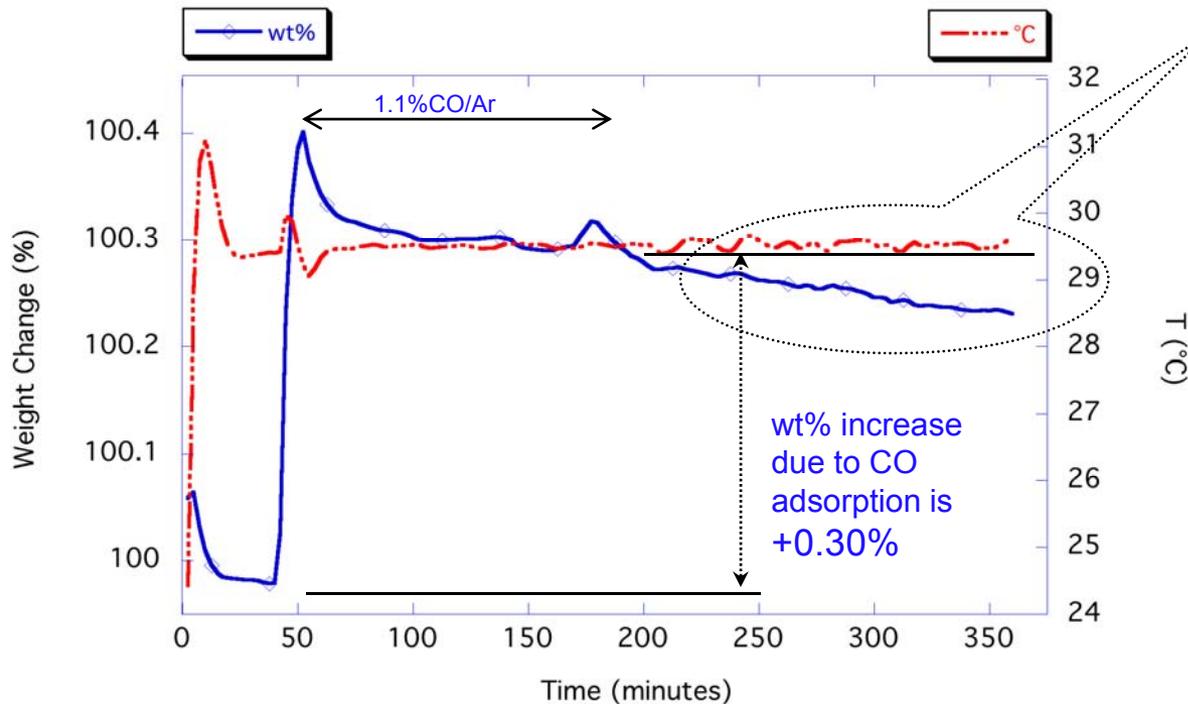
% increase due to CO adsorption on a Pt basis is + 5.97 wt% (immediately after CO absorption.)

Pt (5wt%)/Al$_2$O$_3$; cleaned; 120.613mg

25°C, 5K/min to 30°C; isothermal

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Technical Accomplishments–
20% Pt/C ETEK
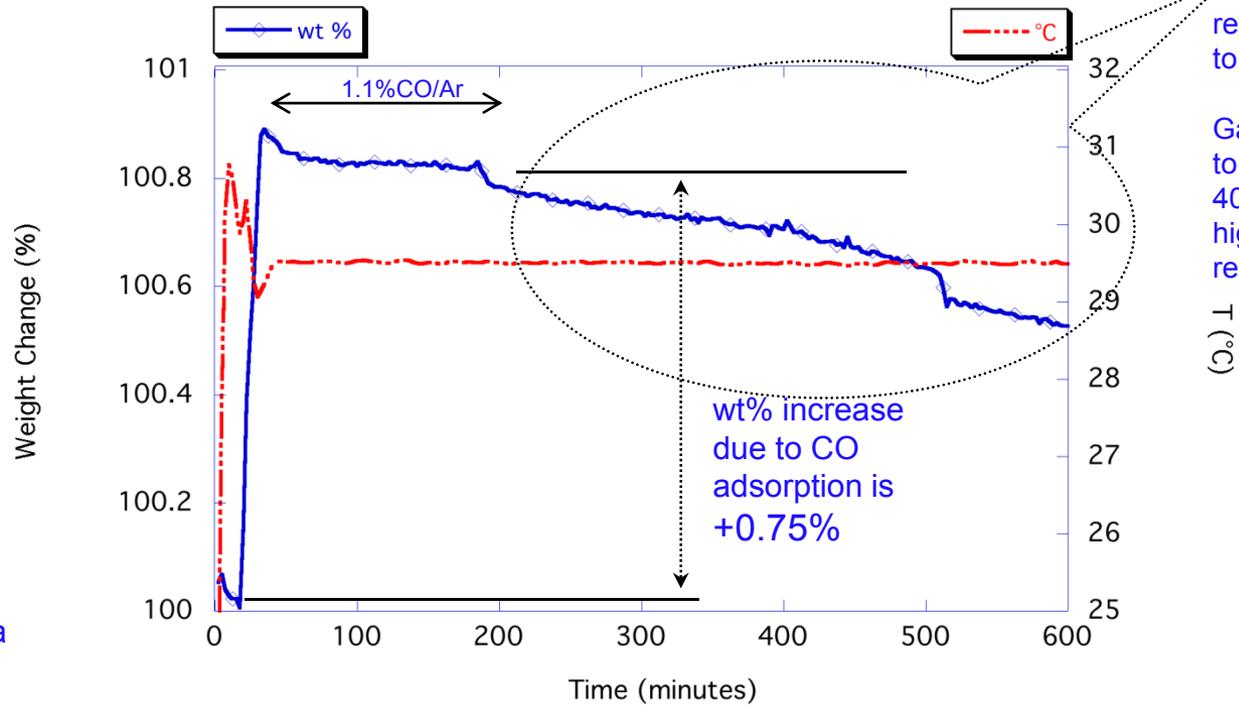
Very similar behavior to Pt on alumina. This will require further investigation to explain. 2X of Pt/Al_2O_3.

Gamma Al_2O_3 is known to hold onto H_2O well 400°C. 85°C may not be high enough to completely remove it from XC-72.

wt% increase due to CO adsorption is +0.75%

% increase due to CO adsorption on a Pt basis is + 3.77 wt% (immediately after CO absorption.)

ETEK Pt (20wt%)/XC-72; cleaned; 123.286mg

25°C, 5K/min to 30°C; isothermal

Summary and a note on experimental error

- **On Pt Basis, CO coverage and calculated SA***
  - HiSpec™ 1000   = +0.72wt%, 25.1m^2/g
  - Pt (5wt%)/Al_2O_3 = +5.97wt%, 210 m^2/g
  - ETEK Pt(20)/XC-72 = +3.77wt%, 132 m^2/g

- Both Pt/Al_2O_3 and ETEK catalysts showed a high rate of weight loss after CO flow was terminated (approx. 20 and 40µg/hr respectively). This requires further investigation.
- Worst case drift rates due to temperature-induced gas flow variations have been measured on the order of 7-8µg/hr with the average observed to be around 2-3µg/hr.
  - Potential error of 0.04% for the sample sizes and durations used in this work.
- Drift is cyclic (T & P) and averaged over several days is less than 1µg/hr.

* using a value of 1.63×10^{-19}m^2/CO molecule calculated from the work of K. Shinozaki, T. Hatanaka, and Y. Morimoto, "Pt Ultilization Analysis Using CO Adsorption," ECS Transactions, 11 (1) (2007) 497-507.

Future Improvements to Gravimetric Capability

- Mass flow controllers to remove temperature- (and barometric pressure-) induced drift.

- Gas supply bottles must be isothermal.

- Netzsch Aëolos quadrupole mass spectroscopy system has been added to the STA-449 to correlate mass loss to gas species during cleaning, adsorption, and to probe any surface reactions occurring on the catalysts.

- Other QMS applications are being developed and applied at present time.

Technical Accomplishments
H$_2$S Methods Update

- Analytical technique using commercial Ag/AgS ion probes to trap and concentrate trace amounts of H$_2$S present in gas streams and measure accumulated [S$^=$] with low error.

- Low concentrations of H$_2$S may be measured by concentrating in a high pH chemical trap with anti-oxidant additives over a known period of time (Orion® SAOB diluted 50 vol%).

  - Integration followed by lead nitrate titration using ion probe to determine endpoint.

  - Cumulative errors determined for titration process (including errors assoc. with volume meas., preparation of [Pb^{2+}] titrant, etc.) is 2%.

- Method successfully used to measure trace quantities of H$_2$S permeating through Nafion® polymers .

  - Methods used for N117, N112, and N212 membranes at 25°C

  - 50 cm^2 with GDL (no catalyst), 1000ppm and 96 ppm sources of H$_2$S used, mixed from pure H$_2$S

26°C

Orion SAOB
1M NaOH + EDTA
+ ascobic acid
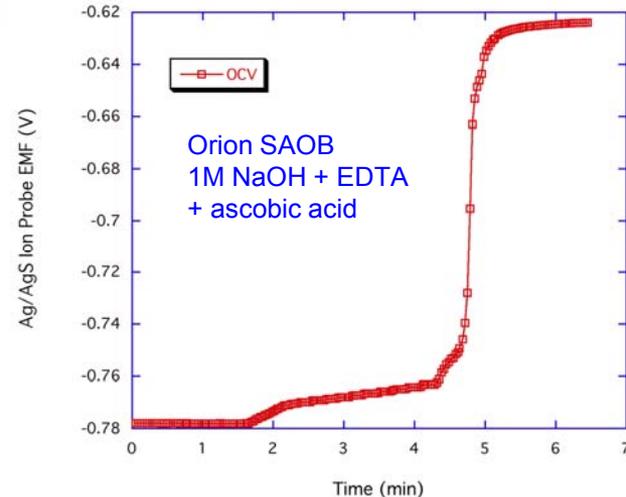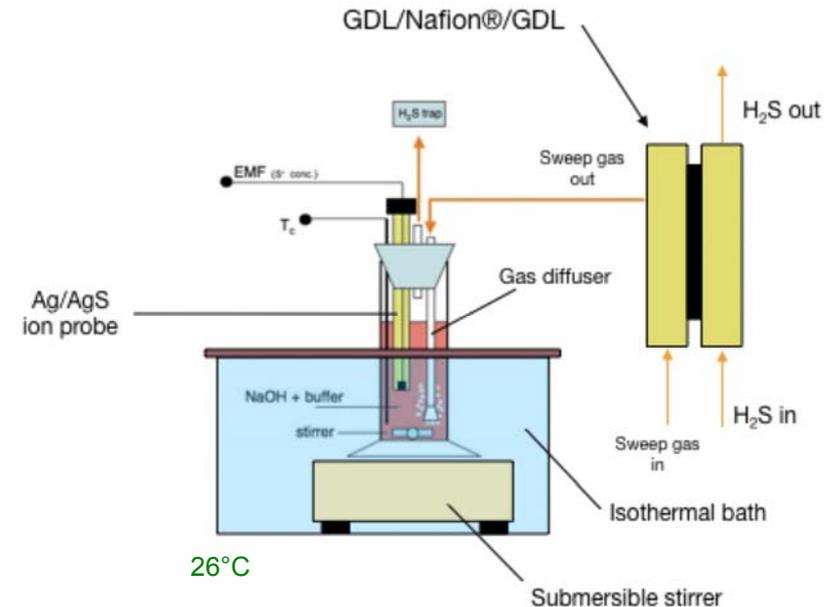
Sample titration of a 60ml trap used to capture H$_2$S permeating through N112 at a rate of 40 ng/s.

Technical Accomplishments
Complementary Sulfur Analytical Technique
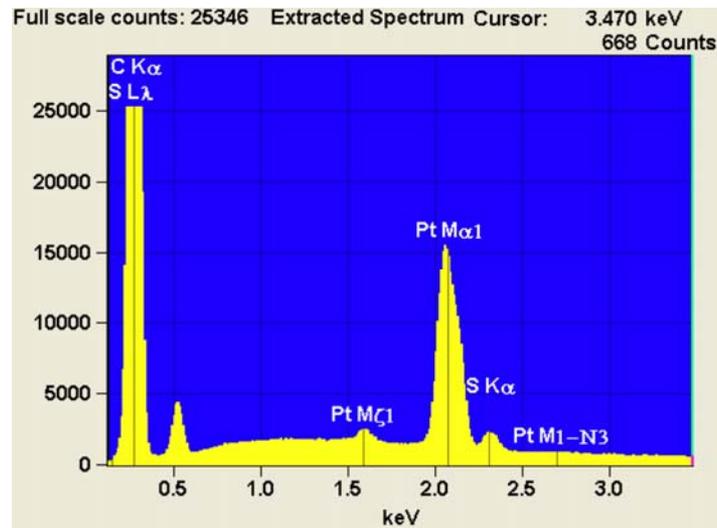
As received S from carbon support
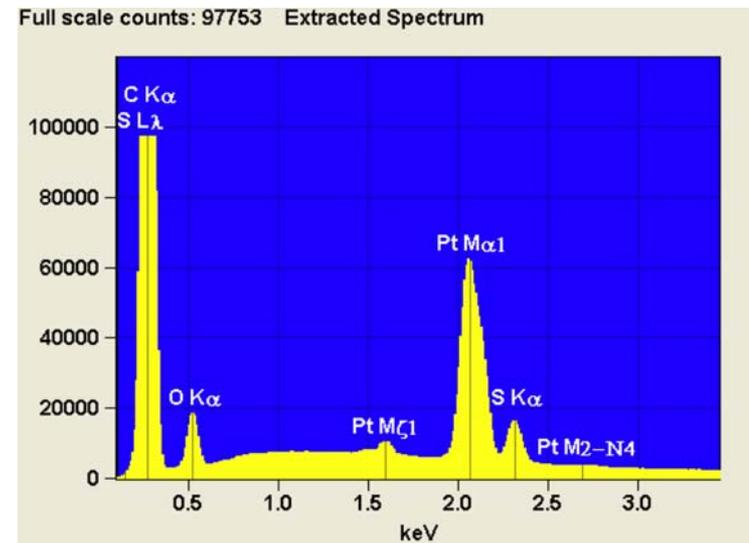
After H$_2$S Exposure carbon

ESEM shows 2% S$_{wt}$ gain after Pt/C which agrees with
LANL-developed ultra-low H$_2$S analytical technique
similar conditions

Technical Accomplishment
Ammonia Method Development
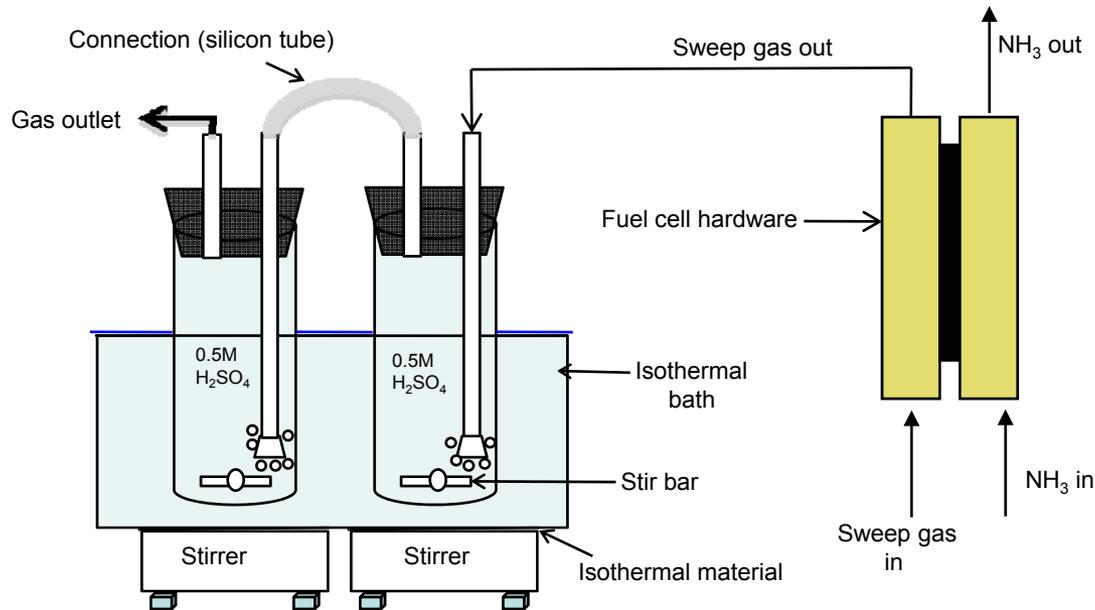
Erlenmeyer in series configuration, immersed in a water bath at 10-15°C while collecting the outlet gas

The ammonia quantified by modified ASTM method for ammonia/nitrogen in water

Ammonia Method

The ammonia in solution permeates through the membrane and dissolves in the internal filling solution (0.1M NH_4Cl solution), reacting reversibly with water and altering the pH of the internal solution.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$
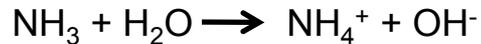
- The working electrode potential, sensitive to OH^-, is governed by Nernst equation,

$$E = E_0 - S \log [OH^-]$$

Since the filling solution has a sufficiently high concentration of NH_4Cl:

$$[OH^-] = [NH_3] \times K_{eq}$$

the electrode response to ammonia is also

$$E = E_0^1 - S \log [NH_3]$$

Electrode

Hydrophobic gas-permeable membrane
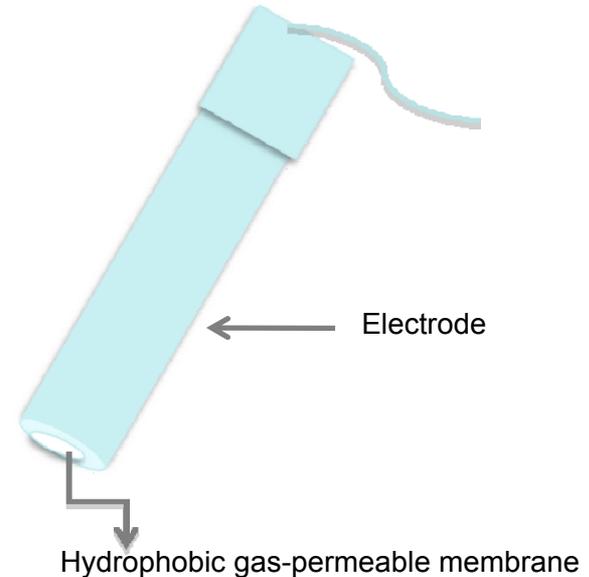
Equilibrium equation:

$$K_{eq} = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Carbon Monoxide Results
Concentration, Temp, Pt loading

1 ppm CO
5 ppm CO
10 ppm CO

80°C

30°C
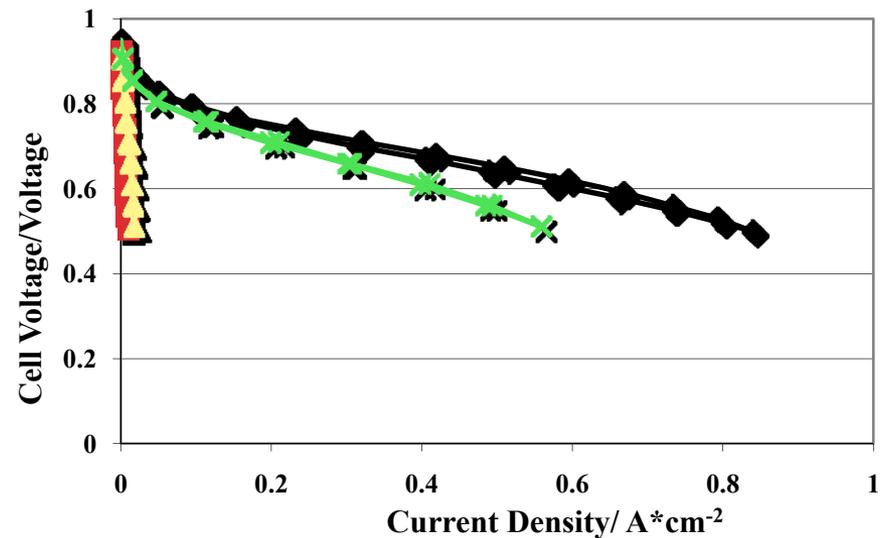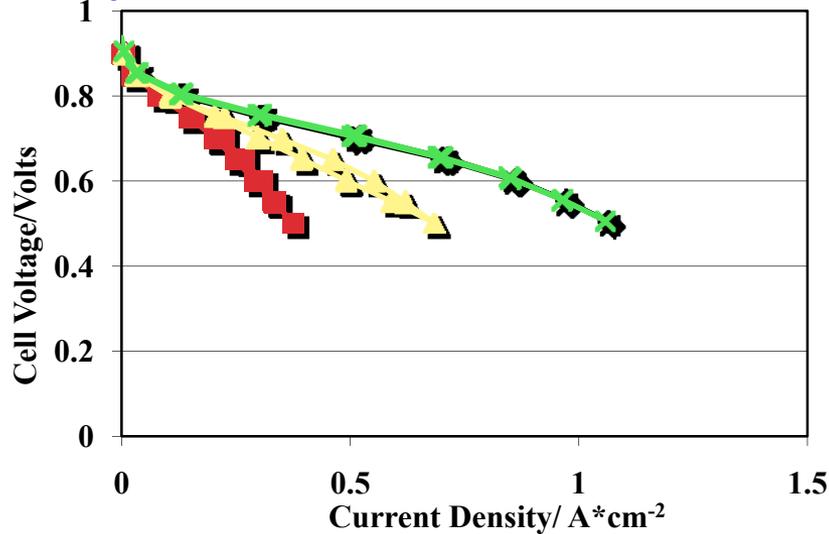
50cm², N112, P: 30/30 psig
H_2/Air: 400/2100 sccm
100% RH

- The increase in CO concentration translates to an increase in performance loss
- At low Pt loadings* and 80°C; tolerance to 1 ppm CO is achievable
- Clearly as the temperature decrease so does the CO tolerance this maybe problematic during start-up.

Carbon Monoxide Results
Concentration, Temp, Pt loading

1 ppm CO
5 ppm CO
10 ppm CO

80°C

A/C: 0.1 mg Pt/cm²

Cell Voltage/Volts

Current Density/ A*cm⁻²

A/C: 0.1/0.2 mg Pt/cm²

Cell Voltage/ Volts
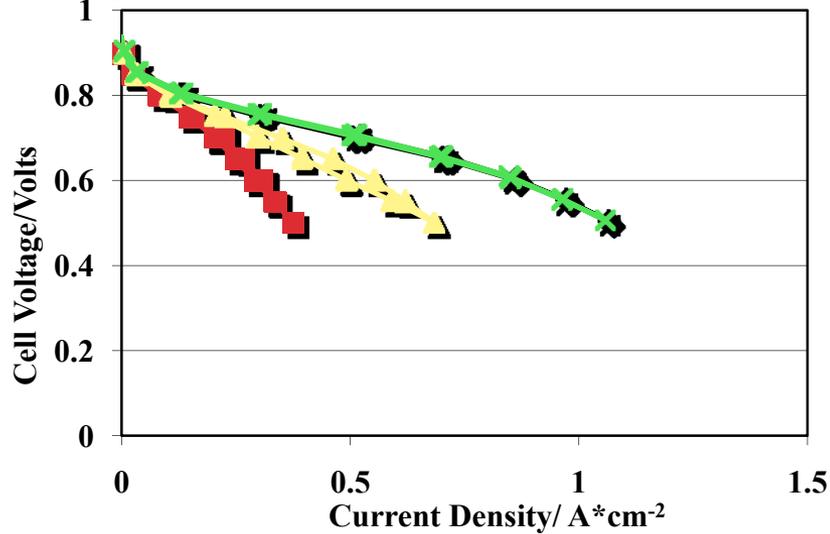
Current Density/ A*cm²
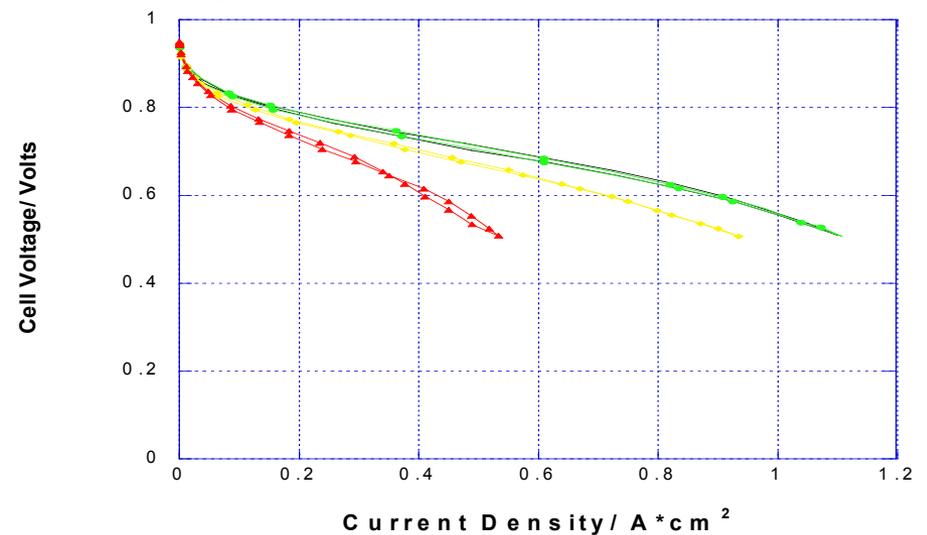
50cm², N112, P: 30/30 psig
H_2/Air: 400/2100 sccm
100% RH

- Clearly changing the cathode loading does not impact the CO tolerance.
- Results nearly identical for two different FC with 0.1 mg Pt/cm² on the anode

H₂S Results

100 ppb H₂S
- X-axis: Time (h), 0 to 140
- Y-axis: Voltage (V) @ 40A / Volts, 0.3 to 0.7
- Labels: H₂S on, H₂S off

250 ppb H₂S
- X-axis: Time (h), 0 to 40
- Y-axis: Voltage(V) @ 40 A, 0 to 0.7
- Label: H₂S on

100 ppb H₂S for 100hrs
- X-axis: VOLTAGE/ VS HRE, 0 to 1.5
- Y-axis: CURRENT DENSITY (A/cm²)
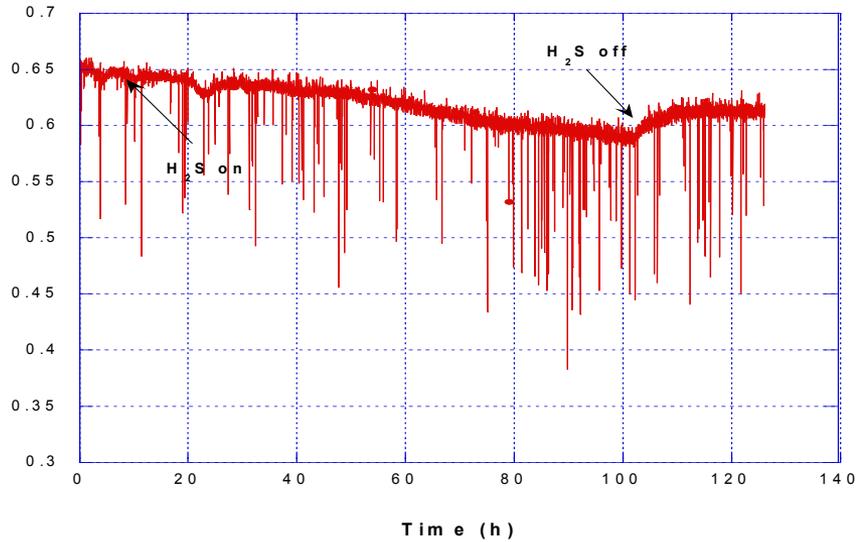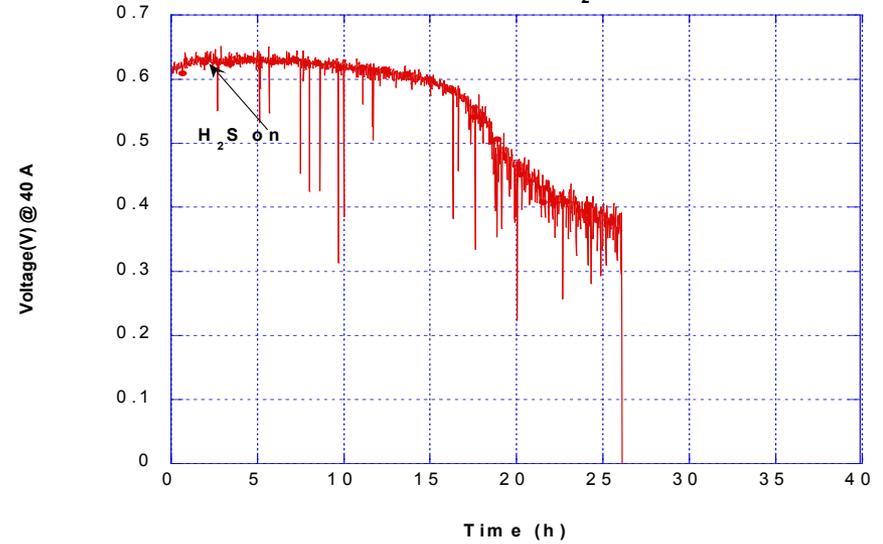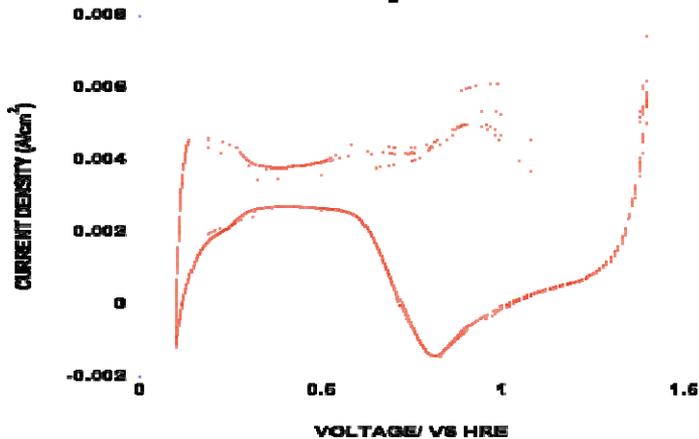
2 mil, /0.1/0.2 mg Pt/cm²
80°C, 100% RH, 30 psig

H₂/N₂: 500 sccm; 80°C, 100% RH(sat)
Scan rate: 20 mV/S, Sweep 0.1-1.4 V

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H₂S Results

0.5ppm H₂S poisoning for 3.5h at 60A

λH$_2$=2.28, Air=2100sccm
T=80/105/80C
P=30/30psi

H₂S on

H₂S off

C V

Voltage@60A (Volts)

Time (hours)

0.5ppm H₂S poisoning for 3.5h at 40A

H₂S on

H₂S off

C V

λH$_2$=2.28, Air=2100sccm
T=80/105/80C
P=30/30psi

Voltage@40A (Volts)

Time (hours)

0.5ppm H₂S poisoning for 3.5h at 20A

H₂S on

H₂S off

C V

λH$_2$=2.28, Air=2100sccm
T=80/105/80C
P=30/30psi

Voltage@20A (Volts)

Time (hours)

CR050609_anodeCV_0.5 ppm H₂S @40A for 3.5h
+3.5h recovery

Current Density (A/cm²)

Voltage (Volts)

H$_2$/N$_2$: 500 sccm; 80oC, 100% RH(sat)
Scan rate: 20 mV/S, Sweep 0.1-1.4 V

- Voltage response for 0.5 ppm H₂S short term exposure at different currents
- Cyclic Voltammetry used to oxidize S-species from Pt surface (cleaning?)

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H$_2$S Results
Current dependence/Normalized voltage

0.5 ppm H$_2$S for 3.5 hrs

Legend:
- Norm V @ 20A
- Norm V @ 40A
- Norm V @ 60A

H$_2$S on

Normalized Voltage vs. Time/hours

2 mil, 0.2 mg Pt/cm^2
80°C, 100% RH, 30 psig
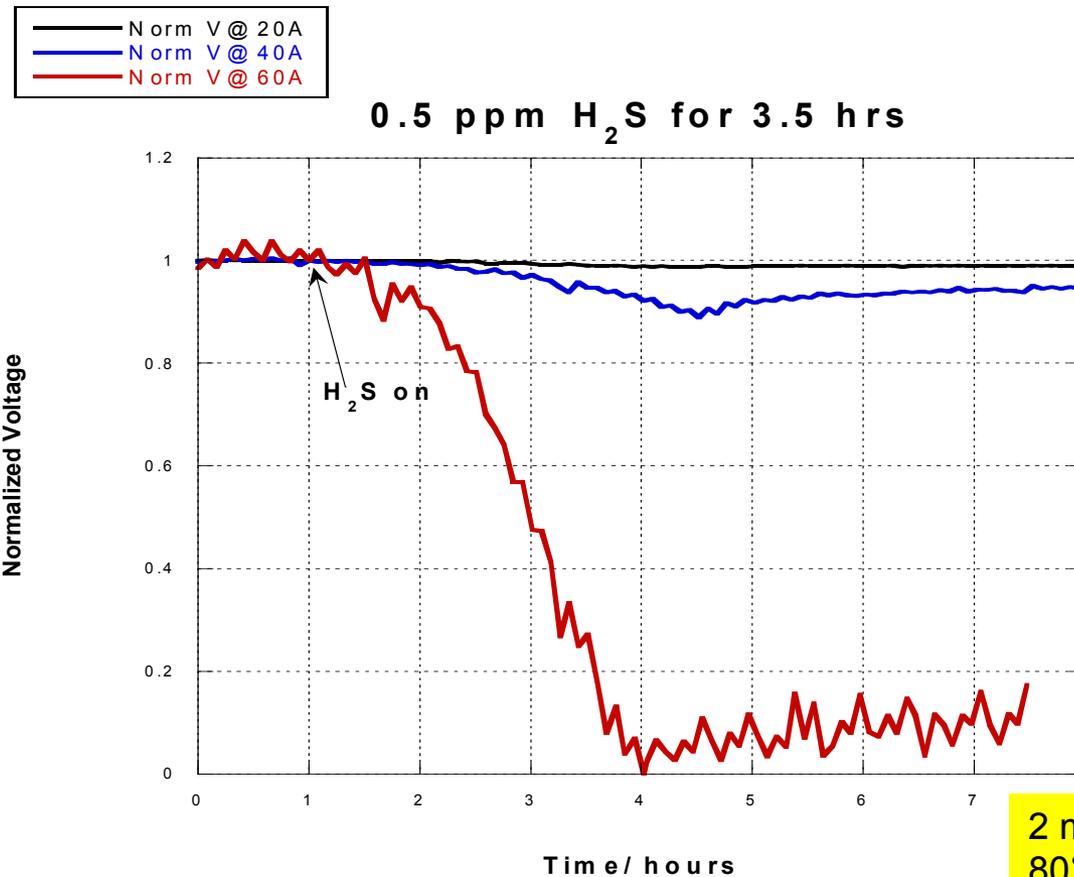
• Performance degradation more pronounced at higher currents (i.e. low voltages.)
(Voltage-dependence and/or S-crossover)

Ammonia Studies

1 ppm NH$_3$, 40A, 80°C, 100% RH
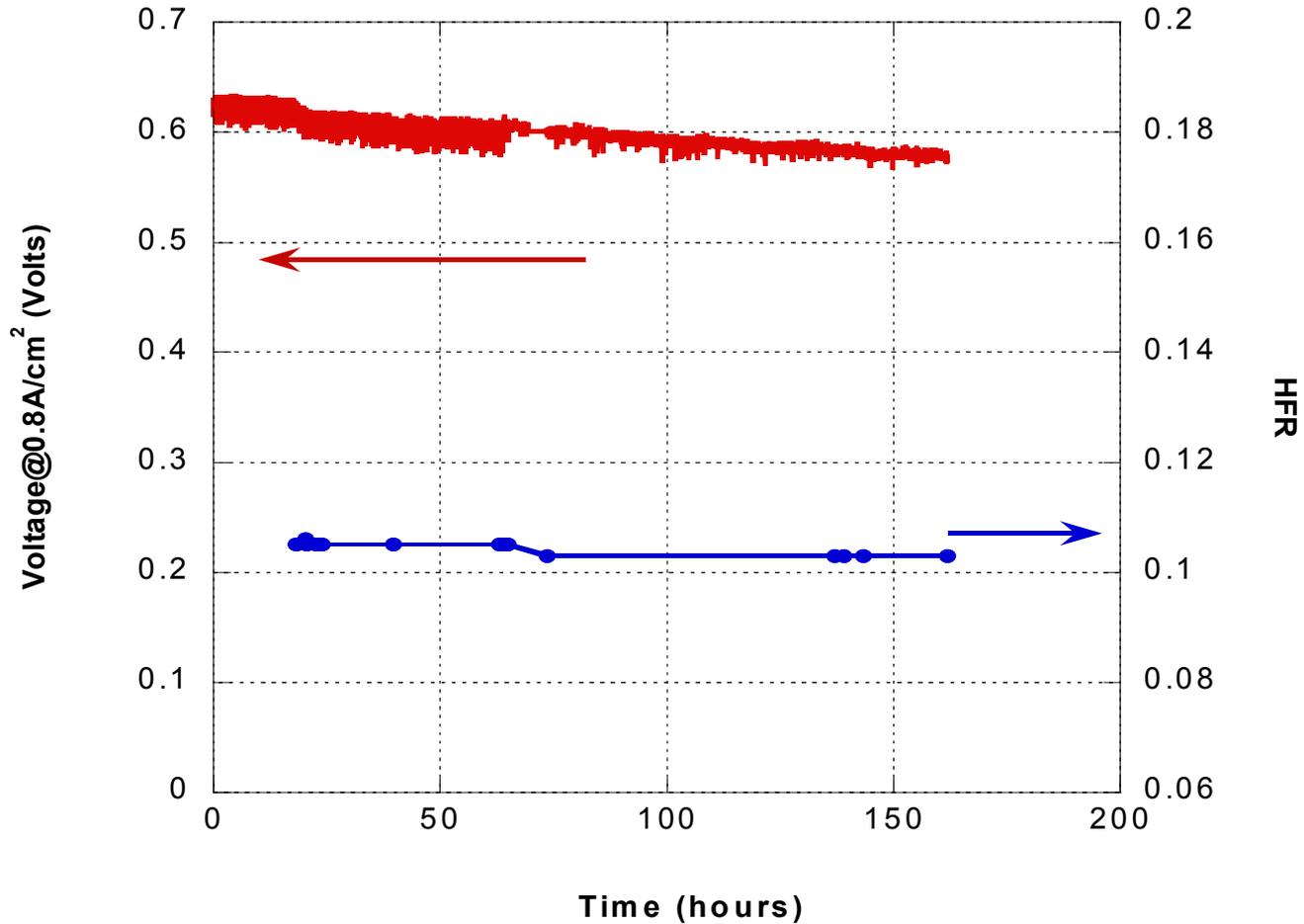
Voltage response over time for 1 ppm NH3, HFR remain constant

Combined Ammonia Studies

Effects of 10ppb H_2S and 1ppm NH_3 Mixture

Effects of 100 ppb CO and 1 ppm NH_3 Mixture
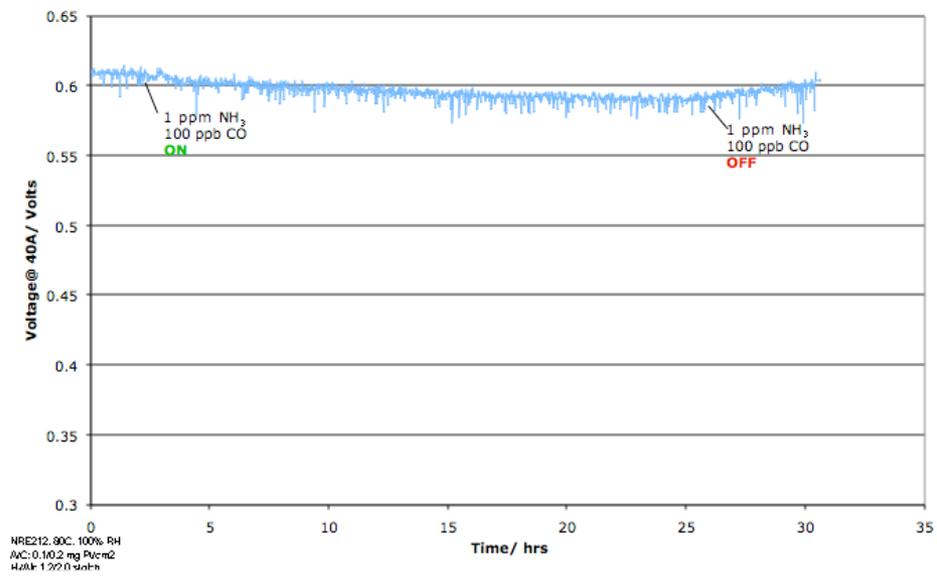
Mixture of 100 ppb CO: 4 ppb H_2S: 1 ppm NH_3
A/C: 0.1/0.2 mg Pt/cm²
80°C, 100% RH, 83% Utilization

- NH_3 showed 20 mV loss in 24 hrs
- H_2S/NH_3 mixture showed 38 mV losses in 24 hrs
- CO/NH_3 mixture showed 20 mV losses in 24 hrs
- CVs show minimal adsorbates, HFR constant

- $CO/H_2S/NH_3$ shows 52 mV losses over 70 hrs
(HFR increased 0.003 Ω* cm²)~ 2.4 mV loss

- *Sources of Losses?*

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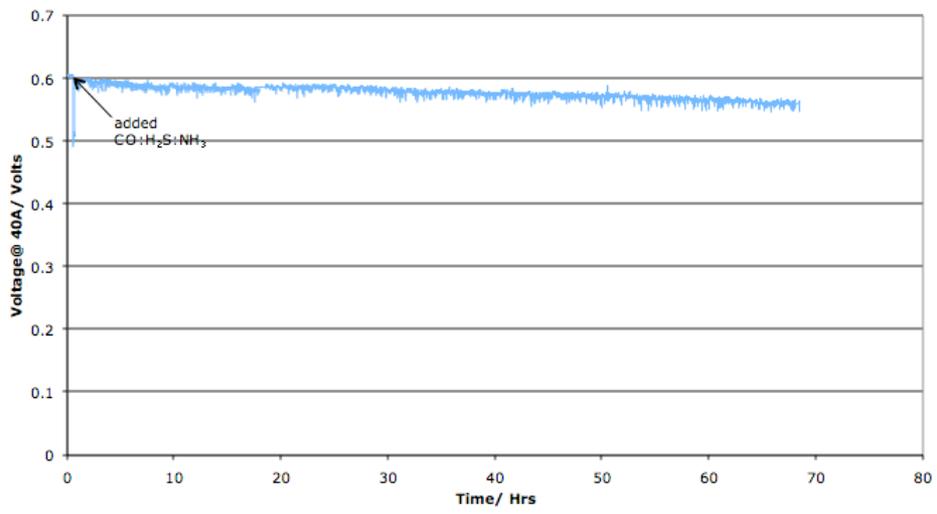
Technical Accomplishments Summary

- *Completed DOE round robin study by including data sets from NIST and the final from LANL*
- Analytical method for measuring trace levels of Sulfur developed. Now being used to quantify S permeation rates.
- Tested critical constituents (CO, H_2S, and NH_3) individually and in combination

Future Work

- Optimization of our analytical method for H_2S and modifying it for in-line analysis.
- Complete initial development of ammonia analytical method
- Continue testing the critical constituents (CO, H_2S, and NH_3) and populating the test matrix.
- Continue providing data sets and interacting with FC modelers.

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