DOE Hydrogen Program

Hydrogen Fuel Quality

The Year In Review

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Los Alamos National Laboratory

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Project ID # SCS4

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Overview

Timeline

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

Barriers

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

Budget

- Total project funding: $1,100K
  - DOE share: 100%
  - Contractor share
- Funding received in FY07: $250K
- Funding for FY08: $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-07	Milestone: Evaluate sensitivity of H2S specific ion analysis methods. Completed
Mar-08	Milestone: Evaluate cross interference effects of H2S specific ion analysis methods. Completed
Jun-08	Deliverable: Report on analytical methods development. Completed Milestone: Determine tolerable impurity level specifications for hydrogen fuels. Completed sulfur Milestone: Evaluate sensitivity of NH3 specific ion analysis methods. In progress*
Sep-08	Milestone: Evaluate cross interference effects of NH_3 specific ion analysis methods. Milestone: Demonstrate proof of concept of CO analysis by electrochemical methods.

* Status as of 4/18/08

Technical Approach

- Conduct gauge studies with testing labs and address experimental differences, thus increasing the confidence in the data.
- Create and standardize a Data Reporting Format
- Develop and test new analytical methods for detecting ppb levels of contaminants.
- Test the critical constituents (NH_3, CO, and H_2S) and provide data sets to FC modelers to establish predictive mechanistic models.

LANL's role in understanding the impact of fuel impurities

On PEFC Performance

On Developing Codes and Standards

***About the Fuel Impurities Effects*:**

The focus is to understand the fundamental interactions and mechanism of impurities on fuel cell performance, including the investigation & development of mitigating strategies and recovery techniques. These efforts are geared towards meeting DOE's 2010 and 2015 Pt loadings. Data generated in these activities are directly communicated to the modeling effort.

Subtask 2.1: Fuel Quality Impacts

- to gain confidence in fuel cell results from the different test labs involved in hydrogen quality efforts by conducting a gauge study. (DOE Round Robin)
- to provide all the relevant information necessary for reproducing experiments and, more importantly, to supply useful information to modelers, MEA manufacturers, hydrogen suppliers and OEMs.

Subtask 2.2: Analytical Methods Development

- to develop and/or modify existing analytical techniques to detect fuel impurities in the ppb (10^{-9}) range.
- to test and determine the impact of CO, H_2S, and NH_3 in the fuel stream in order to develop a hydrogen fuel quality standard.

These analytical techniques will develop the tools to be able to accurately measure impurities at the proposed standards level

The two tasks are separate but complimentary in that they leverage one another. The Fuel Impurities solicitation winners participated in the LANL-led DOE Round Robin to ensure consistent testing procedures and data collection. The learnings from the Fuel Impurities Efforts help establish testing priorities in the Hydrogen Quality effort.

This effort consists of several collaborators:
UConn, Clemson, SRNL, University of S. Carolina, NIST, and HNEI.

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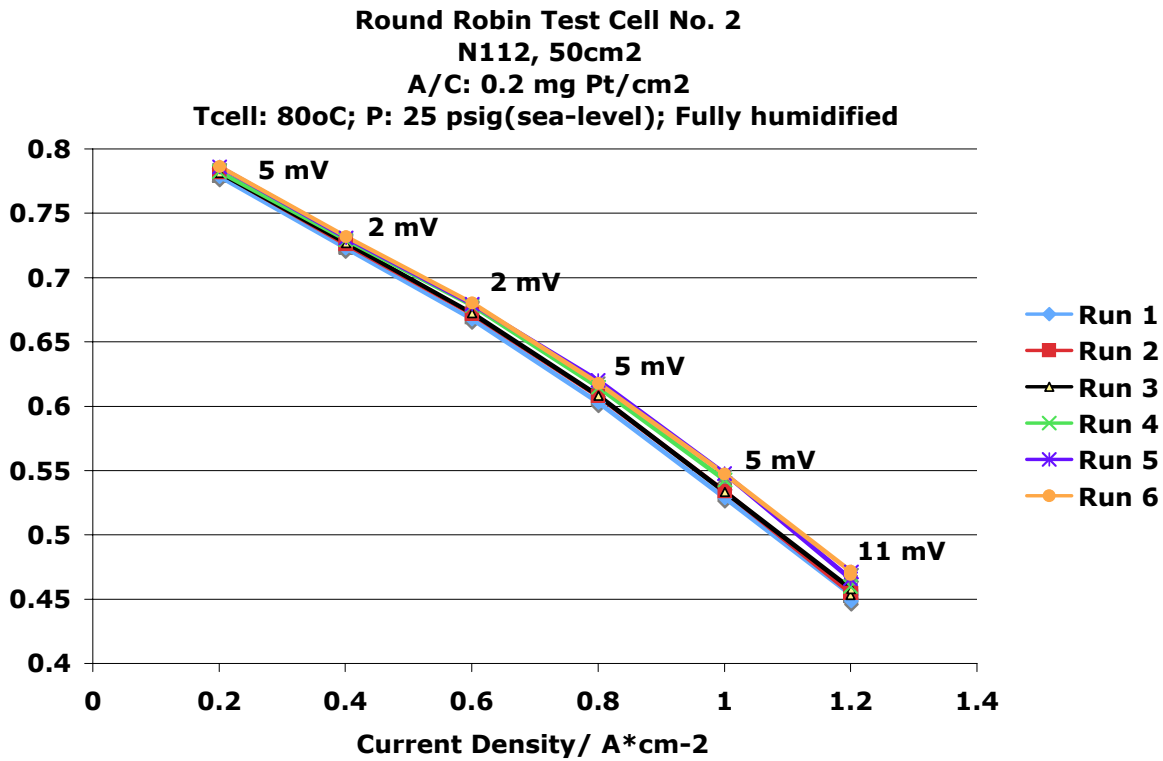
Technical Accomplishments

DOE Round Robin Results

The VI-curves were:

- Taken after completing a break-in procedure (0.6V for 1 hr then cycled 20 minutes at 0.5 and 0.7V for 6 hrs, overnight at 30A (cc))
- Run in constant current mode using 1.2/2.0 stoichs (H_2/Air) until **deviation ≤ 5 mV from the previous VI-curves at multiple points (Pressurized and Ambient)**



The average of the last 3 VI-curves was submitted for a Round Robin Study.

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Technical Accomplishments

DOE Round Robin Results, Cont.

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- Taken after completing a break-in procedure (0.6V for 1 hr then cycled 20 minutes at 0.5 and 0.7V for 6 hrs, overnight at 30A (cc))
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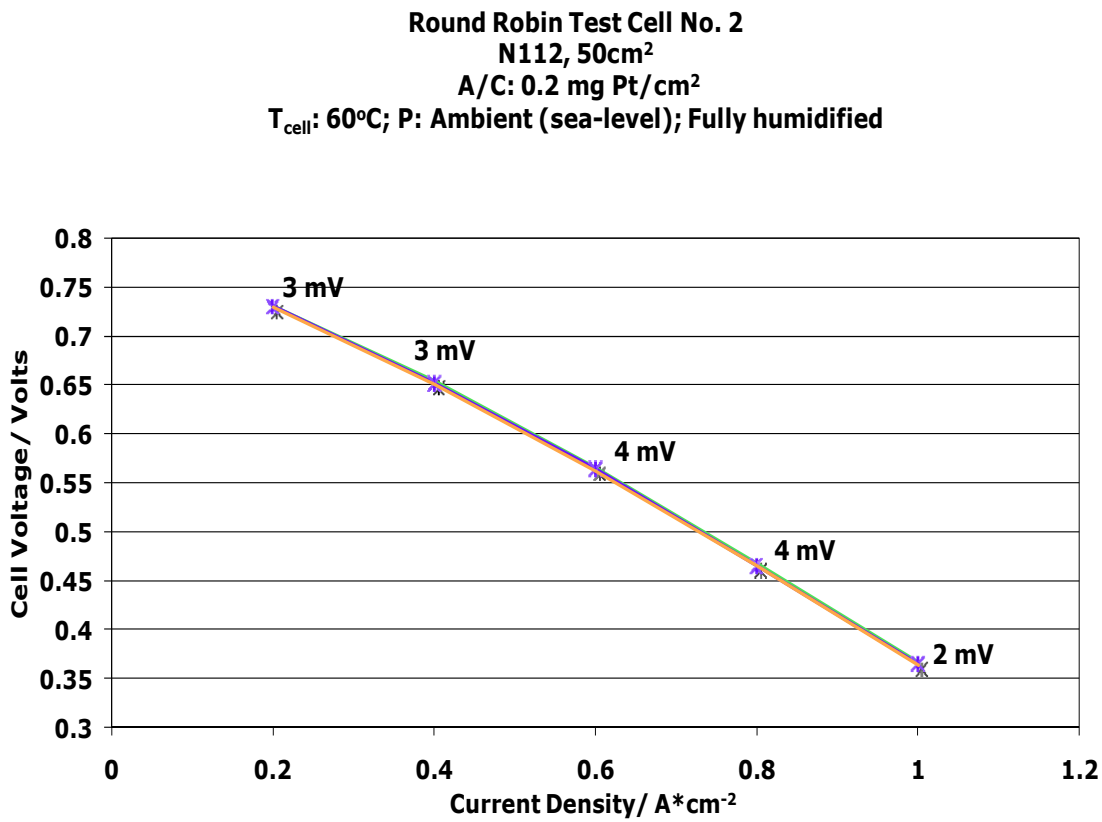

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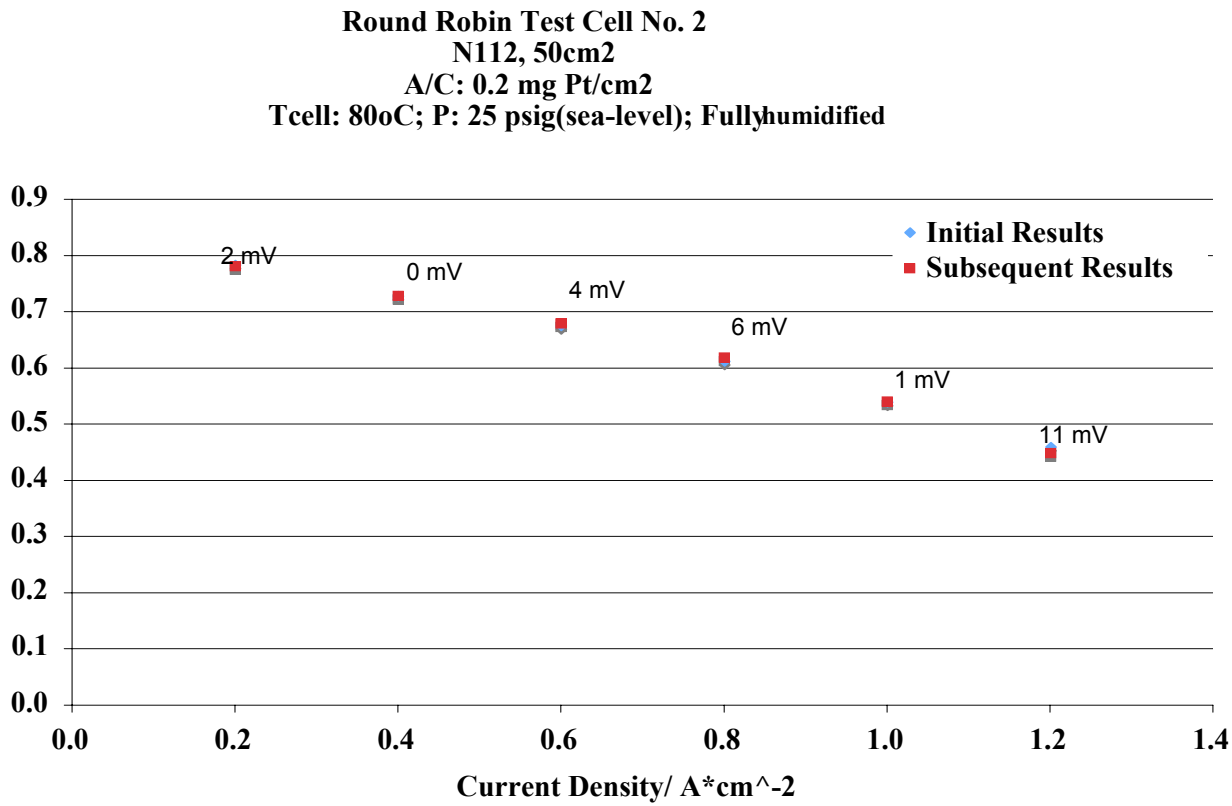
Technical Accomplishments

DOE Round Robin Results, Cont.



- Before and after tests showed nearly identical results, thus making the round robin results valid for comparison.
- Largest difference observed in Mass Transport Region
- Further analysis/tests to probe those differences

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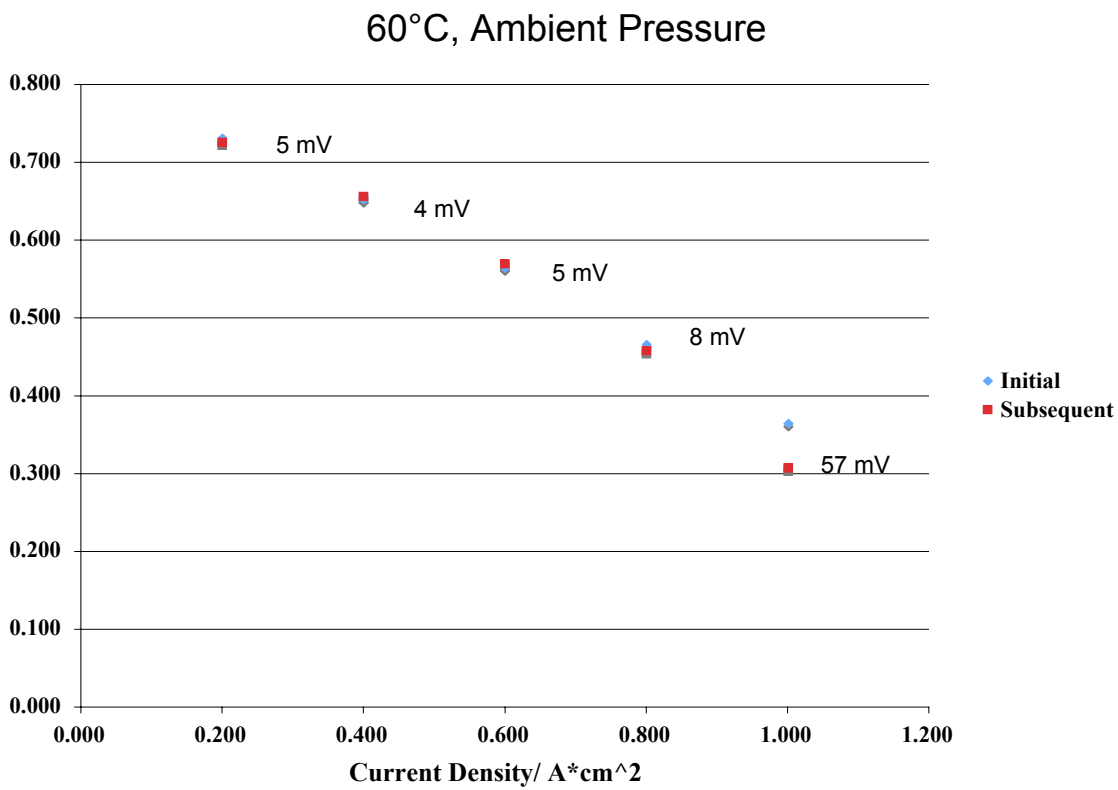
Technical Accomplishments

DOE Round Robin Results, Cont.



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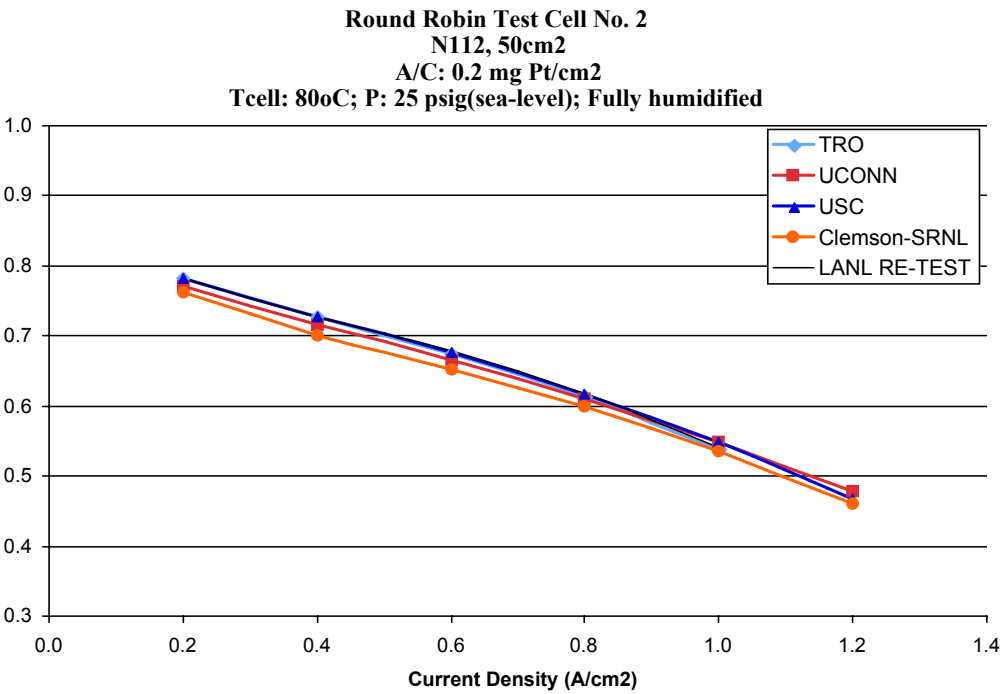
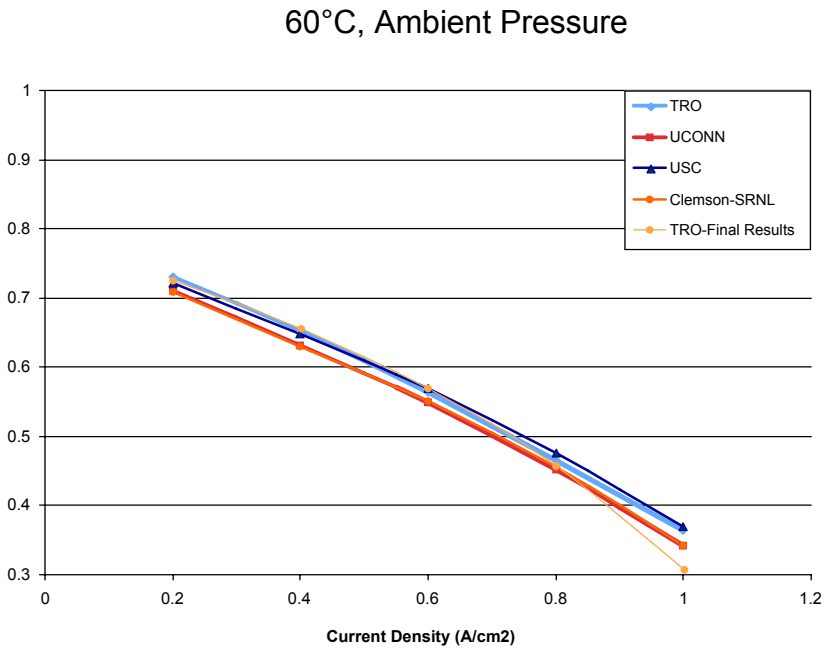
Technical Accomplishments

DOE Round Robin Results, Comparisons





- Overall good agreement between sites, discussions are on-going to address differences.
- Other test sites have expressed interested in the cell and are scheduled to test.
- Final Report in progress

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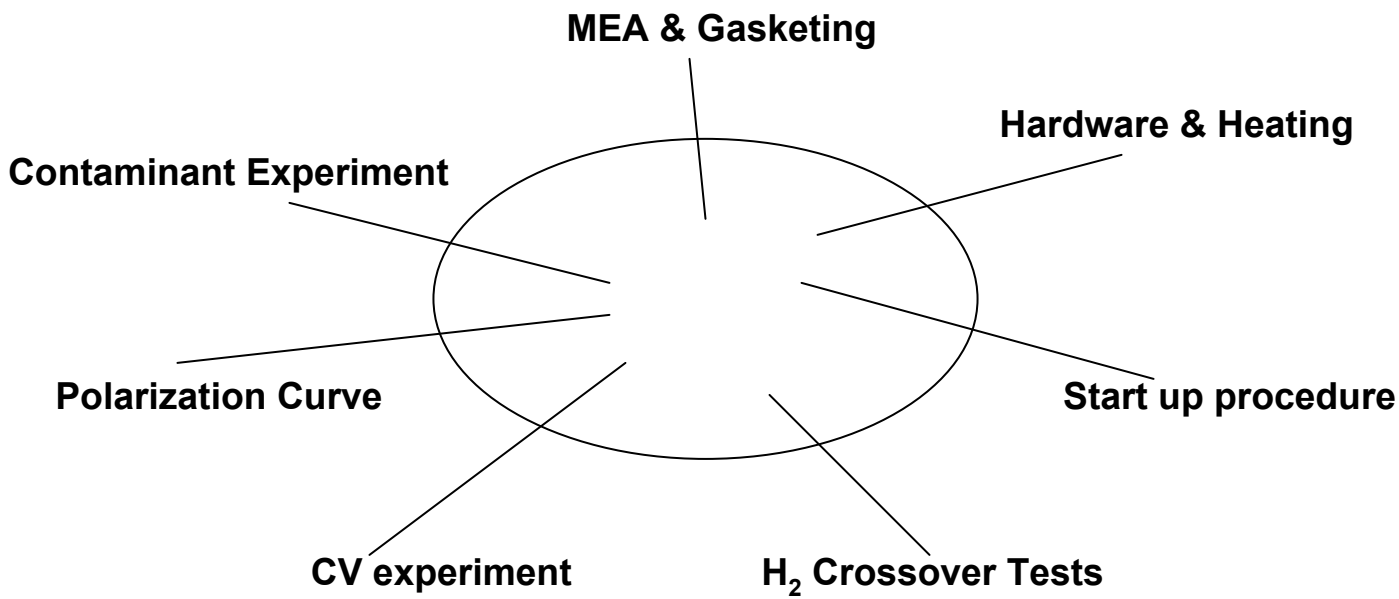
Data Reporting Format



The document's objective is to describe in detail all the information necessary to describe and/or reproduce the performed contaminant experiment

Data Reporting Format

excerpt from start-up procedure

FC Operating Conditions	
Diagnostic Identifier (e.g. MEA 012)	LANL_TR040908
Gas Type	
Anode Gas Composition & Quality (e.g. 100% H_2, 99.999%)	electrolysis grade
Cathode Gas Composition & Quality (e.g. oiless compressor, in-house produced)	oiless compressor
Stoichiometry Mode	
Flow Tracking (yes / no)	yes
Flows	
Anode Stoich (e.g. 1.2 or N/A)	1.2
Cathode Stoich (e.g. 2.0, or N/A)	2
Anode Fixed Flow (e.g. 1200 sccm, or N/A)	n/a
Cathode Fixed Flow (e.g. 3 NL/min, N/A)	n/a
Minimum Flow	
minimum anode flow setpoint (e.g. 80 sccm, or flow at 0.2 A/cm^2)	80 sccm
minimum cathode flow setpoint (e.g. 80 sccm, or flow at 0.2 A/cm^2)	343 sccm

Temperatures	
Cell (°C)	80°C
Humidification	
Anode Humidifier w/o Contaminant (°C)	80°C
Anode Humidifier w Contaminant (°C)	by pass
Anode RH (%)	100%
Cathode Humidifier (°C)	80°C
Cathode RH (%)	100%
Pressures	
Anode Inlet (psia)	
Anode exit (psia)	30
Cathode Inlet psia)	
Cathode exit (psia)	30
Start-Up Procedure (e.g. Company A's Protocol, cycling from 0.2-0.7V until currents stabilize)	LANL protocol

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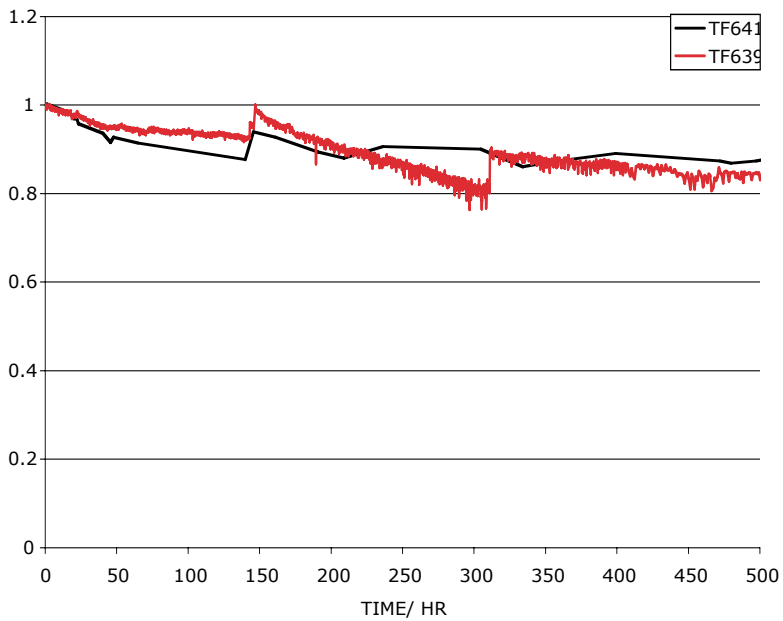
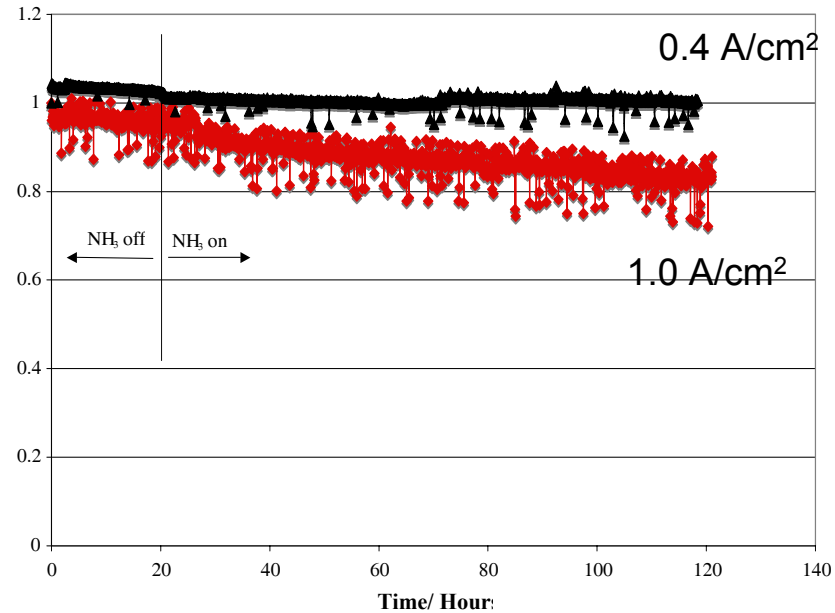
Ammonia Studies

Effects of 1ppm



N112, 50cm^2, 80°C
A/C: 0.2 mg Pt/cm^2
40 A(cc), fully humidified



N112, 50cm^2, 80°C
A/C: 0.1/0.2 mg Pt/cm^2
40 A(cc), fully humidified

The graph on the left shows reproducibility after two different cells were exposed to 1 ppm NH_3. Losses observed were ~70 mV.

The graph on the right shows the impact of NH_3 at 0.4 and 1 A/cm^2. Clearly, the losses become more pronounced at the higher current density. The data show that with more water, the NH_4^+ migrates to the cathode faster.

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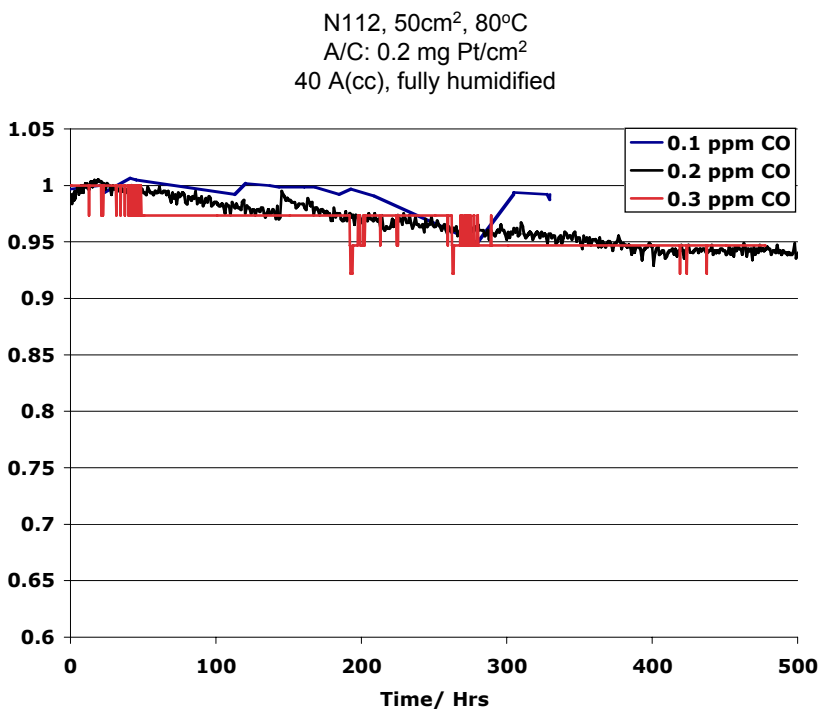
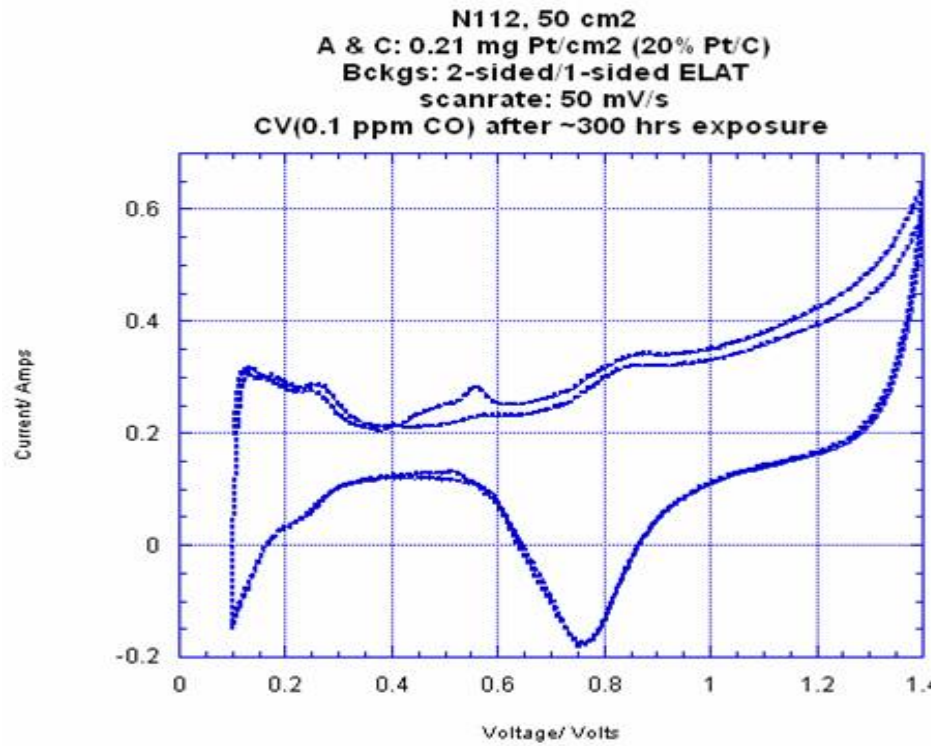
Carbon Monoxide Studies





- 100 ppb CO showed ~5 mV loss over 300 hrs
- 200 and 300 ppb CO showed ~30 mV
- Some CO adsorption detected by CV

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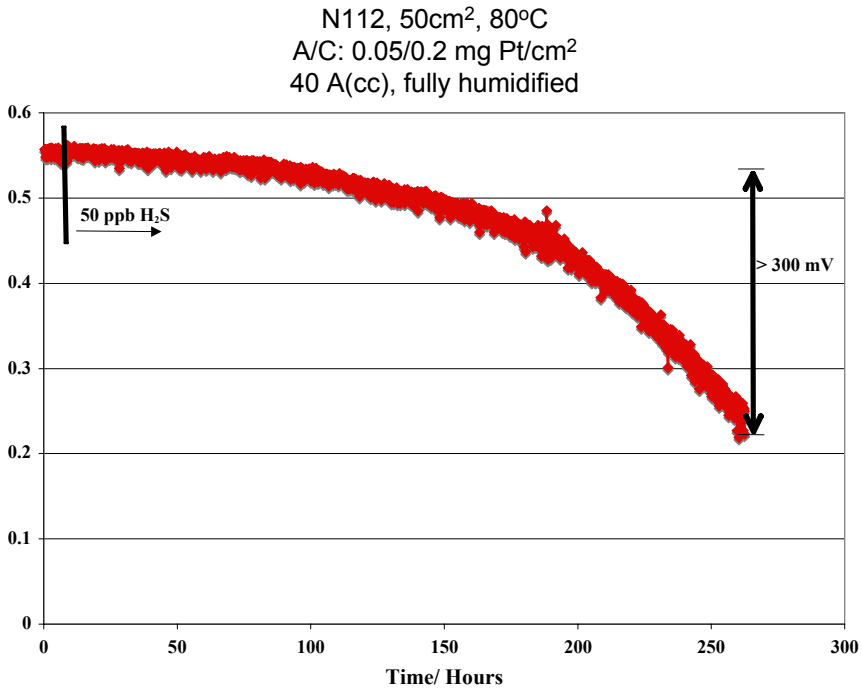
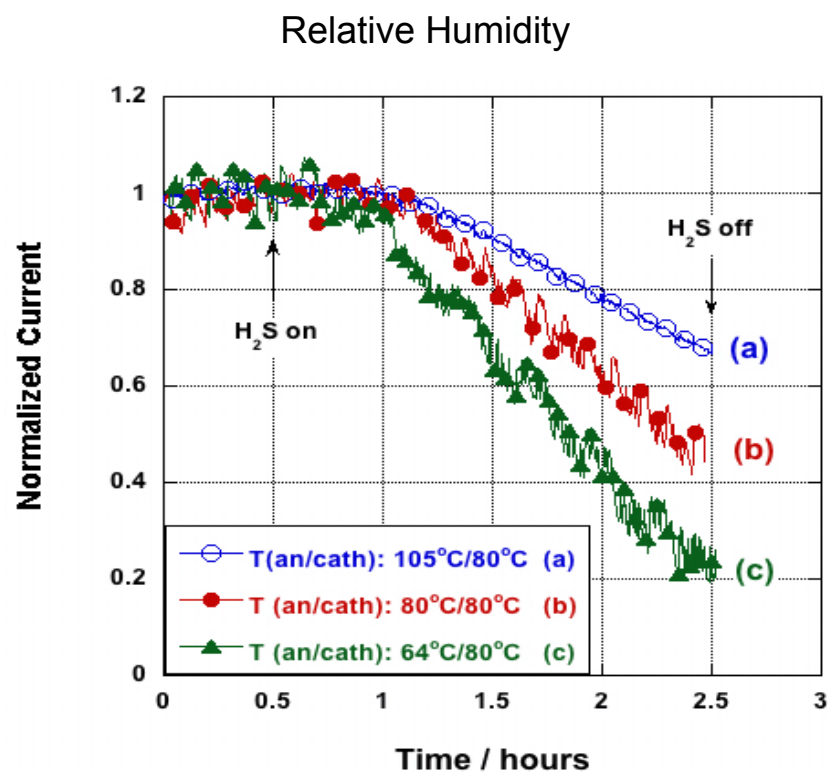
H_2S Studies





- Sulfur chemisorption onto Pt-sites deactivating the catalyst for hydrogen dissociation
- Other in-house results indicate sulfur crosses over to the cathode
- Low levels of sulfur can disable a fuel cell
- An increase in local water decreases the sulfur impact

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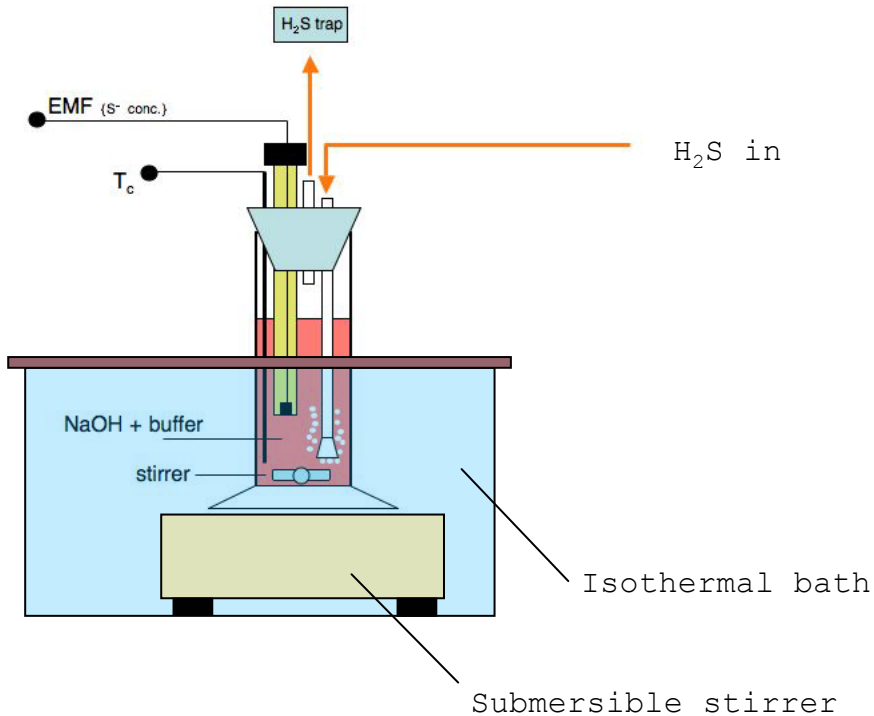
Analytical Methods for ppb H_2S Determination

- Chemical trap used to capture all H_2S
  - pH>12 to insure $S^=$ species in solution (1M NaOH + ascorbic acid and EDTA); flow rates optimized for 100% capture of H_2S
- Ag/AgS electrode, sulfide ion probe
  - Mode 1: EMF converted to $[S^=]$ using calibration data for qualitative determinations
  - Mode 2: Electro-titration: Pb^{+2} titration is used in combination with EMF endpoint determination to validate mass of H_2S captured
- Isothermal measurement to ensure accurate calibration is maintained
- H_2S delivery to experiment must be optimized to prevent adsorptive losses



$$\frac{d[S^=]}{dt} = \frac{[H_2S] * Flow\ rate * \frac{1\ mole}{22{,}400\ ml}}{V_{trap}}$$

$[S^=]$ may be found using probe EMF and an accurate calibration against standards using $E = E_o + S\mathrm{Log}_{10}X$ where

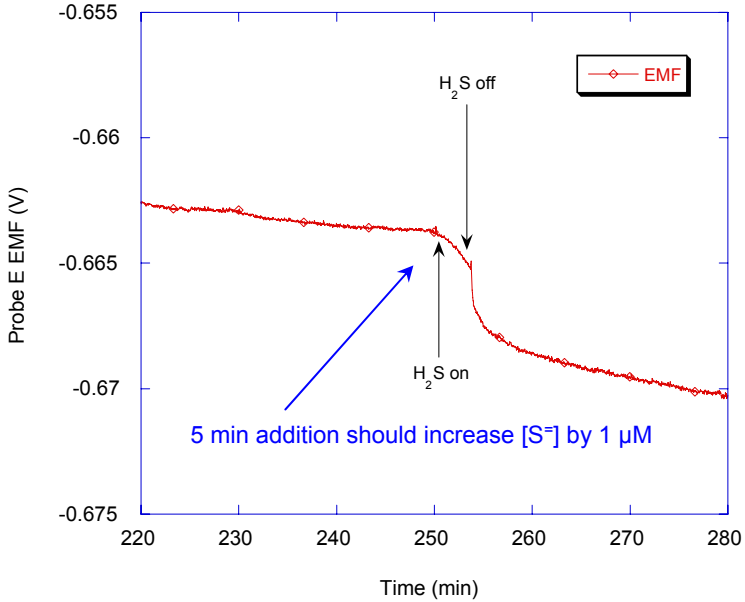
E = measured electrode potential
E_o= reference potential set by ref. solution
S = electrode slope (typically -27 to -30 mV)
X = activity of $S^=$ in solution

Commercial Ion-Selective Probes

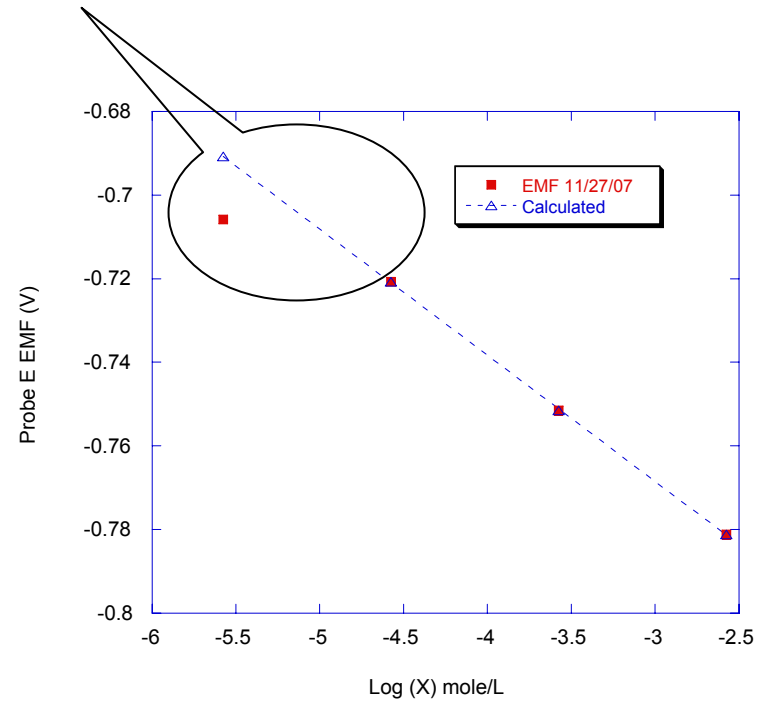
- Not suitable to directly measure [$S^{=}$] even when concentrating with a trap
  - Problems with probe sensitivity at low sulfide ion concentrations
    - Addition of small quantities of H_2S in trap can be seen as a change in EMF but calculation of [$S^{=}$] from these small EMF changes is overwhelmed by a summation of many errors
  - One may only obtain a calibration "window"
    - Repeated testing of commercial probes shows that only an average calibration curve may be obtained
  - Probe drift during extended immersions in trapping solution
    - Long immersions in solutions with a fixed [$S^{=}$] show drift versus time
  - Accuracy of sulfide ion concentration in solutions used for standardization
    - Na_2S and $Na_2S{\bullet}9H_2O$ typically used to prepare standard solutions may contain large percentages of excess water and even sodium sulfate
    - Calibration standards prepared using calculation of initial [$S^{=}$] based on weight is not acceptable
  - H_2S delivery to experiment must be optimized to prevent adsorptive losses

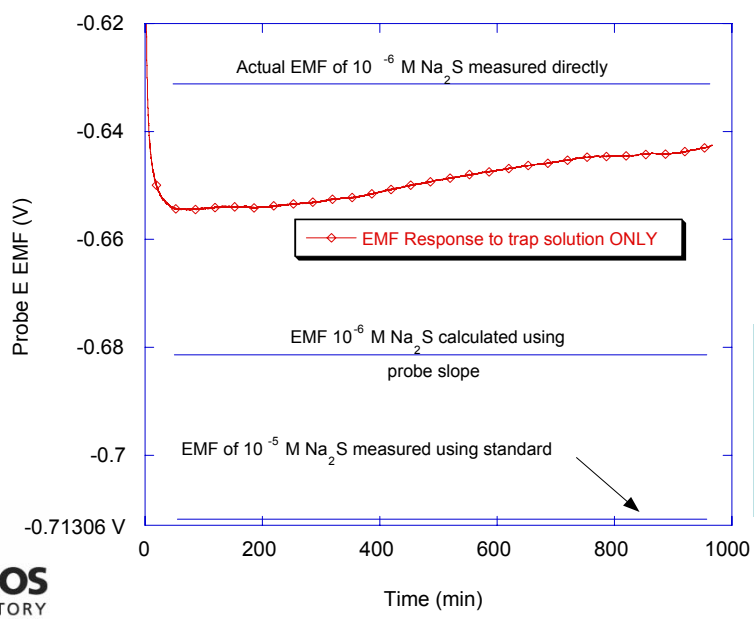
Experimental Evidence

5 ppm of H_2S in Ar can easily be seen by ion probe.



Problem: Commercial sulfide ion probes begin to lose sensitivity below 10^{-5} M [$S^{=}$]





These data to the right clearly demonstrate that the commercial ion probe is unable to differentiate a premixed 10^{-6} M [$S^{=}$] from neat buffer solution.

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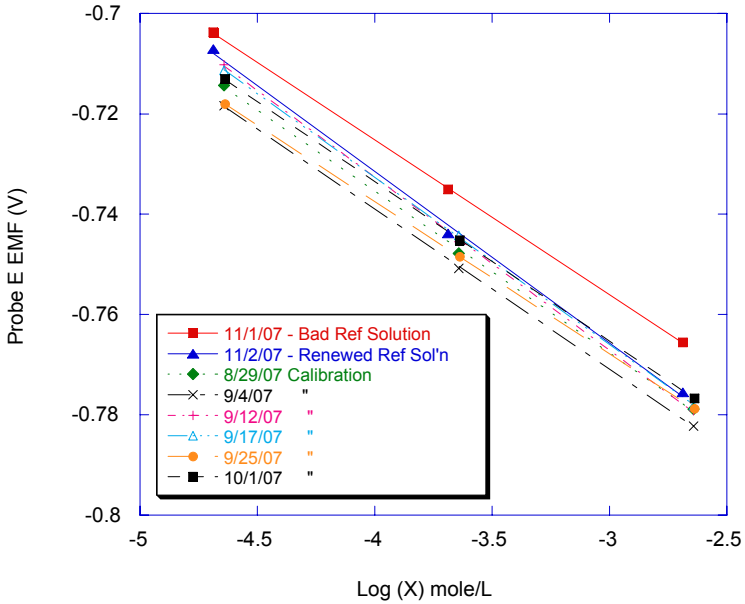
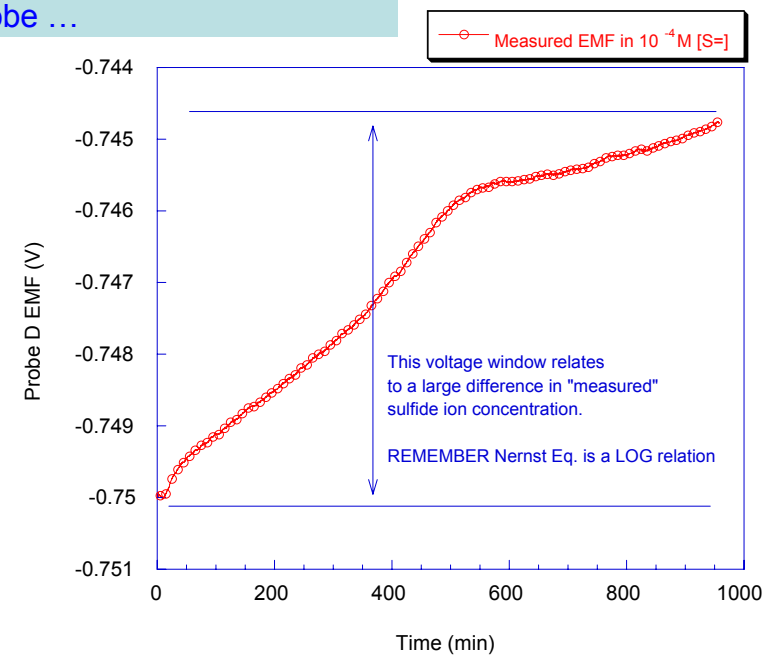
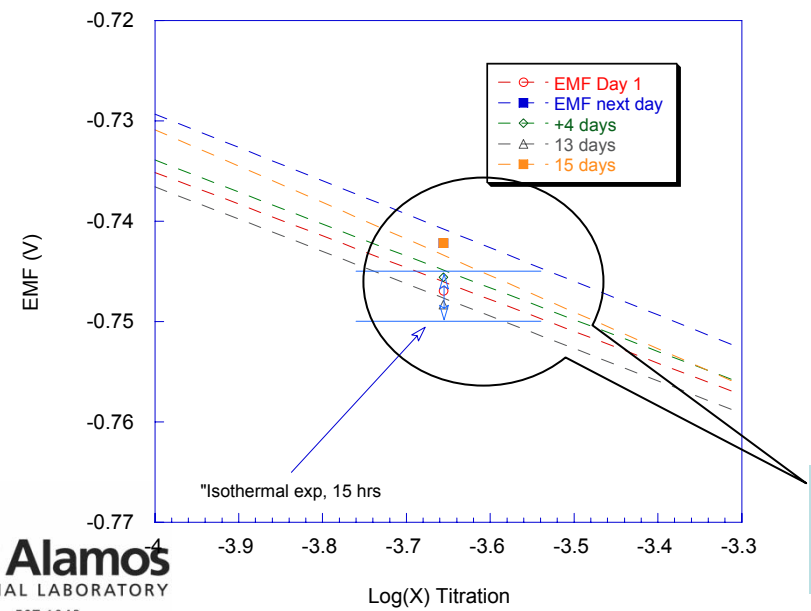


Tracking of calibration curve data over numerous preparations of standard solutions show that there is an average EMF associated with each decade of [$S^=$] ion concentration. Also, this plot shows how the KNO_3 reference solution must be periodically serviced.

Taken together …

… with experiments that document the inherent drift in the ion probe …





…means that a measured EMF does not lead to a well-defined [$S^=$].

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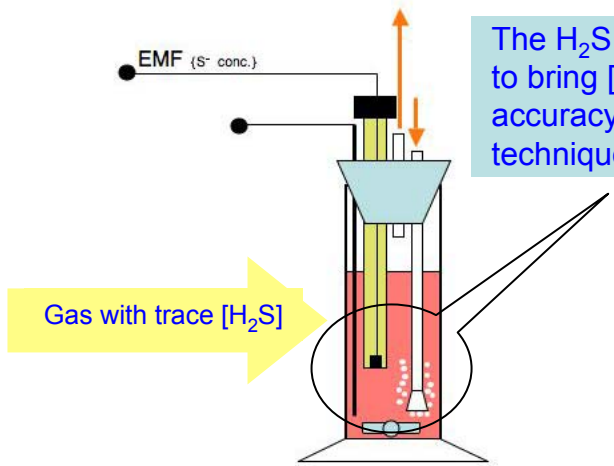
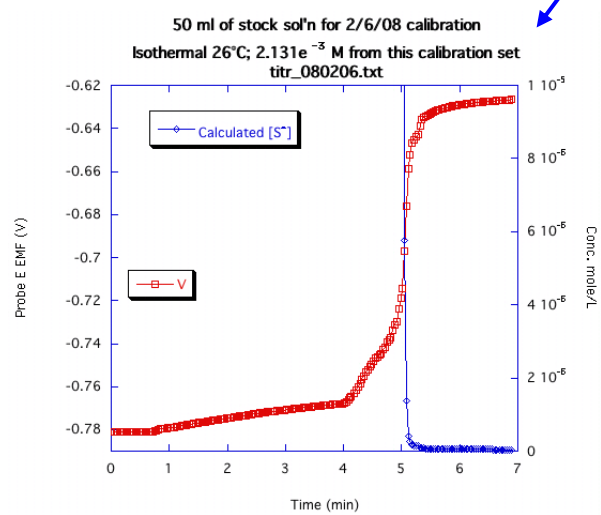
Knowing the origin of these errors, new analytical H_2S techniques have been developed using selective ion probe techniques.

- Titrations performed using the ion probe as an end point indicator greatly improves the accuracy and precision of the sulfide ion probe measurement.
  - Dropwise additions of known quantity and $[Pb^{+2}]$ of lead nitrate or lead perchlorate titrant permit calculation of $[S^{=}]$.
- Well defined $[Pb^{+2}]$ titrant solutions may be easily prepared.
  - No water uptake in the salt.
  - Commercially prepared lead perchlorate solutions available.
- Isothermal operation (26°C).
- Quick analysis means no time for probe drift.
- Calibration curve and standards are <u>not necessary</u>.
- Accurate gas flow control corrected for temperature and pressure using precision MKS mass flow controllers.



The H_2S is integrated long enough to bring $[S^{=}]$ into range of high accuracy for the ion probe titration technique.

Once enough H_2S has been trapped, perform titration and calculate $[S^{=}]$.



E.g. 100ppb H_2S in Ar could be measured within a day's integration time.

Precise measurement of time and flow rate and $[S^{=}]$ using ion probe titration methods permits calculation of concentration of trace H_2S in gases, crossover rates, surface area probe, etc.

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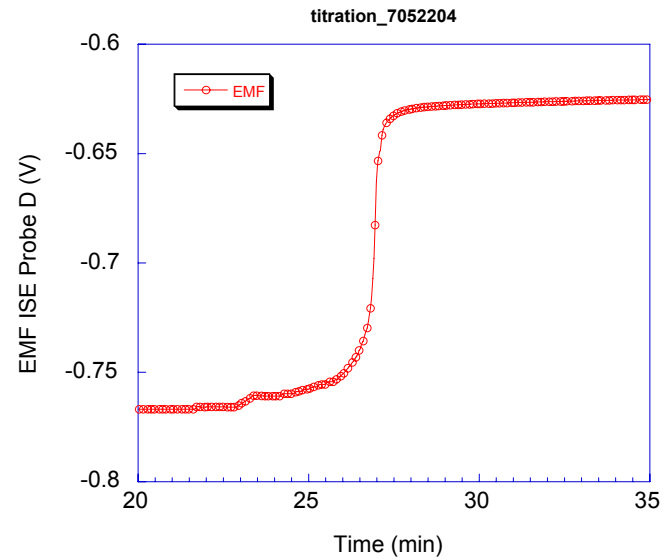
Experimental verification of [$S^{=}$] calculation using [Pb^{+2}] titration

- Use of $Pb(NO_3)_2$ at a concentration 10x of anticipated [$S^{=}$] may be titrated using the ion probe as an endpoint indicator.
- The first application was to accurately measure the true Na_2S concentration being used as stock standard for probe calibration.
- TGA analysis of Na_2S "anhydrous" from Alfa contained
  - 4 wt% H_2O
  - 19 wt% Na_2SO_4
  - Possibility of inert substances?



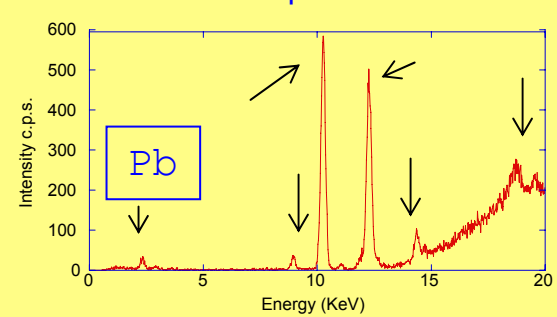
- [$S^{=}$] was measured by ISE probe titration using [Pb^{+2}] of $3.089e^{-2}$M
  - Theoretical [$S^{=}$] correcting mass of Na_2S for water and sulfate content :

    $2.02e^{-3}$M
  - Using titration curve data (right) :

    $2.00e^{-3} \pm 4.24e^{-5}$ M

Error reflects error in volume measurement and TGA analysis of lead salt.

XRF is being used to corroborate titrations of µM or lower solutions



Titrated solutions may be analyzed for PbS precipitate.

The presence of Pb on trapped in filter paper confirms the presence of S.

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Technical Accomplishments Summary

- Completed DOE Round Robin Testing
- Developed a Data Reporting Format
  - Accepted by ISO TC197 Working Group 12
  - Proposed for adoption as part of standard
- Developed analytical method for measuring and determining ppb levels of sulfur
- Tested critical constituents (NH_3, CO, and H_2S)

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Future Work

- Complete final report on DOE Round Robin Testing
- Finalize the Data Reporting Format
  - Awaiting input from Japan, Europe, and Korea
- Optimize our analytical method and modify it for the other critical constituents
- Continue testing the critical constituents (NH_3, CO, and H_2S) and populating the test matrix
- Continue providing data sets and interacting with FC modelers