2012 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Program Annual Merit Review and Peer Evaluation Meeting

Hydrogen Safety, Codes and Standards: Sensors

DOE Program Manager: Antonio Ruiz

Presented by: Eric L. Brosha

Project Team Members: Eric L. Brosha[1], Cortney Kreller[1], Fernando H. Garzon[1], Robert S. Glass[2], Rangachary Mukundan[1], Catherine G. Padro[1], and Leta Woo[2]

[1]Los Alamos National Laboratory
Los Alamos, New Mexico
[2]Lawrence Livermore National Laboratory
Livermore, California

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Project ID# SCS004

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Overview

- **Timeline**
  - Start: Summer FY 2008
  - Finish: FY 2013
  - 80% Complete

- **Budget**
  - Total project funding
    - DOE share: $3950K
  - Funding received FY11: $550K
  - Funding for FY12: $500K
    - $300K LANL
    - $200K LLNL

- **MYRD&D Barriers** (2011)

✧ A: Safety Data and Information: Limited Access and Availability

✧ C: Safety is Not Always Treated as a Continuous Process

✧ K: No Consistent Codification Plan and Process for Synchronization of R&D and Code Development

✧ L: Usage and Access Restrictions

- **Partners**

– Project lead: Fernando H. Garzon (LANL), Robert Glass (LLNL)

– Custom Sensor Solutions, LLC – Commercial electronics developer

– BJR Sensors, LLC

– Commercial Industry Partner: ElectroScience Laboratories (ESL) Corp - Commercial prototype engineering

– NREL: Codes & Standards field performance evaluation/validation team member

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Relevance – Objectives

- Develop a low-cost, durable, and reliable Hydrogen safety sensor for vehicle, stationary and infrastructure applications, through material selection, sensor design, and electrochemical R&D investigation.

- Demonstrate working technology through rigorous life testing and application of commercial (reproducible) manufacturing techniques.

- Disseminate packaged prototypes to NREL and work toward commercialization by engaging appropriate industry partners. NREL to evaluate sensor performance and ensure adherence to codes and standards, field evaluation, and performance requirements.

- Pursue transfer of the new sensor technology and commercialization through industry partnerships.

Relevance – Technical Performance Requirements
Why does the hydrogen community need better H_2 Safety Sensors?

- An H_2 infrastructure will require improved H_2 safety sensors.
- Most recent confirmation of this view: NREL/DOE Hydrogen Sensor Workshop, June 8, 2011
- 2011 workshop reaffirmed findings of Hydrogen Safety Sensor Workshop, Washington DC, April 3-4, 2007.
- Ultimate Problem: sensor drift leading to false positives and false negatives.

…from Executive Summary – 2011 NREL/ DOE H_2 Sensor Workshop :

"Outstanding sensor shortcomings include the following:

1. *Analytical Performance Parameters*
   - *Response time*
   - *Cross sensitivity*
2. *Operational Parameters*
   - *Cost of maintenance and calibrations*
   - *Alarm thresholds*
3. *Deployment Parameters*
   - *Code requirements*
   - *Placement*
   - *Point sensors vs. wide area monitoring"*

"Overall, if we had access to robust, durable, and cost-effective hydrogen sensors for the ventilation, oxidant outlet, and anode loop applications, we would most likely be using hydrogen sensors in all of these applications … whereas today there is almost always a cost/ benefit trade-off decision made regarding the use of hydrogen sensors in these applications on a platform-by-platform basis."

Robert Holland, P. Eng., C.R.E, Principal Reliability Engineer, Ballard Power Systems

"…I've found that Hydrogen sensors tend to drift leading the user to generally not trust the sensor for small hydrogen leaks. Ideally, I would like a sensor that never drifts and is inexpensive, allowing me to allocate multiple sensors in a large lab…"

Jonathan Malwitz, FuelCell Energy

"…From our point of view there is a need for a low-cost reliable sensor."

Stuart Pass, Teledyne Energy Systems

In addition, **Natalie M. Olds, USCAR,** has voiced concerns about the lack of commercial sensors with required accuracy or speed to test diffusion models for simulating hydrogen release during crash testing of fuel cell vehicles and that without an appropriate sensor to equip test bays and crash vehicles, the models have not been verified experimentally.

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Milestones and Go/No-Go FY11 and into FY12

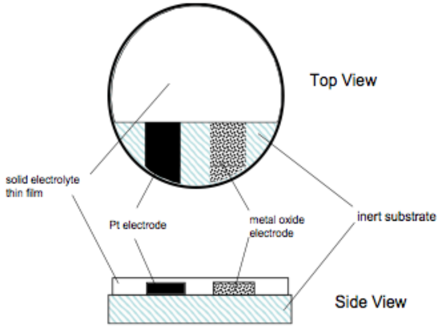
- Completed 1st round of NREL testing.
  - Results were obtained : Expected and unexpected.
  - FY12 sensors AOP Objectives and Milestones were set based on positive feedback.
  - Devices continued to be used through out FY12 for testing and electronics development.
- Designed more advanced sensor substrates incorporating on-board temperature control and completed initial calibration procedures for pre-commercial prototypes.
- Effective prototype packaging scheme adopted for pre-commercial naked sensors.
  - Sensors may be easily transferred to development partners.
  - Sensors may easily be physically handled/manipulated during *real-time* operation.
- Partnered with BJR Sensors and co-developed an algorithm using a novel approach to eliminate the cross interference affecting existing technologies. (see appendix, additional slides)
- Acquired sensor platform costs for large scale-up in production.
- Electronics development requirements defined using NREL feedback.
  - Commercial partner identified: Custom Sensor Solutions, LLC, AZ. USA.
  - Board specifications defined.

Approach: Controlled Interfaces for Sensor Design and Development

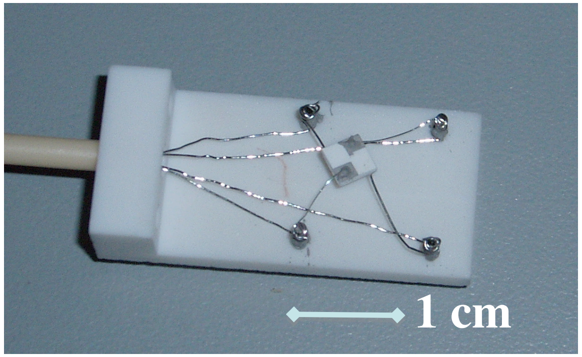
Sensor Technology Selection

- **Derivative of the hugely successful automotive Lambda, potentiometric O_2 sensor.**
- Mixed-potential sensors generate a non-equilibrium potential in the presence of oxygen and a reducing/oxidizing gas.
- Unique class of sensors have been developed that are based on dense electrodes and porous electrolyte structures [1,2].
- Result: stable and reproducible three phase interfaces (electrode/electrolyte/gas) that contribute to their exceptional response sensitivity and stability [3,4].
- Controlled Interface Technology: Conducive to miniaturization, thin film electrodes and electrolyte greatly improve sensor response [5].

- US patents 6,605,202 and 6,656,336, 7,214,333



Schematic of a HC Sensor in planar configuration (US #, 7,264,700).



ITO/YSZ/Pt H_2 safety sensor built on ESL platform.

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Approach: National laboratories lead in development and commercialization of mixed potential sensor technology

- Possibility of mixed potential sensors were an outgrowth of Lambda sensor R&D in early 80's.
- No commercial mixed potential sensors available. Why? A number of non-insignificant issues…

1. Sensor aging
2. Reproducibility problems
3. Selectivity
4. Technology Commercialization

LANL/LLNL R&D has addressed these impediments in ***laboratory devices***.

❖ *Over 70 LANL and LLNL peer reviewed sensor publications and proceedings papers.*

The process of transferring advanced technology to the marketplace raises fresh challenges/renews various problems as devices need to be made to a price point.

e.g. longer term stability, sensor drift, susceptibility to contamination/poisoning, RH effects, T effects, UV exposure, vibration, etc.

- To help in addressing daunting issues related to technology commercialization:
  - ✓ We are working with ESL Electroscience Inc. for mass fabrication of the sensor element.
  - ✓ We are working with Custom Sensor Solutions, LLC to develop electronics to interface the sensor element to the outside world.

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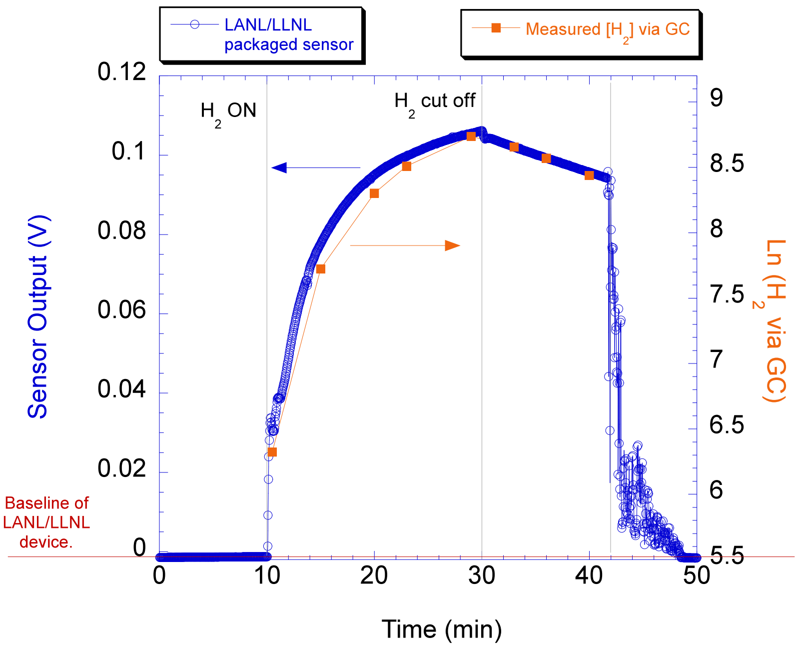
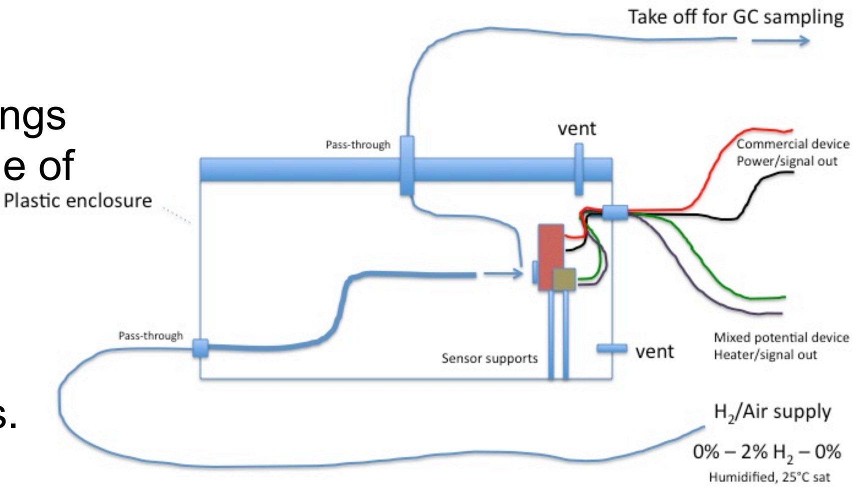
Technical Accomplishments FY11: Static volume sensor testing of pre-commercial prototype against calibrated GC sampling/measurement

- Experiment: Testing LANL/LLNL pre-commercial H_2 sensor in more real-world scenarios.
- LANL/LLNL test sensor performance compared to a $2000, commercially available TCD-based H_2 sensor.
- An air/H_2 stream is introduced at 400cc/min into a 1.7cf Plexiglas enclosure. The mix is injected 8” away from face of both devices with GC sampling inlet located 2” in equidistant position in front of sensors.
- Gas inside enclosure may escape through sampling inlet at top, through 0.25” hole in enclosure above the sensors, or through openings that permit pass-through of cabling on back side of enclosure.
- H_2 is premixed with air and humidified before introduction into enclosure to prevent any possibility of achieving flammable fuel/air ratios.





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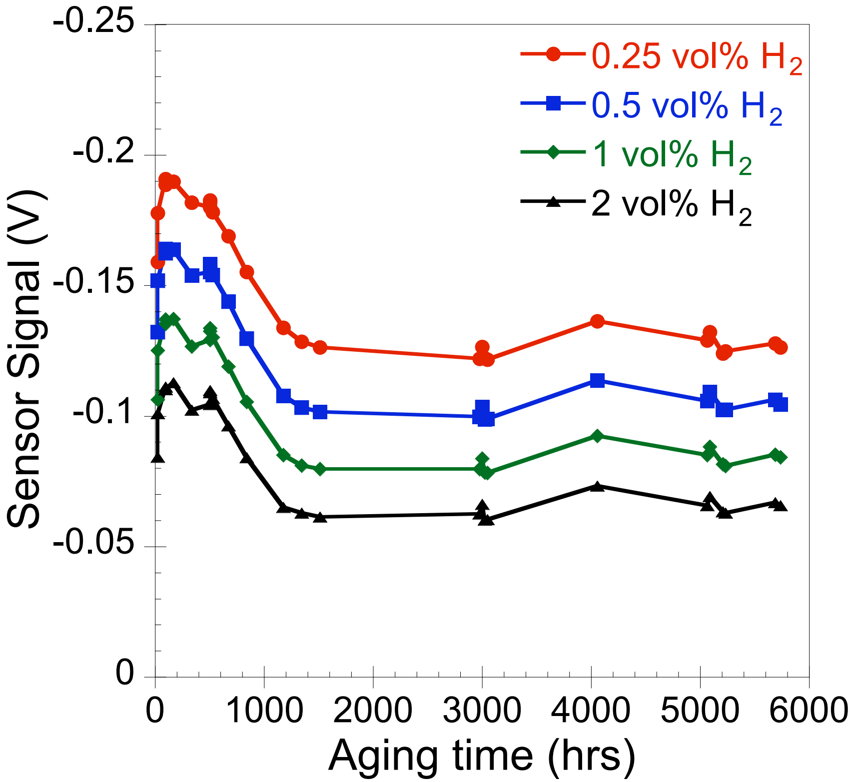
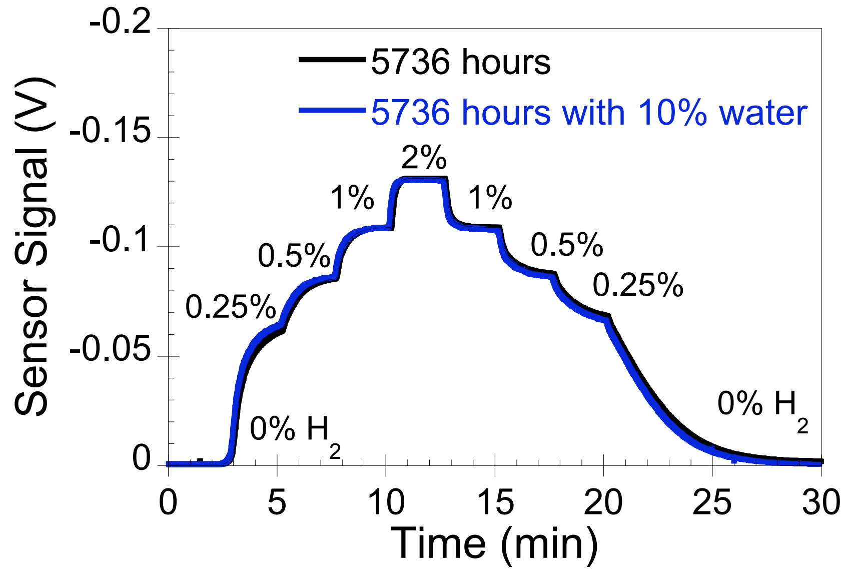
Technical Accomplishments: Evaluation of impregnated prototype to almost 6000 hours with demonstrated humidity tolerance





Excellent humidity tolerance in laboratory testing (no change with the addition of 10% water) confirms results of NREL evaluation

- Laboratory prototype design with impregnated electrodes presented last year (FY11) showed stability and reproducibility to over 3000 hours in laboratory testing – additional testing in FY12 confirms continued stable performance to almost 6000 hours.
- New water injection system established for evaluating humidity tolerance for water variation from 0-10%, which corresponds to the full range relative humidity 0-95% for temperatures up to 90^{o}C – prototype has excellent tolerance to 10% water (~95% relative humidity).

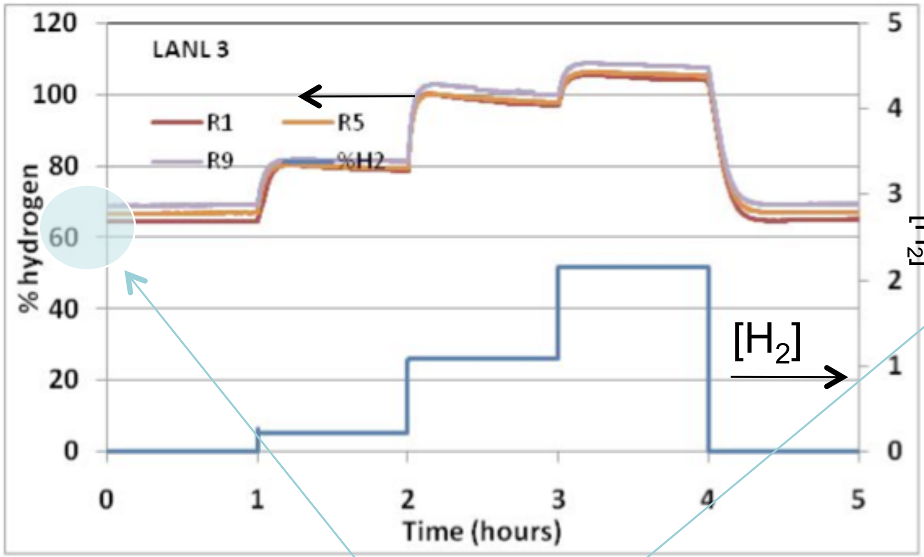
Technical Accomplishments: FY11 testing at NREL

- **Round 1**: H_2 sensor test stand at NREL used to evaluate sensitivity and influence of humidity, partial/absolute pressure, and ambient temperature.
  - ✓ Sensor reproducibly tracked H_2 levels
  - ✓ Demonstrated good sensitivity to H_2
  - ✓ Demonstrated minimal influence of humidity
  - ✓ Demonstrated the anticipated changes in sensor response to changes in the ambient temperature
    - Higher ambient T requires less voltage applied to Pt heater
  - ◎ Witnessed anomalous baseline behavior not seen in LANL or LLNL development testing.
  - ✓ Extreme durability testing
    - Two sensors were operated for extended period of time well outside of original design
- **End of Round 1**: Obtained feedback for planning/design of control electronics:
  - ✧ Temperature feedback and control & isolation of sensor from signal influences from outside world are necessary.

Technical Accomplishments: FY11 testing at NREL cont'd

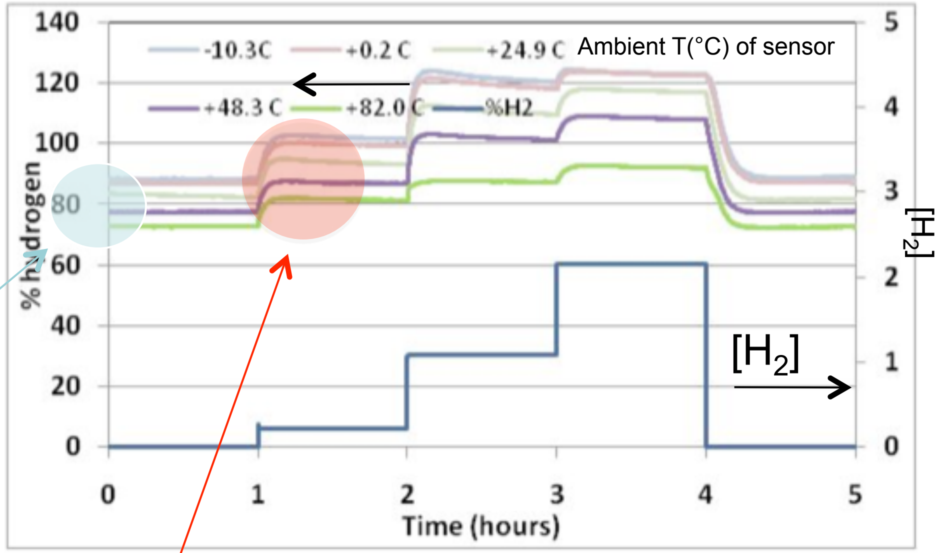
Standard test, response of sensor to increasing $[H_2]$.

Run 1, Run 5, and Run 9 overlay.



Standard test, response of sensor to increasing $[H_2]$.

Background temperature of sensor test chamber increased from -10.3°C to 82°C.



Strange baseline behavior recorded at NREL.

- This could not be explained other than an issue with the system used for data acquisition.

Temperature response: sensitivity increases with decreasing ambient T of the chamber.

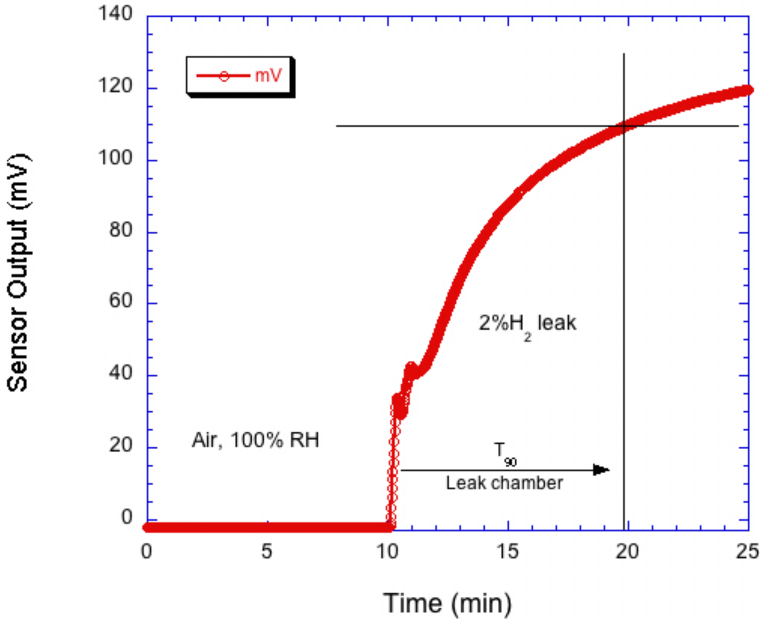
- This can easily be explained and resolved: heater power delivered to Pt heater was fixed during testing. Hotter ambient chamber T means hotter sensor surface T and sensitivity is a function of operating T.

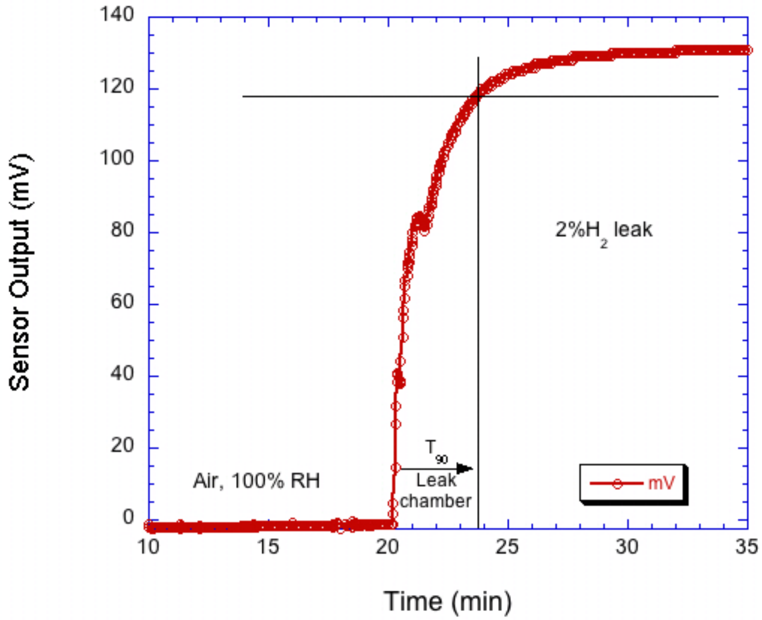
Technical Accomplishments FY12: FY11 testing at NREL follow-up

- Anomalous baseline behavior was recorded for both sensors tested at NREL.
  - Baselines (0% H_2) up to 100mV
  - Heater V increased above 5V in attempt to decrease baseline value.

- Sensors returned to LANL showed none of this behavior.
  - Normal response (*see bottom right*) compared to initial response (*see top right*)
  - Difference due to application of high heater power for extended period of time

- Results of NREL operating sensors well outside normal conditions:
  - Negligible change in sensitivity to identical H_2 concentrations during simulated leaks.
  - Device responded more quickly to H_2 filling the leak chamber.





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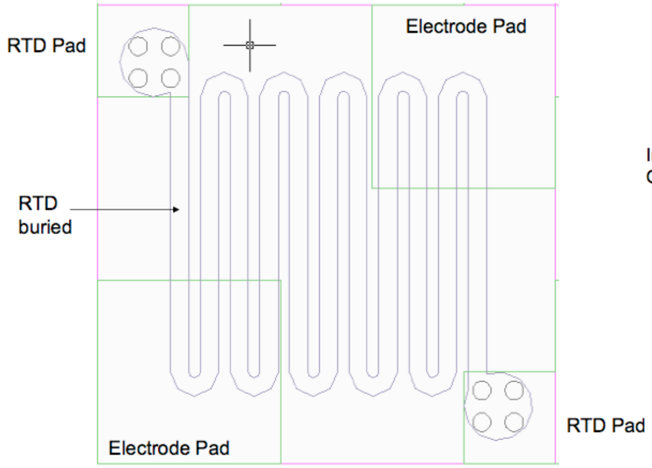
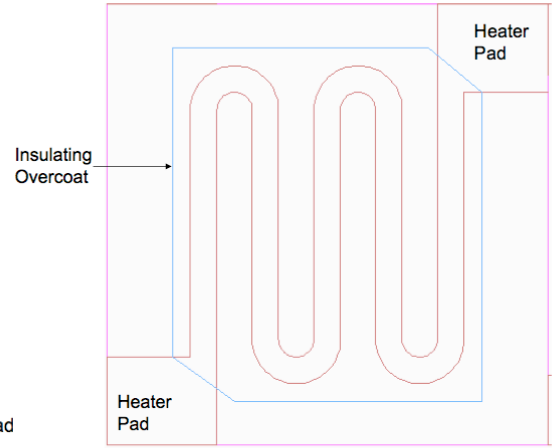
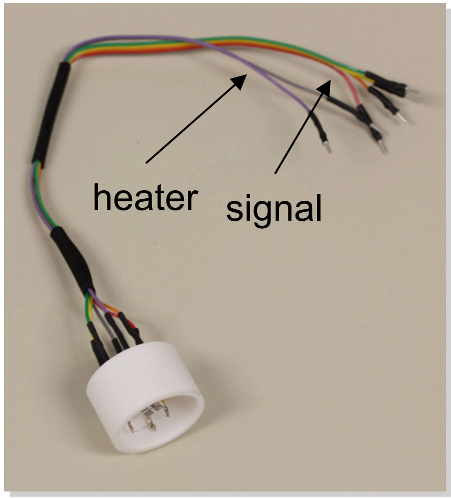
Technical Accomplishments FY12: Developed method for on-board temperature control using advanced sensor platform

Top surface of ESL substrate

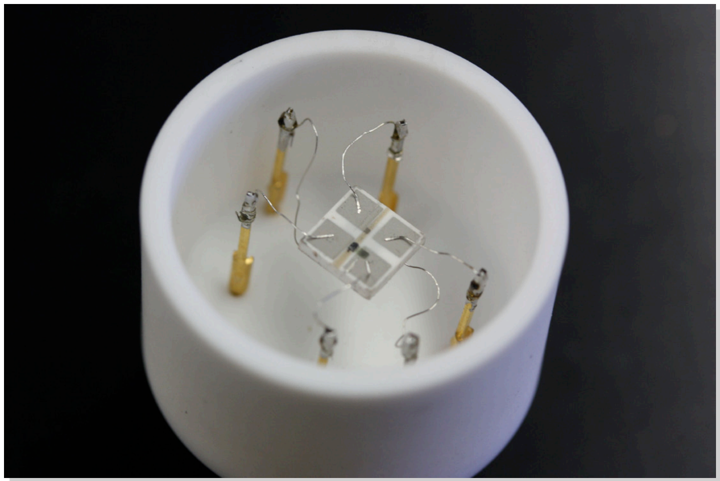


Bottom surface of ESL substrate



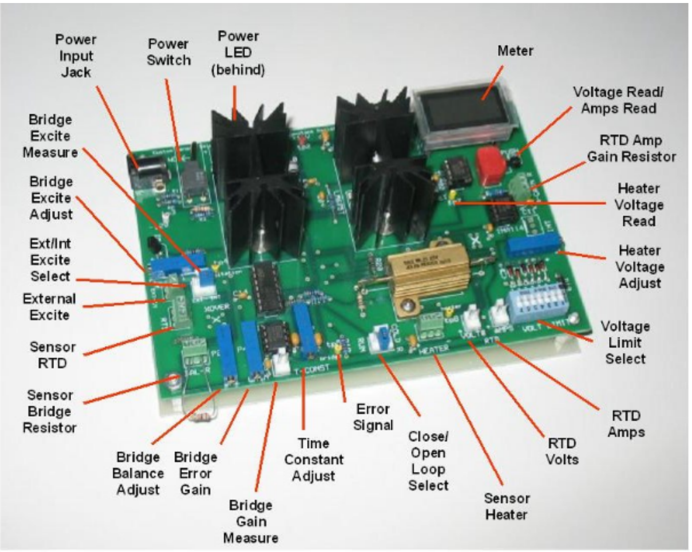


- More advanced sensor platform was developed by industry partner ESL Electroscience: a resistive temperature detector (RTD) was incorporated into the prototype sensor.
    - The RTD was buried into the alumina directly beneath the top surface layer containing the sensor elements.
    - The RTD introduced two extra leads to the prototype configuration, in addition to the two leads for the sensor elements and two leads for the heater, for a total of six leads.

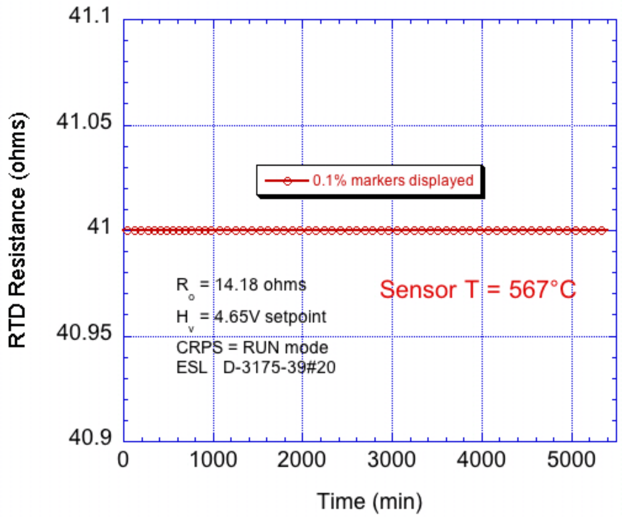


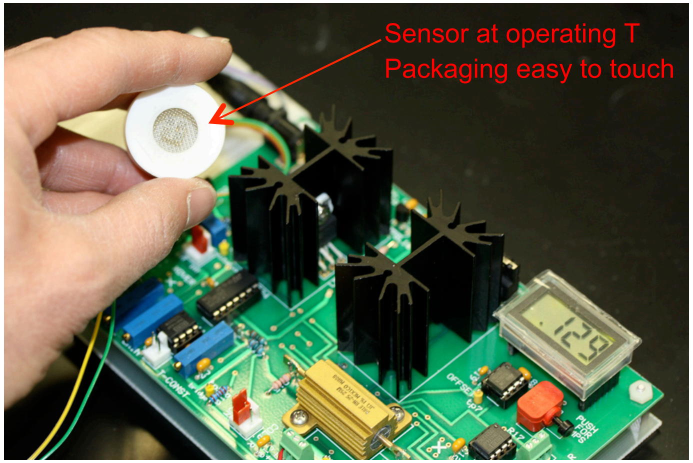
Technical Accomplishments FY12: Heater control prototype electronics

- Constant Resistance Power Supply prototype designed by Custom Sensor Solutions
- Designed to use output of buried RTD embedded in the ESL sensor platform.
- Designed to handle power requirements of pre-commercial mixed potential electrochemical sensors.
- This model is now a stock item available to researchers.



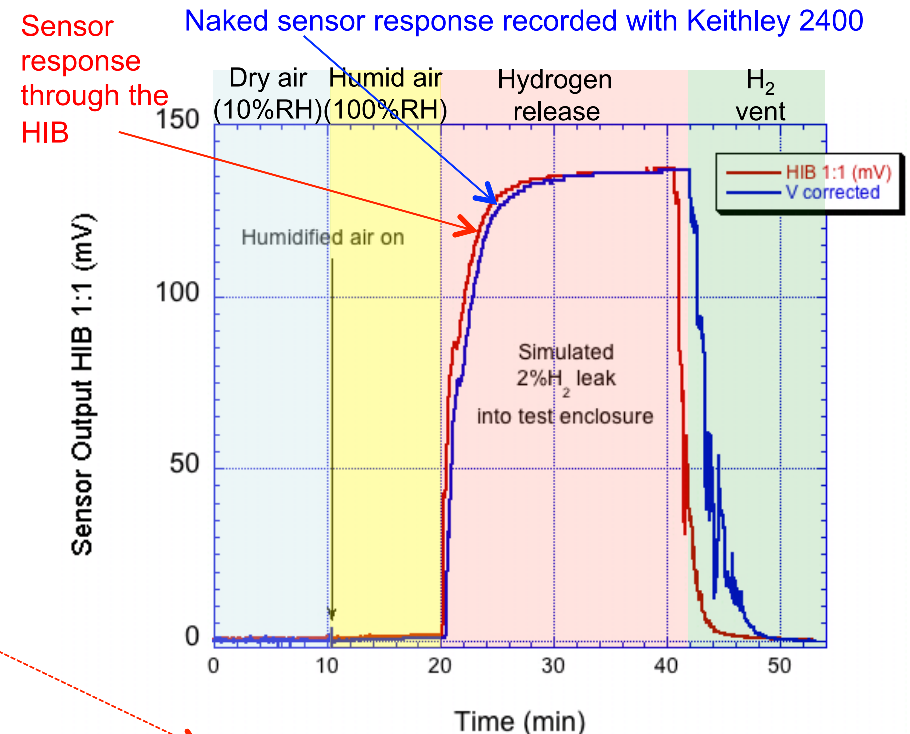
Weekend stability test of new ESL platform using heater control board.
- quiescent conditions

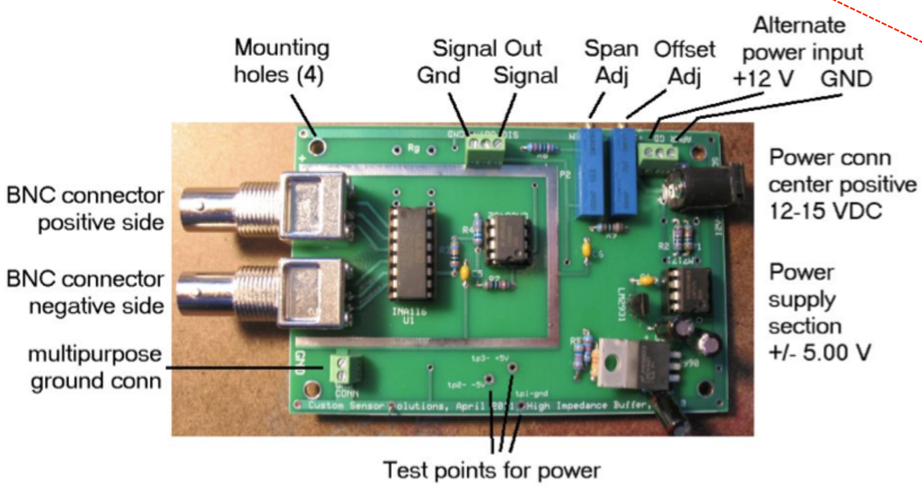


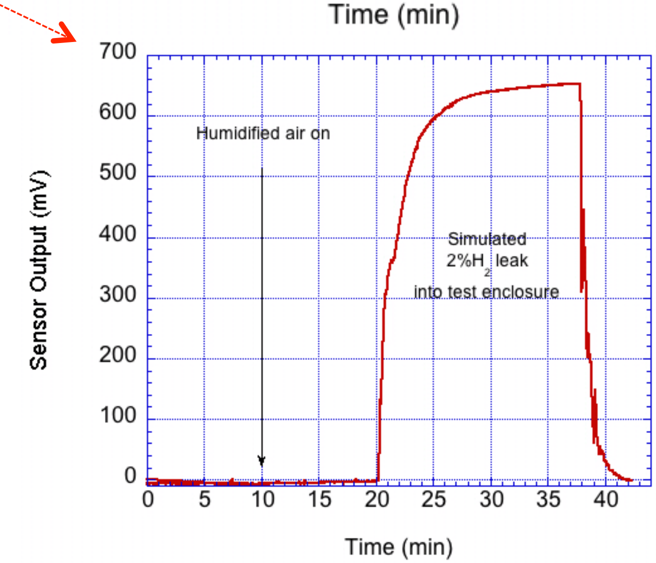


Technical Accomplishments FY12: High impedance buffer (HIB) board prototype electronics

- Designed by Custom Sensor Solutions to isolate the naked sensor element from the "outside world."
- **Right:** HIB protects sensor response yet does not alter the sensor response.
- Experimental board built around the Burr Brown INA116 electrometer amplifier.
  - Minimizes leakage between the electrodes, from sensor itself to the electrometer circuit.
  - Built-in offset and span adjustment







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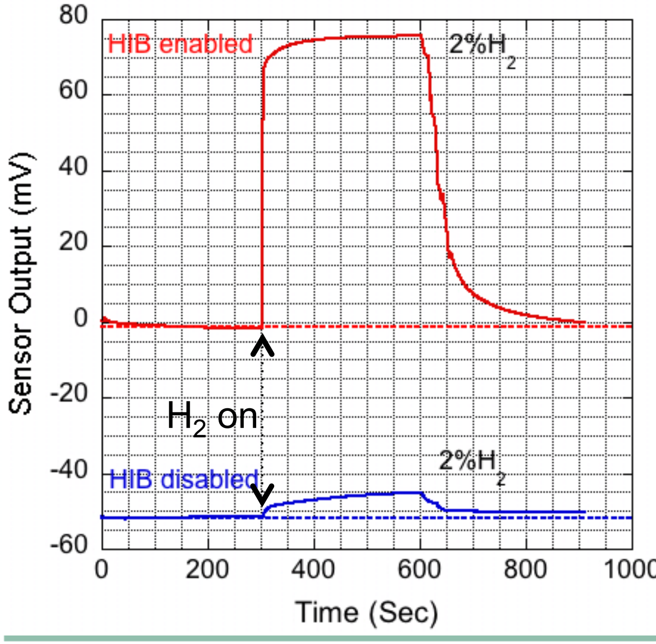
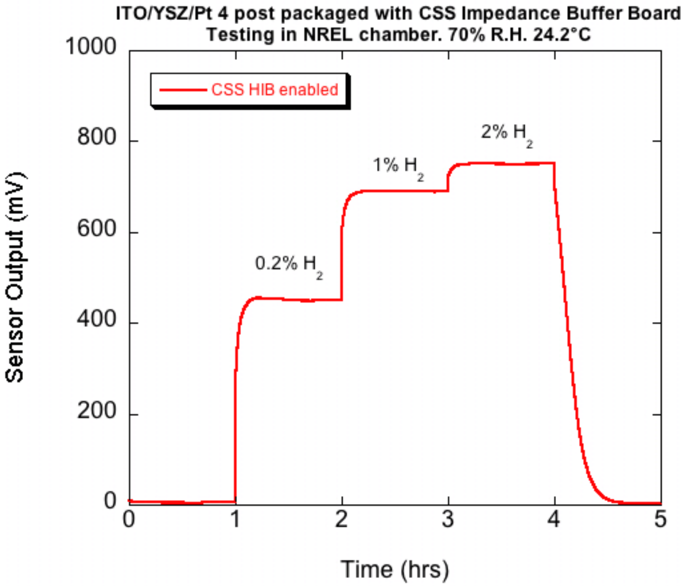
Technical Accomplishments FY12: Initiation of 2nd round of NREL testing started before AMR

- 4 of the 4 original Round 1 NREL sensors return to Golden for testing.
  - 1 test "mule"
  - Return of NREL#3 to investigate baseline anomalies after LANL re-cert.
  - 2 new devices – extensively tested at LANL
- 3 new H_2 sensors incorporating RTD taken to NREL for testing.
  - Temperature feedback for both manual and electronic control of sensor T
- Electronics pressed into service with the sensors:
  - Impedance buffer boards placed into NREL test chamber with packaged sensors.
  - Without HIB boards, anomalous baseline behavior and poor response characteristics seen in 1st round of NREL testing were reproduced.
  - HIB board successfully protects sensor from data acquisition system altering response while preserving and amplifying sensor output.



Correct sensor output obtained using Impedance buffer board without use of offset and gain.

Anomalous baseline behavior and poor signal reproduced without impedance buffer.

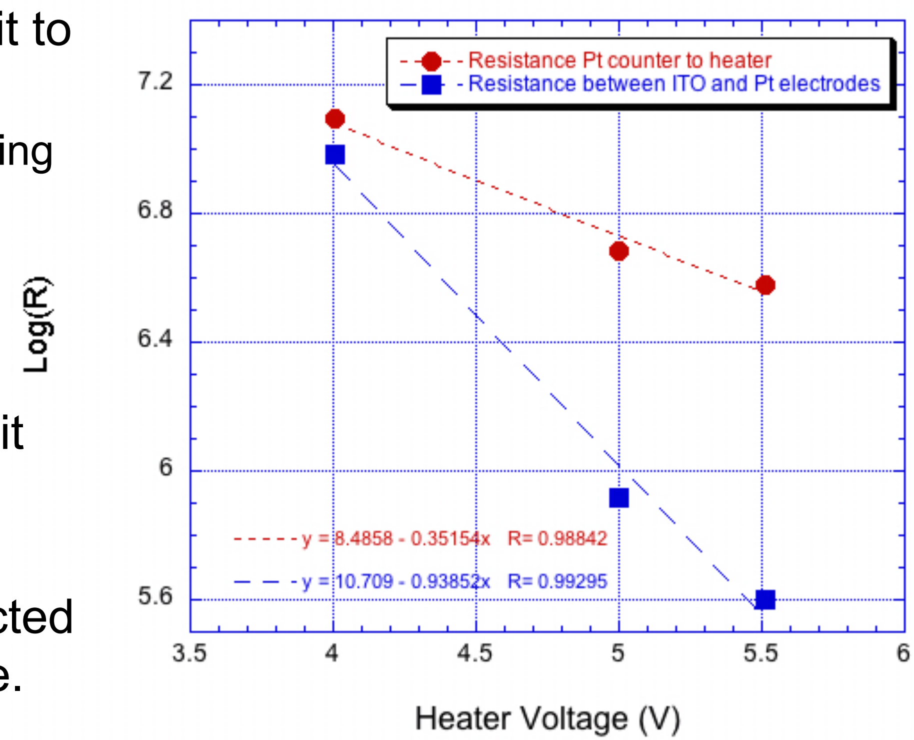


HIB board incorporates amplifier to permit user to adjust gain of output.

Very high signal to noise!

Technical Accomplishments FY12: NREL Round 2 – Identification of issues to resolve in pre-commercial ESL platform in FY13

- Ionic current/leakage from heater circuit to the sensor electrodes.
  - Identified very quickly in HIB board testing at LANL
  - Compositional change/impurity levels introduced semi-conducting or ionic currents
- "Communication" between heater circuit and sensor electrodes interferes with performance of HIB circuits.
- Identified problem with ESL and instructed course of action to ameliorate the issue.
- Problem easily solved based on performance of previous gen of ESL devices.
- **Example of the "two steps forward, one step back" nature of bringing new and advanced technology to market.**



* Previous ESL four post platforms (w/o RTD) measured <u>open circuit</u> at all T below 800°C.

Collaborations

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Fundamental electrochemical sensor R&D, establish proto-type designs, packaging, and testing

NREL NATIONAL RENEWABLE ENERGY LABORATORY

Codes & Standards field performance evaluation/validation team member

Lawrence Livermore National Laboratory

Materials selection, sensor design, durability investigations, and life testing

Federal Laboratories within DOE Hydrogen and Fuel Cells Programs

Industrial Partners:

BJR sensors Sensor Technology

Pulse discharge technique for improving accuracy

Custom Sensor Solutions, Inc. ...since 1997

Hardware for sensor control electronics

ESL ElectroScience

Manufacturing, scale-up, engineering processes

Proposed Future Work:

- Remainder of FY2012 and FY2013:
  - Run full standard H_2 Sensor NREL protocol on LANL/LLNL/ESL mixed potential–based H_2 safety sensors.
  - Collate and analyze data with NREL.
  - Prepare report on testing results and outline path forward.
  - Continue to work with NREL to develop testing protocols for mixed potential type electrochemical gas sensors.
  - Continue to test and improve prototype circuit board and electronics designed for mixed potential type sensors. Optimize design, improve performance, reduce cost, reduce size and power consumption.
  - Seek commercial development partners with commercialization achievements in hand.

Summary

- ✓ All FY12 Milestones are on target to be completed before end of project.
- ✓ A viable H_2 safety sensor technology has been developed on a pre-commercial sensor platform that continues to improve.
- ✓ Platform prototype advanced to incorporate temperature feedback.
- ✓ FY12 data show durability of Pt heater is excellent and RTD output is stable overtime.
- ✓ Round 1 NREL testing valuable: Resolution of problems identified at NREL; testing data have spurred electronics development while producing valuable durability information.
- ✓ Anomalous NREL baseline and signal issues reproduced and solved. Prototype electronics were developed, tested, and implemented.
- ❑ NREL Round 2 tested initiated on March 13 to be followed by full protocol testing summer of FY12.

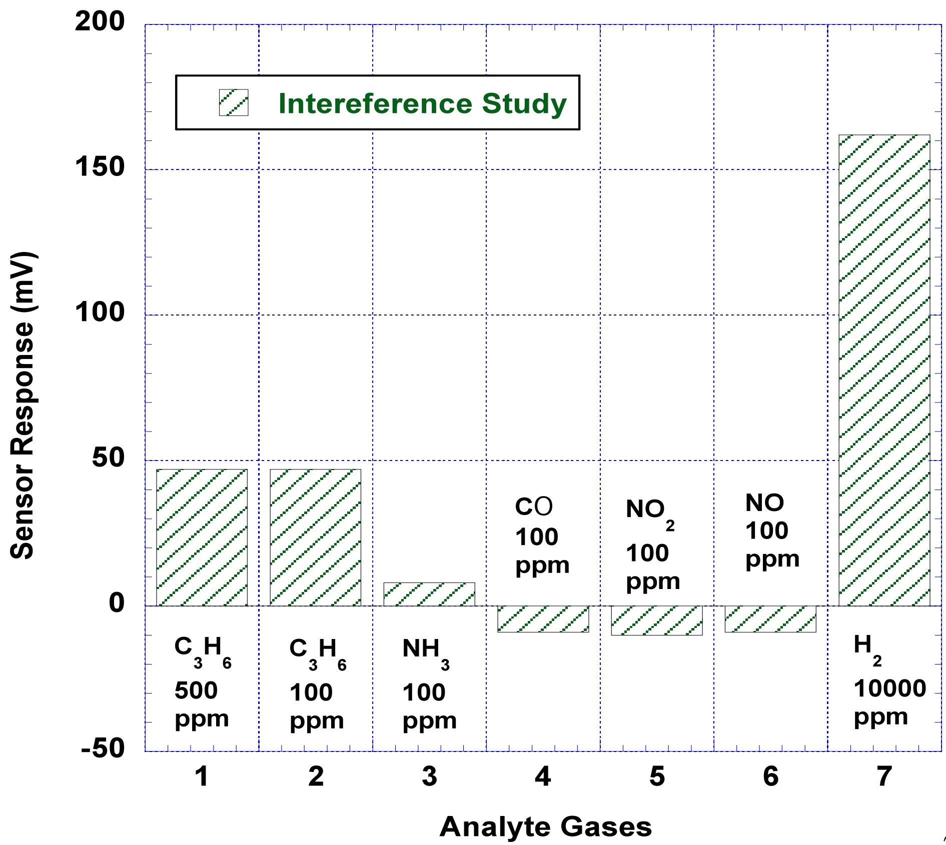
Technical Back-up Slides

Technical Accomplishments: Milestone for Interference/cross sensitivity progress

- Cross sensitivity is often an issue with chemical sensors.
- Mixed potential sensors are not immune.
- Gas that can be oxidized or reduced may interfere with target gas.

- Pre-filters or catalysts before the sensor electrodes is one possible solution.
  - e.g. some CO detectors, NO_x sensors, etc.
  - These approaches typically reduce sensitivity or increase response time.

- Need a new, higher performance approach.



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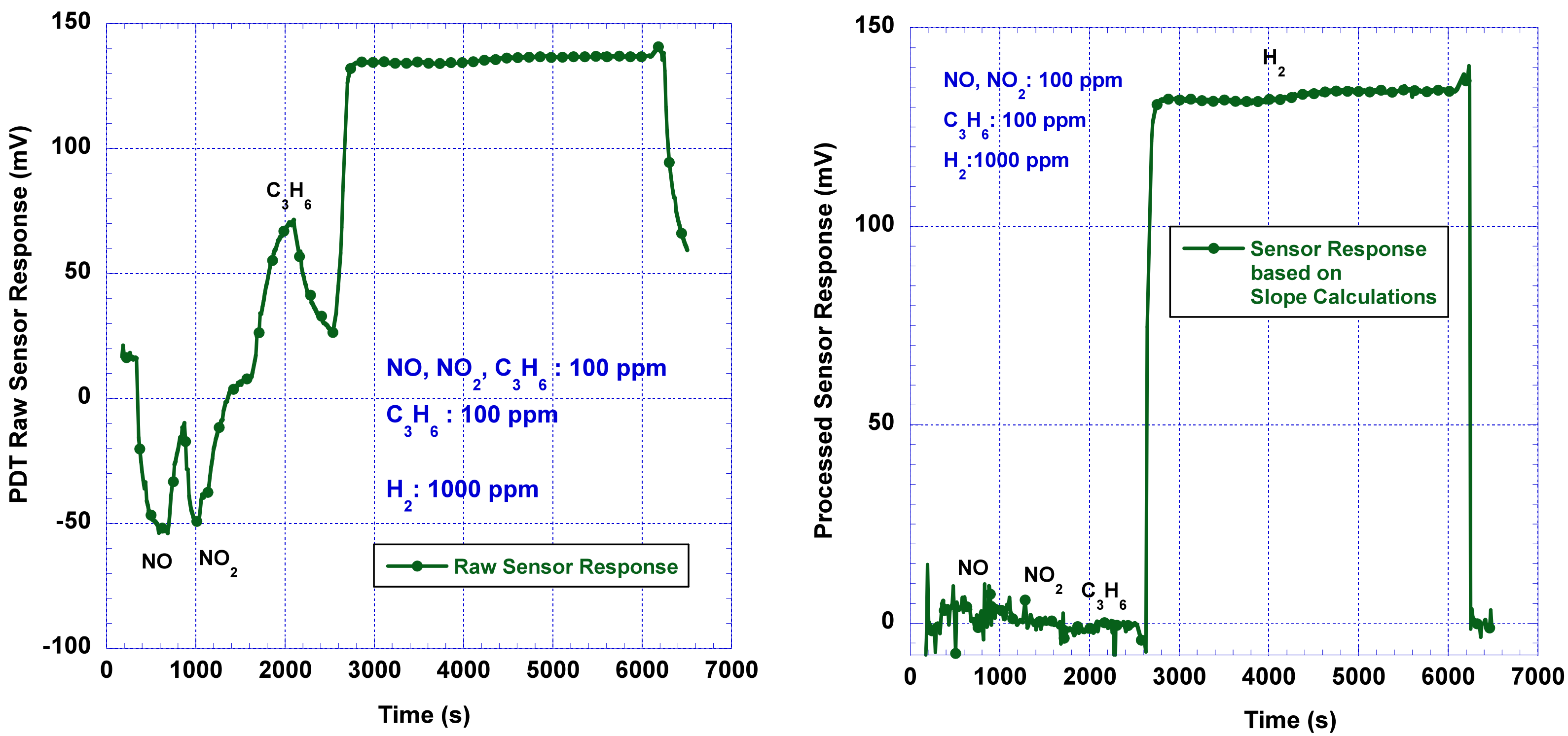
Technical Accomplishments: Collaboration BJR Sensors LLC utilizing Pulse Discharge Technique (PDT) combined with unique properties of the LANL/LLNL pre-commercial sensor prototype



- Unique property of the LANL/LLNL H_2 sensor lends itself well to a new approach to Lambda sensor signal conditioning developed by BJR (Patent no. 7,585,402).

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Approach: Why the National Laboratories' Involvement?

- Robust efforts in electrochemical sensor R&D since 1990. Fundamental scientific study in solid-state ionics, electrochemistry and engineering.
- Projects in CO, NMHCs, NO_x, SO_x, fluoride ion, H_2, and explosives sensor development
  - Delphi/LANL CRADA
  - USCAR CRADA (LANL & LLNL)
  - DOE EERE ARES
  - LANL LDRD
  - DOE OVT (LANL & LLNL)
  - LANL Royalty Funding/Tech Transfer
  - LLNL Royalty Funding/Tech Transfer
  - LANL Warfighter Support
- Over 70 (non LANL/LLNL overlap) peer reviewed journal and proceedings papers on sensors
- Total of 10 US sensor patents issued
- LLNL Tech Transfer (NO_x sensor technology)
- 1999 R&D 100 Award for "The Sulfur Resistant Oxymitter 4000™"

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