

2011 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Annual Merit Review and Peer Evaluation Meeting

Hydrogen Safety, Codes and Standards: Sensors May 9-13, 2010

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Project ID# SCS004

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Overview

- **Timeline**

- Start: Summer FY 2008
- Finish: FY 2012
- 70% Complete

- **Budget**

- Total project funding
 - DOE share: \$3400K
 - Equal budgets for LANL and LLNL
- Funding received FY10: \$700K
- Funding for FY11: \$550K
 - \$350K LANL
 - \$200K LLNL

- **MYPP Barriers**

- D. Liability Issues
- E. Variation in Standard Practice of Safety Assessments for Components and Energy Systems

- **Partners and Collaborators**

- Project lead: Fernando Garzon, LANL; Robert Glass, LLNL
- BJR Sensors, LLC
- Commercial Industry Partner: ElectroScience Laboratories (ESL) Corp - Commercial prototype engineering
- NREL: Codes & Standards field performance evaluation/validation team member

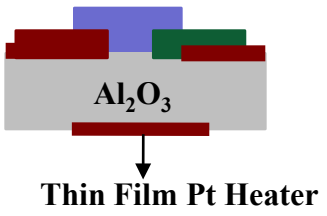
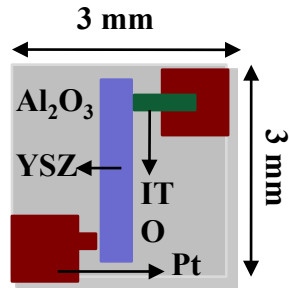
Relevance – Objectives

- Develop a low cost, low power, 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 ultimately commercial parties interested in testing and fielding advanced commercial prototypes. Pursue transfer of the technology to industry.
- Seek NREL help and guidance to evaluate sensor performance and keep us on track vis-à-vis adherence to codes and standards and field evaluation, performance requirements.

Relevance – Technical Performance Requirements

Why does the hydrogen community need better H₂ Safety Sensors?

Sensitivity: 1 vol% H ₂ in air	Temperature: -40°C to 60°C
Accuracy: 0.04-4%, ±1% of full scale	Durability: 5 yrs without calibration
Response time: < 1 min at 1% and < 1 sec at 4%; recovery < 1 min	Low cross-sensitivity to humidity, H ₂ S, CH ₄ , CO, and VOCs



Major Milestones and Go/No-Go FY10/11

- Completed testing of FY09 and FY10 laboratory and pre-commercial prototypes for long-term evaluation (>3000 hrs, LLNL and 4000hrs, LANL including T cycling) including comparison of mixed potential and impedance modality in laboratory prototypes: down-select to mixed potential.
- For laboratory prototypes, evaluated impregnated composite electrodes for better long-term stability and **demonstrated stability and reproducibility to over 3000 hrs in laboratory testing.**
- **Designed more advanced sensor substrates incorporating on-board temperature control** and completed initial calibration procedures for pre-commercial prototypes.
- Effective packaging scheme adopted for pre-commercial prototypes.
- Partnered with BJR Sensors and co-developed an algorithm using a novel approach to **eliminate the cross interference affecting existing technologies.**
- Fabrication of multiple pre-commercial prototype devices for NREL testing; six devices prepared with high level of reproducibility.
- **1st Round of devices shipped to NREL for testing;** devices returned and durability studied.
- **Positive NREL feedback already used to improve sensor platforms** and to prepare for Round 2 NREL testing – focus on electronics.
- **Explored sensor costs for large scale-up in production.**
- Remainder of FY11 into FY12: Sensor electronics for Round 2 NREL testing, protocol for on-board temperature control, updating existing packaging scheme to incorporate electronics and temperature control, continue electrochemical and long-term aging evaluation of both pre-commercial and laboratory prototypes, continue cross-sensitivity studies to ensure desired sensor performance and accuracy.

Approach: Controlled Interfaces for Sensor Design and Development

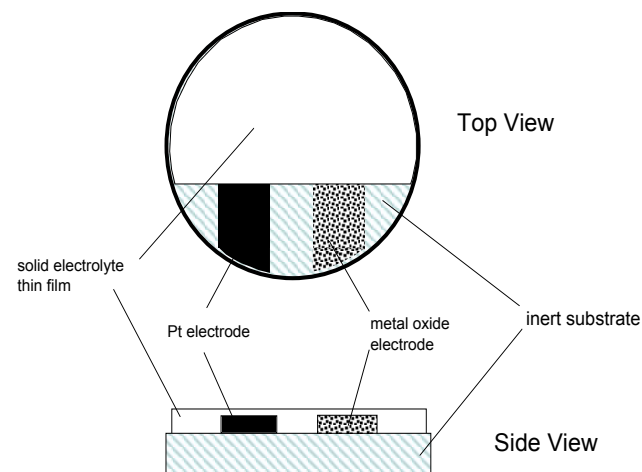
Why this technology?

- **Derivative of the hugely successful automotive Lambda, potentiometric O₂ 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].



Controlled Interface Sensors:

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



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

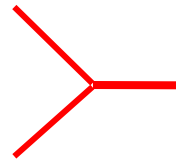
Approach: Using the Capabilities of our National Laboratories

- 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, H₂, 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
 - LANL Warfighter Support
- Over 60 (non LANL/LLNL overlap) peer reviewed journal and proceedings papers on sensors
- Total of 10 US sensor patents issued.
- 1999 R&D 100 Award for “The Sulfur Resistant Oxymitter 4000™” - a Joint R&D Entry with LANL and Rosemount Analytical Co.

Approach: Using the Capabilities of our National Laboratories

- Possibility of mixed potential sensors were an outgrowth of λ -sensor R&D in early '80's.
- No commercial mixed potential sensors available. Why?

1. Sensor aging
2. Reproducibility problems
3. Selectivity
4. Manufacturability



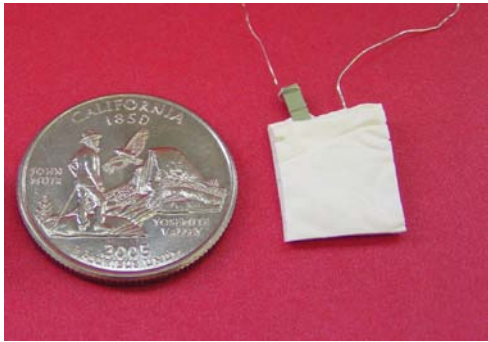
LANL/LLNL R&D has addressed these impediments.



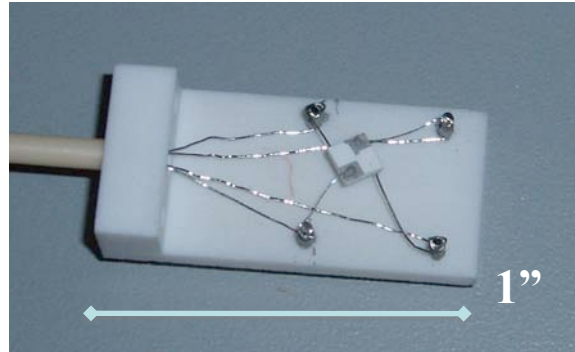
We now turn our attention to this one.

- Sensor design and materials requirements are different (BACKWARDS!) from materials technology, inks, tapes, methods, etc. developed for λ -sensors.
- We are working with ESL Electroscience Inc. to solve/develop new capabilities to address these remaining issues.
- We are working with NREL as code & standards field performance evaluation/validation team member.

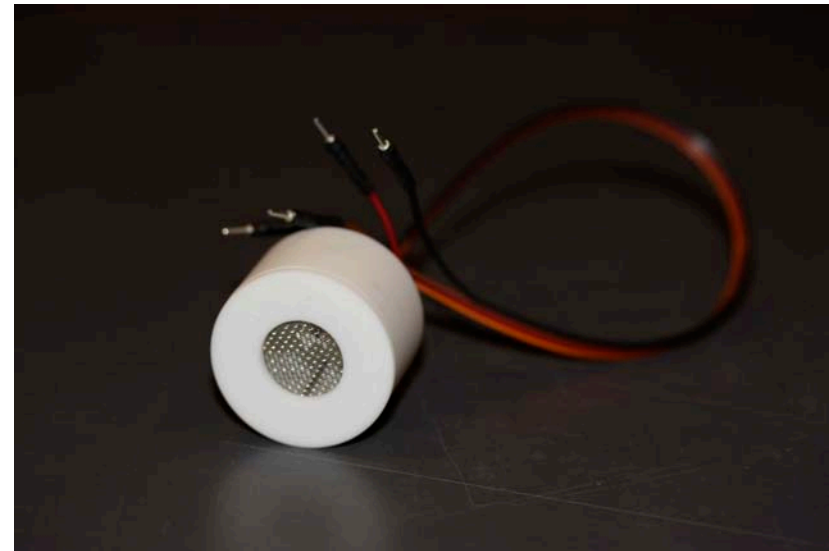
Approach: Milestone met for progress towards commercialization, materials engineering and working with industrial partner



1st Generation device – tape cast using ITO electrode and controlled interface approach. **Externally-heated** with tube furnace (30lbs): **120V, 8A**. A quarter illustrates size of sensor. FY09.



Pre-commercial mixed potential sensor in thick film version on ESL fabricated platform (LANL specs). **Power requirements: 6.5V, 0.75A** Presently designing self-contained fixture so that sensors may be distributed to testing partners in FY11.



Pre-commercial ceramic packaging/sensor supported by 4 posts. **Power requirements: 5.0V, 0.65A**. Pre-commercial prototype easily handled and many placement options – easily test in static or flow environments. FY11.

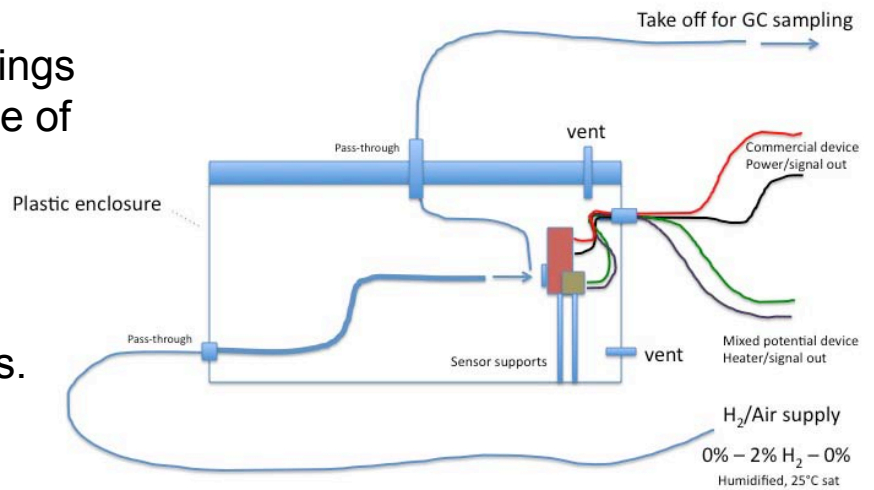
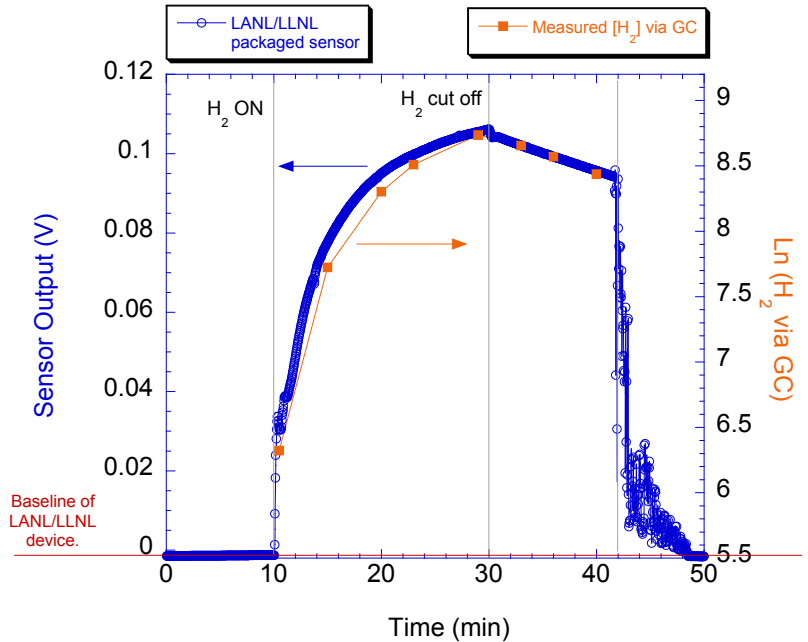
- Sensors require packaging to protect device, facilitate handling, transport, and testing by other entities.
 - Prerequisite for testing bench by NREL.
- Permits testing outside of a tube furnace/flow condition: Static testing/enclosure testing with H₂ source.

Approach: Technology adequate to meet low-cost goal?

- Technology a derivative of automotive O₂ sensor: Large #'s & low cost.
- 1st 20 prototype platforms – 4 post – were ordered in a single lot.
 - \$461.25 EA
- Pt screen print ink largest cost driver for the sensor platform.
- Budgetary estimate performed by ESL:
 - **100K** pieces, **\$0.75 to \$1.25 EA**
 - **500K** pieces, **\$0.60 to \$0.90 EA**
- Pre-commercial sensors prepared in this project required additional steps of sputtering ITO working electrode and YSZ electrolyte.
 - Must be factored in.
 - YSZ may be screen printed.
- Reasonable to guess at an upper bound of ITO/YSZ deposition of increasing sensor cost by 10x?
 - E.g. **\$6.00 - \$9.00**/sensor or in the range of a modern lambda sensor.

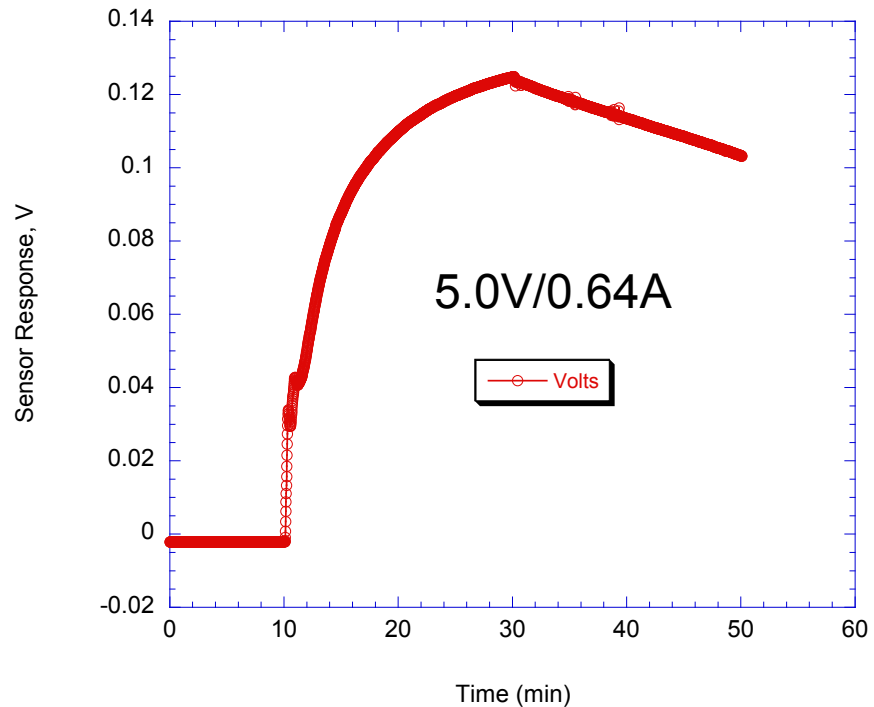
Technical Accomplishments: Static volume sensor testing of pre-commercial prototype against calibrated GC sampling/measurement

- Experiment: Testing LANL/LLNL pre-commercial H₂ sensor in more real-world scenarios.
- LANL/LLNL test sensor performance compared to a commercially-available TCD-based H₂ sensor.
- An air/H₂ stream is introduced at 400cc/min into a 1.7cf plastic 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 the permit pass-through of cabling on back side of enclosure.
- H₂ is premixed with air and humidified before introduction into enclosure to prevent any possibility of achieving flammable fuel/air ratios.

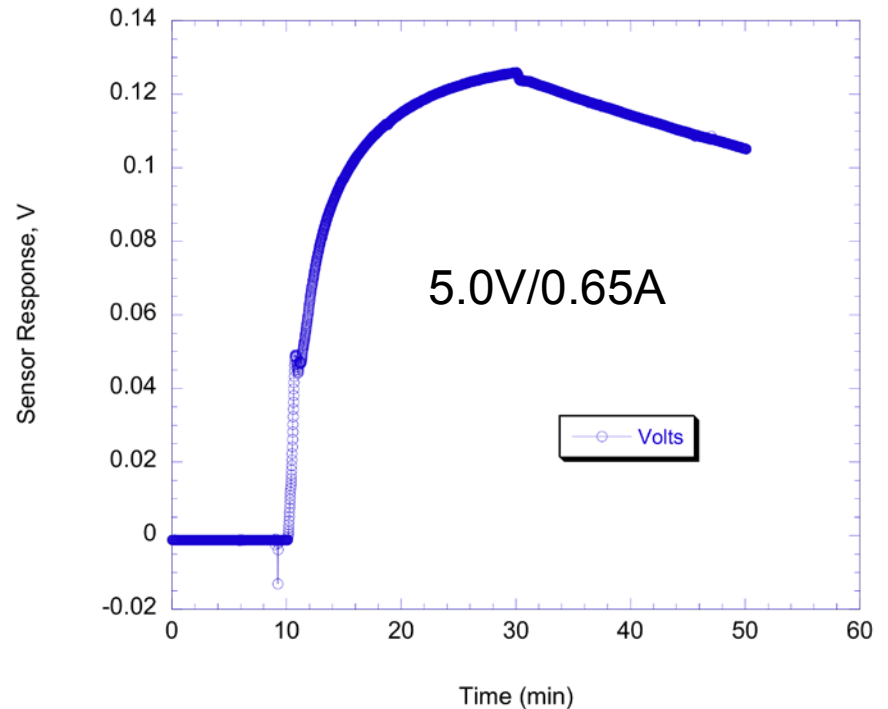


Technical Accomplishments: Packaged device reproducibility of pre-commercial prototype sensors

ITO/Pt-P Device #1



ITO/Pt-P Device #2



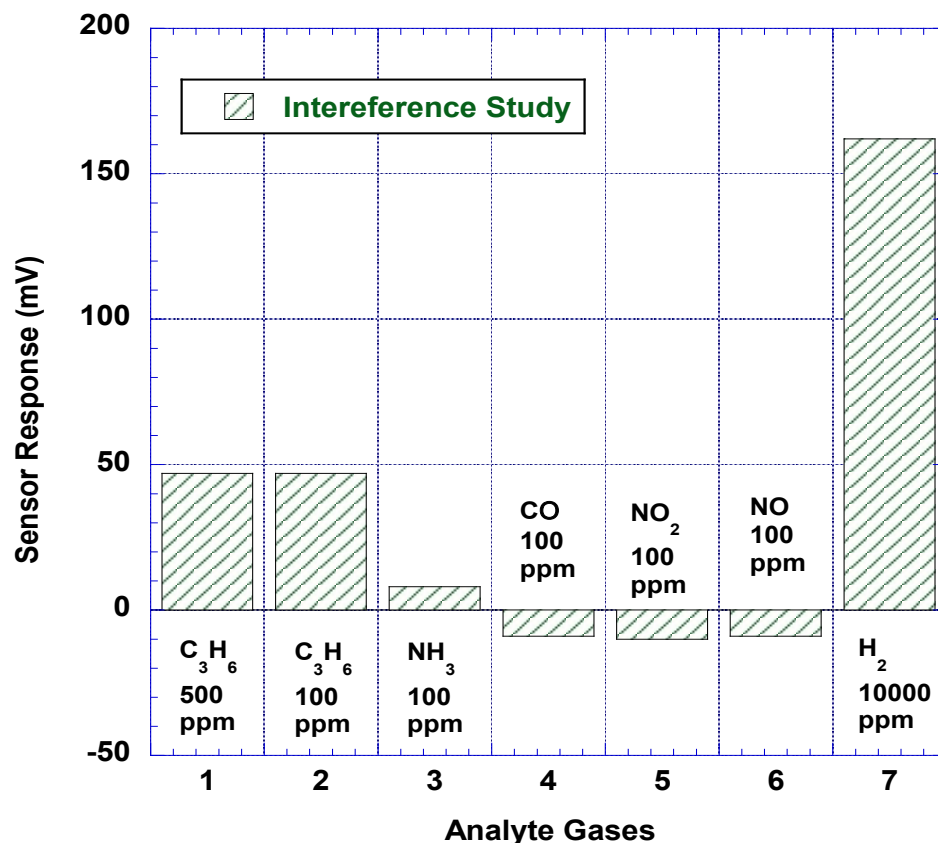
- Packaged pre-commercial prototype sensors have reproducible sensing characteristics.
- Biggest contributor to device-to-device reproducibility is variation in ESL heater R and placement of sensor within packaging; e.g. Temperature.

Technical Accomplishments: Milestone for transfer of packaged, pre-commercial prototype sensors to NREL for independent validation

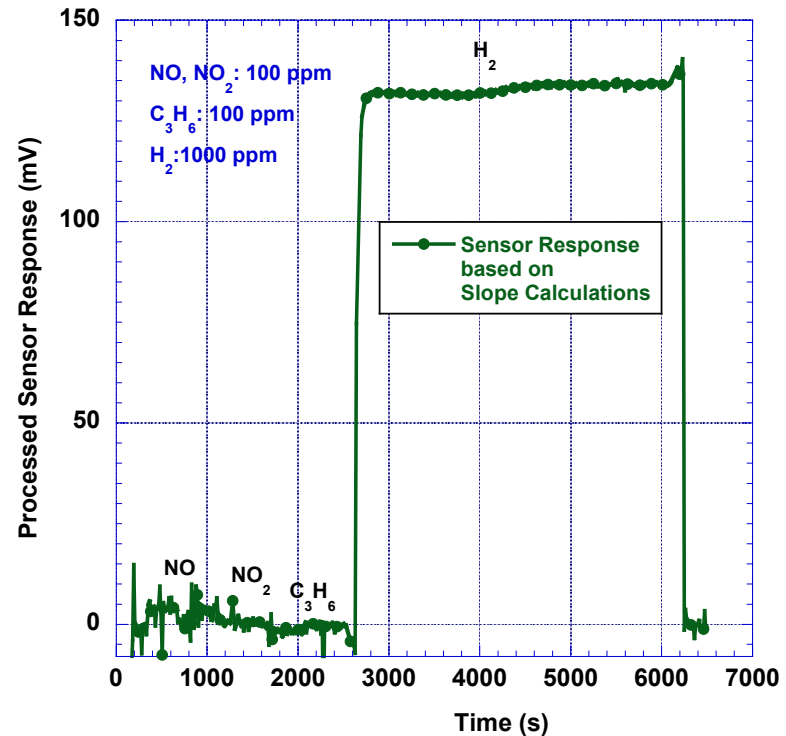
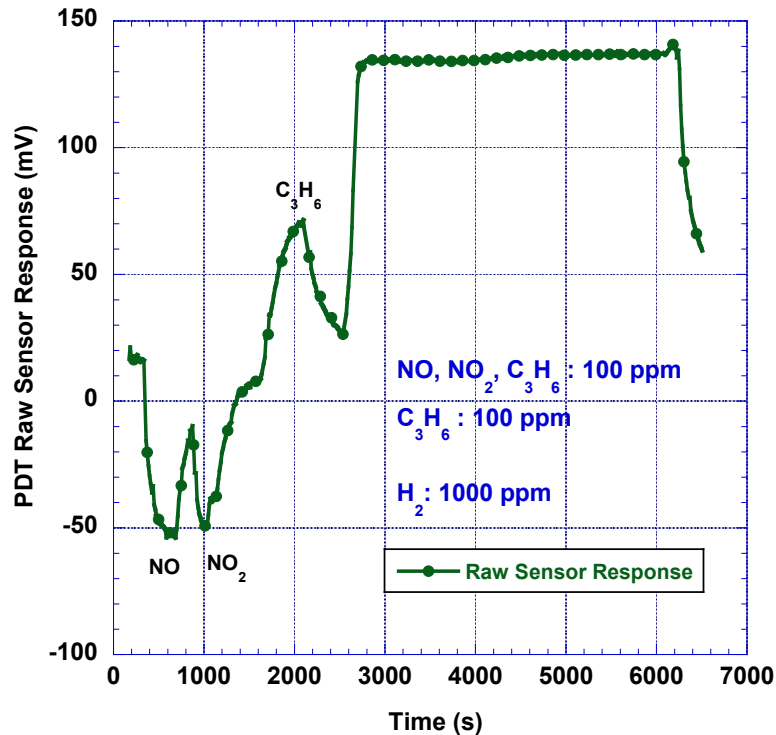
- 2 packaged H₂ sensors and sent to NREL (Oct 2010) for testing (Jan 2011).
 - 1 failed lead wire due to mechanical stress.
 - Resolved: replaced with backup sensor.
- LANL sensor packaging mated to NREL sensor test rig.
- H₂ Response, RH influence, response to H₂ partial and absolute pressure, ambient T sensitivity tested.
- The Good: H₂ response with insensitivity to changes in RH and T.
 - Behaves as predicted to ambient T changes – will be solved with RTD and active sensor T set point.
 - Behaved with anticipated response characteristics.
- The Bad: Unexplained anomalous baseline behavior never before seen at LANL or LLNL.
 - Sensors returned post-testing, and retested at LANL: anomalous baseline behavior is *not* a property of the sensors.
 - Resolution: fabricate input and signal conditioning circuit for high impedance sensor with scaling and offset capability, shielding, and heater power.
- The Ugly: NONE!

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.



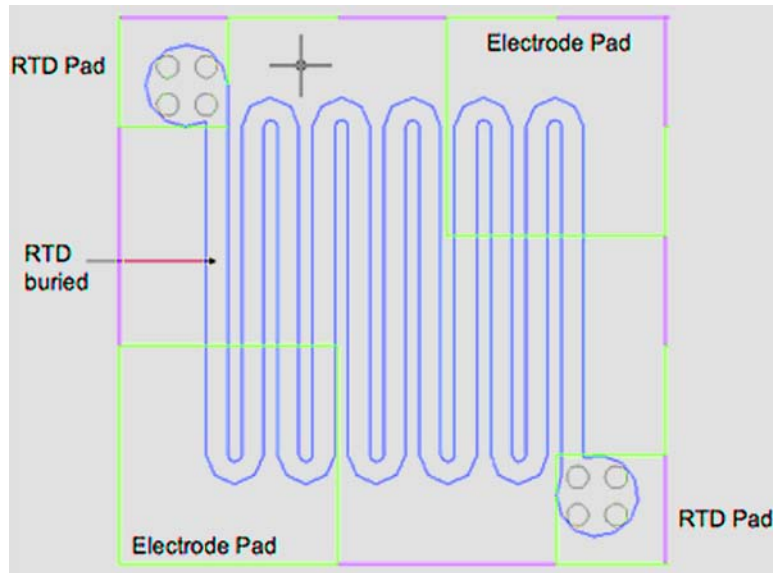
Technical Accomplishments: Collaboration BJR Sensors LLC utilizing Pulse Discharge Technique (PDT) combined with unique properties of the LANL/LLNL pre-commercial sensor prototype



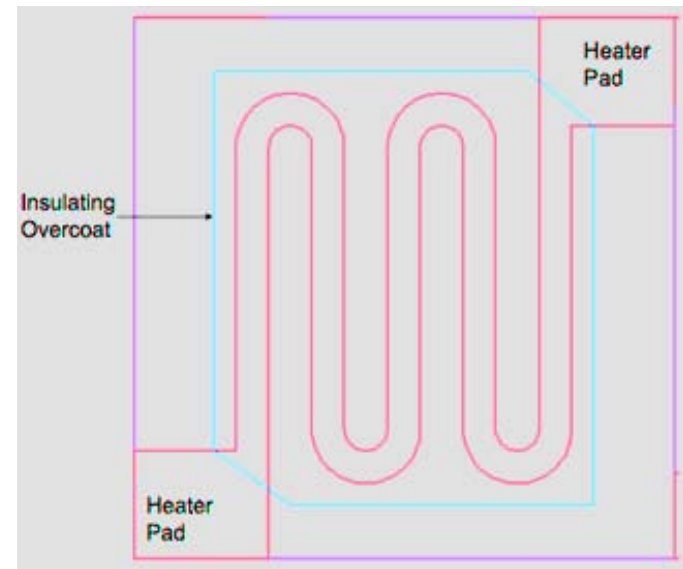
- Unique property of the LANL/LLNL H₂ sensor lends itself well to a new approach to Lambda sensor signal conditioning developed by BJR (Patent no. 7,585,402).

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

Top surface of ESL substrate

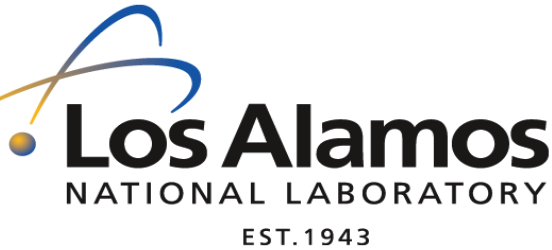


Bottom surface of ESL substrate



- More advanced sensor platform was developed.
- Continuing to work with industry partner ESL Electrosience, 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.

Collaboration and Coordination with Other Institutions



Emphasis: Development of commercial prototypes, packaging and life testing.



Emphasis: Materials selection, sensor design, and alternative modalities.



Emphasis: Codes & Standards field performance evaluation/validation team member.



Emphasis: PDT control/signal processing.



ESL ElectroScience

Industrial Partner
Experts in manufacturing high temperature ceramic materials, scale-up, engineering processes.

Proposed Future Work:

- Remainder of FY2011:
 - Fabricate new sensors on platform with embedded RTD.
 - Using the results from NREL testing, Round 1, improve sensors and packaging.
 - Work with NREL to develop testing protocols for mixed potential type gas sensors.
 - Work with NREL to test prototype circuit board and electronics for mixed potential type sensors.
 - Fabricate electronics to protect sensors from external influences, leakage currents, etc.
 - Impedance matching, signal amplification, etc.
 - Utilize RTD/incorporate active temperature control.
 - Provide sensors and control electronics to NREL for Round 2.

Summary

- All FY11 Milestones are on target to be completed
- A viable H₂ safety sensor technology has been developed on a pre-commercial sensor platform that continues to improve
- Mixed potential-based H₂ safety sensors have been fabricated, packaged and transferred to NREL for testing
- Round 1 complete. Positive feedback used to improve device
 - Electronics necessary and are being designed, and will be in testing phase shortly
 - Move from a naked sensor to near-commercial state
- NREL Round 2: once circuitry, shielding, heater controls are in place.

Back-up Slides

Relevance – Technical Performance Requirements

Why does the hydrogen community need better H₂ Safety Sensors?

“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

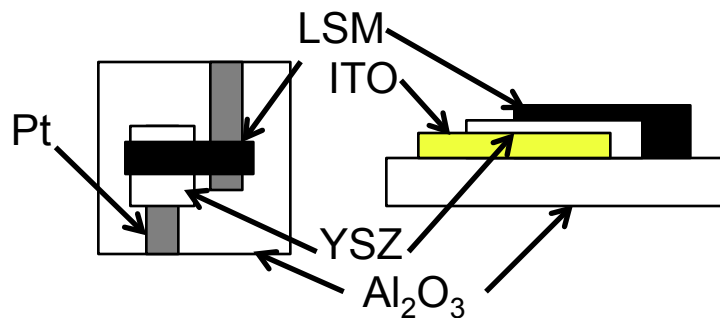
“...From our point of view there is a need for a low-cost reliable sensor.”

Stuart Pass, Teledyne Energy Systems

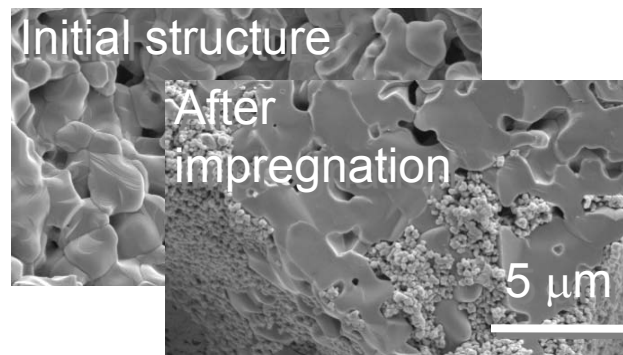
In addition, **Natalie M. Olds, USCAR**, has voiced concerns about the lack of commercial sensors with required accuracy or speed to test diffusion models for simulating hydrogen release during crash testing of fuel cell vehicles and that without an appropriate sensor to equip test bays and crash vehicles,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

Technical accomplishments: Milestone achieved for stability and reproducibility to over 3000 hours of laboratory furnace testing

- Laboratory prototype design presented last year was modified to investigate novel impregnation technique for improving long-term stability.



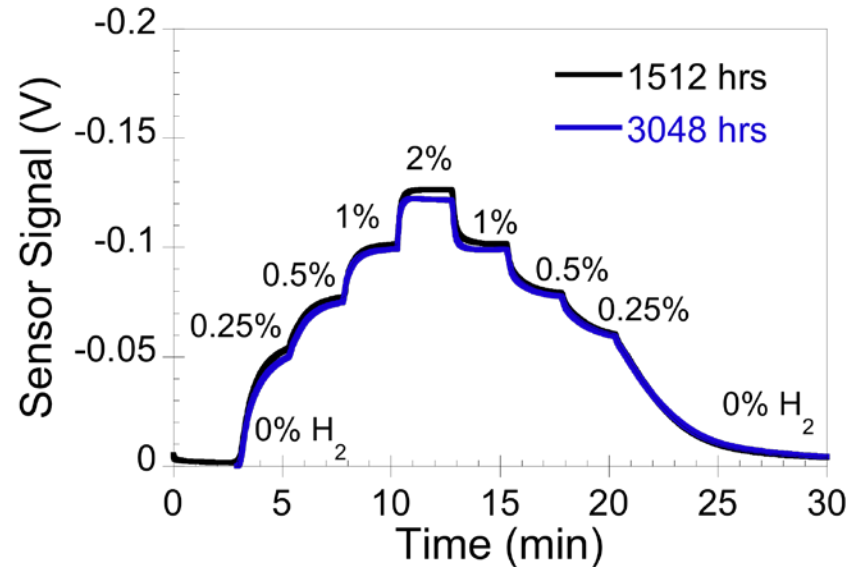
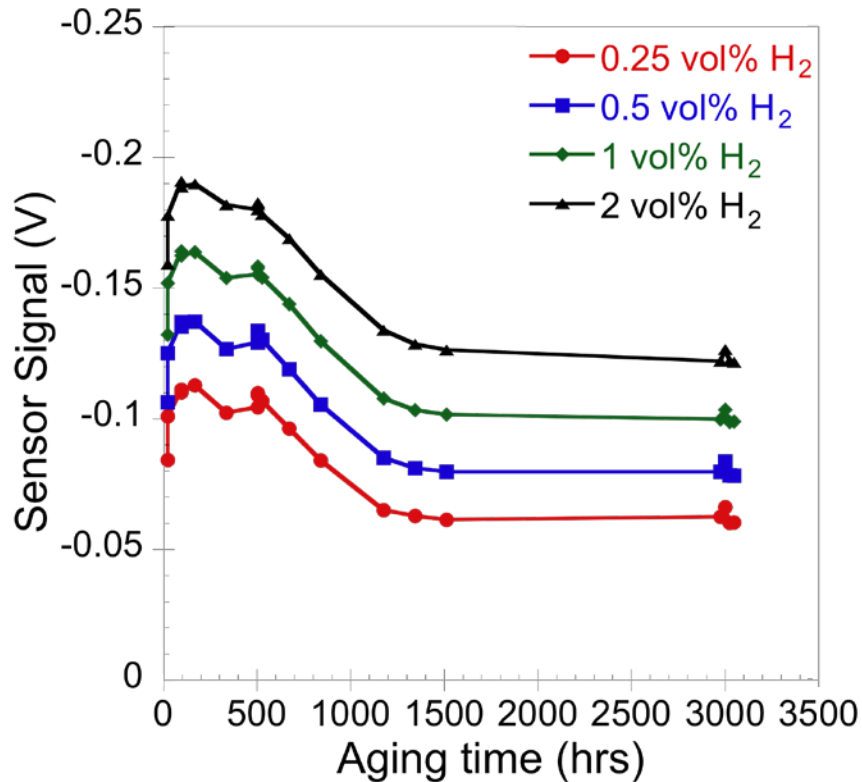
Top and cross-sectional view with tin-doped indium oxide (ITO) and dense LSM electrodes, yttria-stabilized zirconia (YSZ) electrolyte.



Separate low-temperature impregnation was used to introduce ITO into sintered porous YSZ.

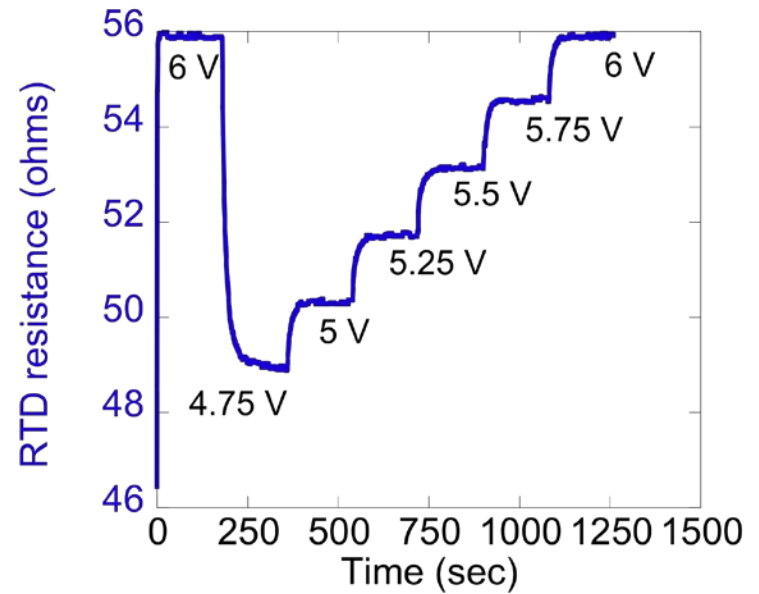
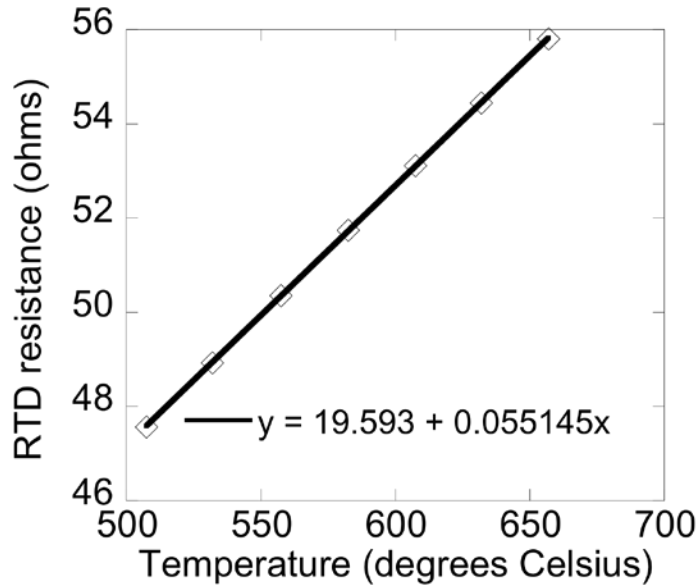
- Using same design as previously investigated, the ITO sensing electrode was replaced with a 50 wt% impregnated composite ITO/YSZ sensing electrode.
 - The porous YSZ was spin coated and initially sintered to 1000C.
 - ITO was impregnated using a 5 wt% nanoparticle solution (50/50 wt% water/ethanol).

Technical accomplishments: Milestone achieved for stability and reproducibility to over 3000 hours of laboratory furnace testing

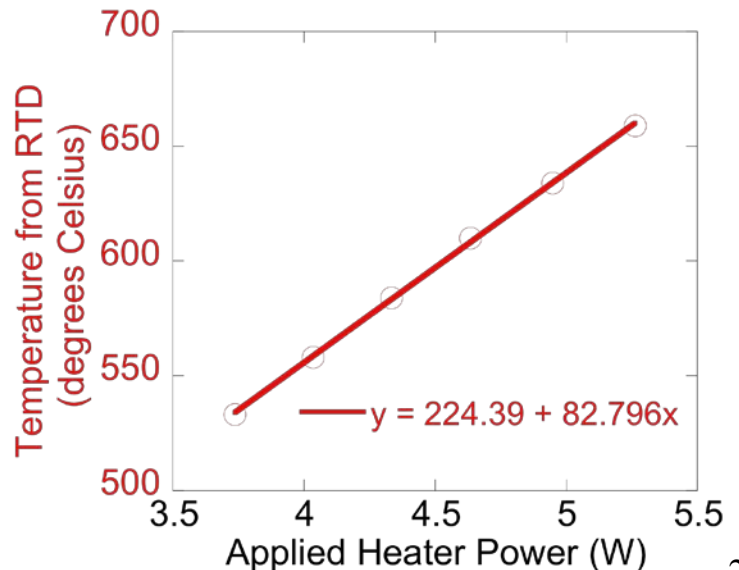


- Laboratory prototype design presented last year (FY10) showed reasonable performance up to ~2000 hours, but then signal magnitude began to degrade.
- The impregnated composite ITO/YSZ sensing electrode had improved stability to over 3000 hours, likely due to better thermal expansion match with YSZ electrolyte.

Technical accomplishments: Developed method for calibrating embedded resistive temperature detector (RTD)

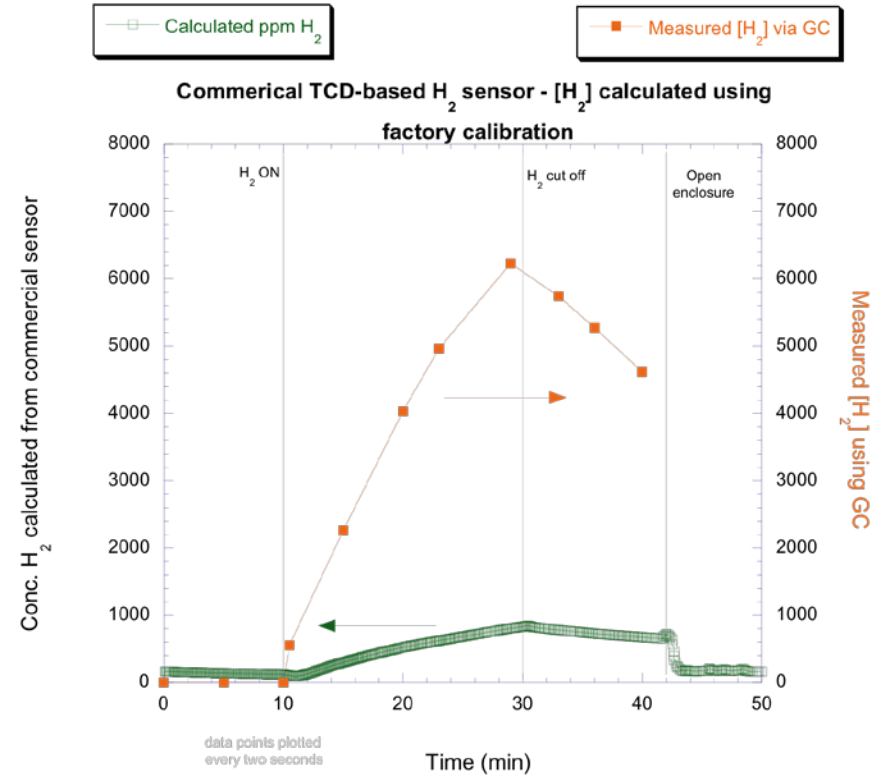
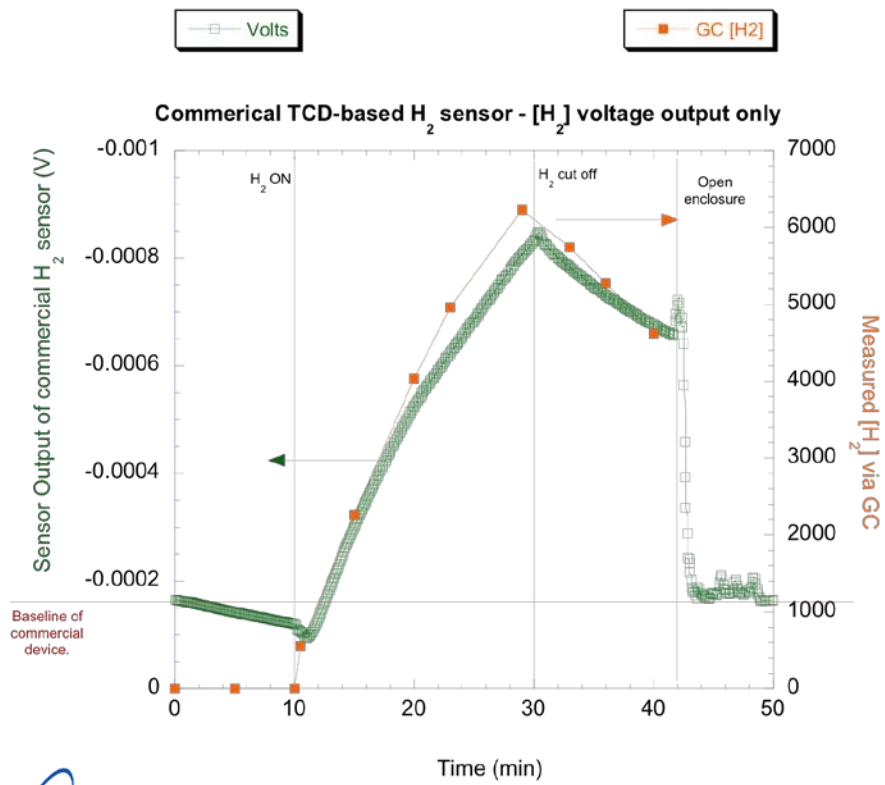


- RTD resistance initially measured using controlled furnace with thermocouple.
- RTD resistance then measured at different heater voltages from 4.75 to 6 V.
- Finally, the RTD resistance was used to find the relationship between the heater power and measured temperature.



Commercial H₂ sensor incorporated into the test chamber to provide feedback and act as a benchmark for the LANL/LLNL pre-commercial device

- TCD linear dependence on P_{H₂}.
- H₂ sensor tracked H₂ levels but factory calibration was in error with the GC analysis.
- Humidity dependence when manufacturer claimed no dependence.
- Baseline zero point in error due to LANL elevation.



References

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