2013 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

P.I. & Presenter : Eric L. Brosha

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May 14, 2013

Project ID# SCS004

Overview

- **Timeline**
  - Start: Summer FY 2008
  - Finish: FY 2013
  - 95% Complete

- **Budget**
  - Total project funding
    - DOE share: $4500K
  - Funding for FY13: $200K
    - $150K LANL
    - $ 50K LLNL

- **MYRD&D Barriers** (2012)

✧ The SCS sub-program will develop hydrogen sensors with the appropriate response time, sensitivity, and accuracy for use in safety applications to reduce risk and help establish public confidence (Table 3.7.6).

Table 3.7.6 DOE Targets for Hydrogen Safety Sensors
Measurement Range: 0.1% - 10%
Operating Temperature: -30° to 80° C
Response Time: Less than one second
Accuracy: 5% of full scale
Gas Environment: Ambient Air, 10%-98% relative humidity range
Lifetime: 10 years
Interference Resistant (e.g. hydrocarbons)

- **Partners**
  - Project lead: LANL and LLNL
  - NREL: Codes & Standards field performance evaluation/validation team member
  - Custom Sensor Solutions, LLC – Commercial electronics developer
  - ESL ElectroScience, Inc. - Commercial prototype engineering
  - BJR Sensors, LLC

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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 performance evaluation in simulated laboratory and field tests, initiate rigorous life testing, and with NREL collaborators to evaluate sensor performance in relation to codes and standards.
- Work toward commercialization by engaging appropriate industry partners, including long-term testing and development of manufacturing methods.
- 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?

- Ultimate Problem: sensor drift leading to false positives and false negatives.
- 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.

…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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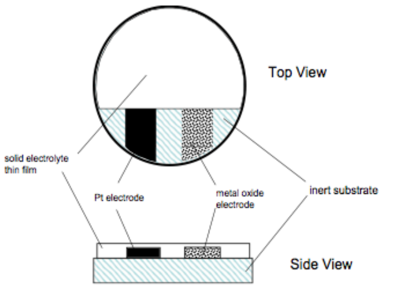
Milestones FY13

- Completed 2nd round of NREL testing.
  - FY13 sensors AOP Objectives and Milestones were set based on positive feedback.
  - Results confirmed identification of source, and ***successful amelioration*** of sensor anomalies reported in FY11 testing.
  - High impedance buffer circuits ***isolated*** electrochemical sensor from leakage currents in NREL DatAcq system.
  - New improvements made to sensors to greatly widen the application environment of the technology.
  - Devices continued to be improved throughout FY12 for testing and electronics development.
- Fabricated more advanced sensor substrates incorporating unitary heater/RTD.
- Working electrode and electrolyte layers deposited using electron beam evaporation.
  - Significantly faster ***and cheaper*** method of manufacture.
  - Already obtained estimated sensor platform costs using scale-up models from ESL: Sensor cost not a barrier.
- New working electrode candidate identified so that sensor may withstand harsh, anaerobic protocol used by NREL.
- Heater electronics designed around unitary device configuration.
- Effective prototype packaging scheme for pre-commercial naked sensors.

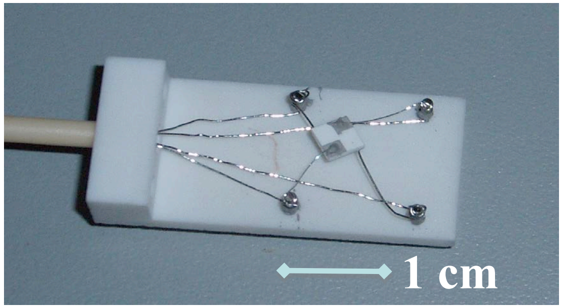
Approach: Controlled Interfaces for Sensor Design and Development

Sensor Technology Selection

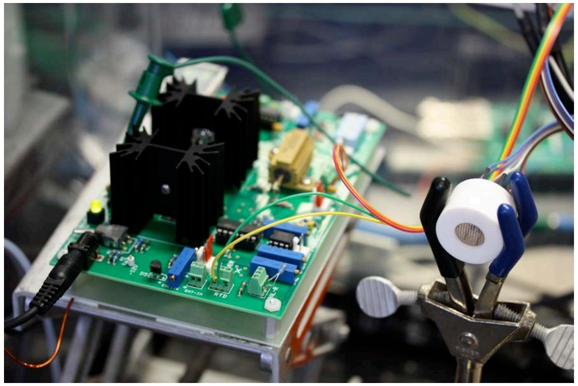
- **Derivative of the hugely successful automotive Lambda, potentiometric O_2 sensor.**
- Mixed-potential sensors generate a non-equilibrium potential in the presence of oxygen and a reducing/oxidizing gas.
- Unique class of sensors have been developed that are based on dense electrodes and porous electrolyte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



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



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



Packaged H_2 safety sensor with prototype control electronics.

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*** and now must impart these accomplishments to commercial prototypes.

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:

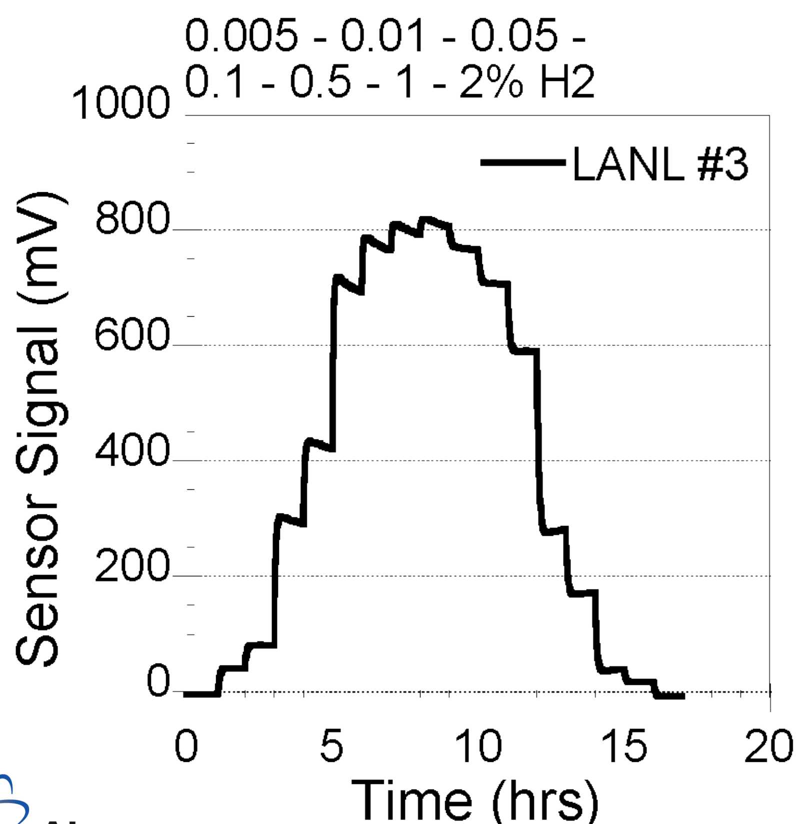
- ✓ ESL ElectroScience, Inc. – lay groundwork for mass fabrication of the sensor element.
- ✓ Custom Sensor Solutions, LLC - develop electronics to interface the sensor element to the outside world.

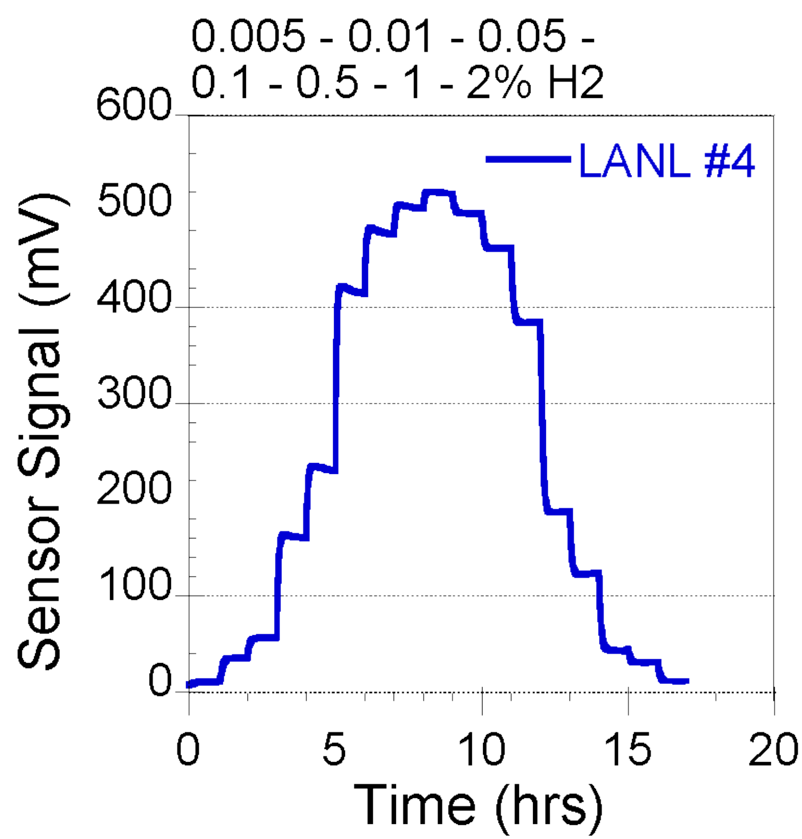
Technical Accomplishments FY12: NREL testing continues to provide valuable feedback validating performance of the technology

- **Round 2**: H_2 sensor test stand at NREL used to evaluate sensitivity and influence of humidity, partial/absolute pressure, ambient temperature, cross interference, and anaerobic operation.
  - ✓ Impedance buffer electronics worked very well as designed, permitted normal sensor operation and testing using NREL systems
  - ✓ Sensor reproducibly tracked H_2 levels, wide range
  - ✓ Demonstrated high sensitivity to H_2 with high signal-to-noise
    - NREL protocol expanded to include lower level [H_2] testing for these devices (high sensitivity and signal-to-noise)
  - ✓ Demonstrated minimal influence of humidity
  - ✓ Conducted extreme durability testing
    - Operated for extended period of time including atmospheric conditions for which they were never designed

Technical Accomplishments: Round 2 testing at NREL – expanded testing in low range devices LANL#3 and LANL#4 (New Results)

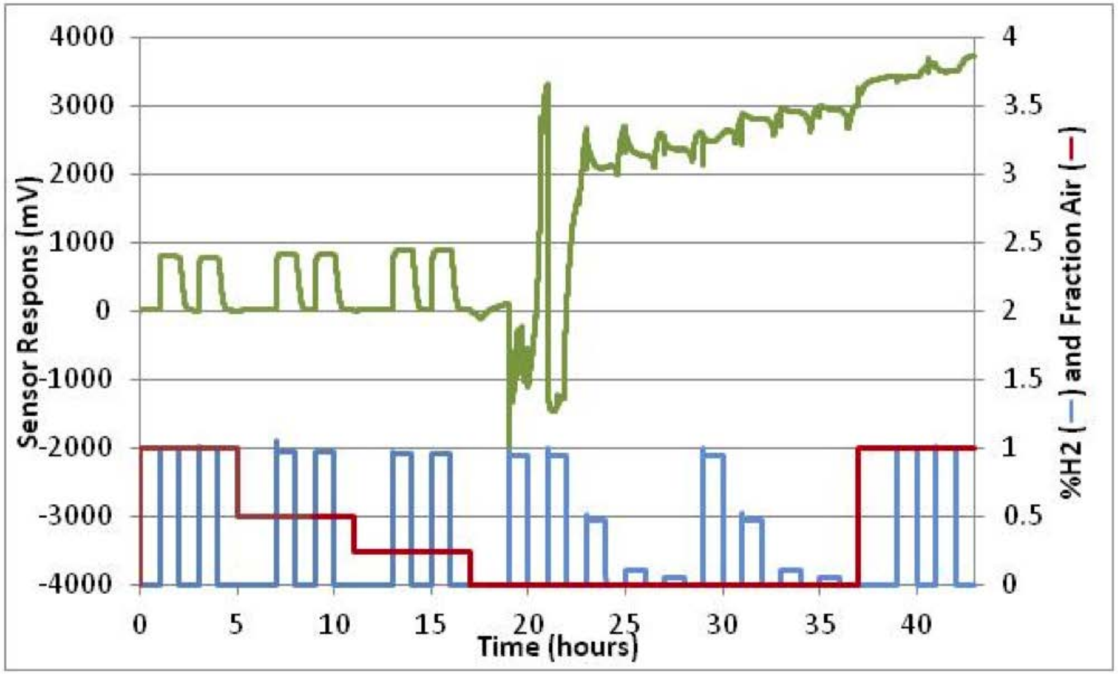
- NREL linear range test
- Normal sensor baseline and response using high impedance buffer electronics
- Sensors #3 & #4 were tested in parallel and showed measureable response at lowest concentration
- Level reproducibility validated in separate experiments
- Sensor gain set-point (HIB) different for each sensor as suggested by NREL: Sensor #3 output from HIB higher than sensor #4 but response is similar in characteristics otherwise.





Technical Accomplishments: NREL Round 2 – results of anaerobic testing and postmortem analysis of LANL#3 device (New Results)

- LANL/LLNL sensor exposed to extremely reducing conditions
- 5V produces ca. 550°C sensor T while PO_2 taken to 0%
- Exposure to H_2 in absence of O_2 lead to permanent alteration of sensor behavior.
- Mixed potential sensors based on oxygen ion conducting solid electrolytes require *some* oxygen in order to function.
- The oxidation state of the ITO material comprising working electrode can easily change under these conditions.
- ITO electrode is the only sensor component that would be affected by these conditions at normal operating temperature.



Conclusions:

✓ NREL test to measure sensor performance in anaerobic conditions. Test shows very little dependence on PO_2 until taken to 0%.

✓ Test shows LANL/LLNL prototype will effectively function and trigger event alarm and continue to function unless anaerobic conditions are established.

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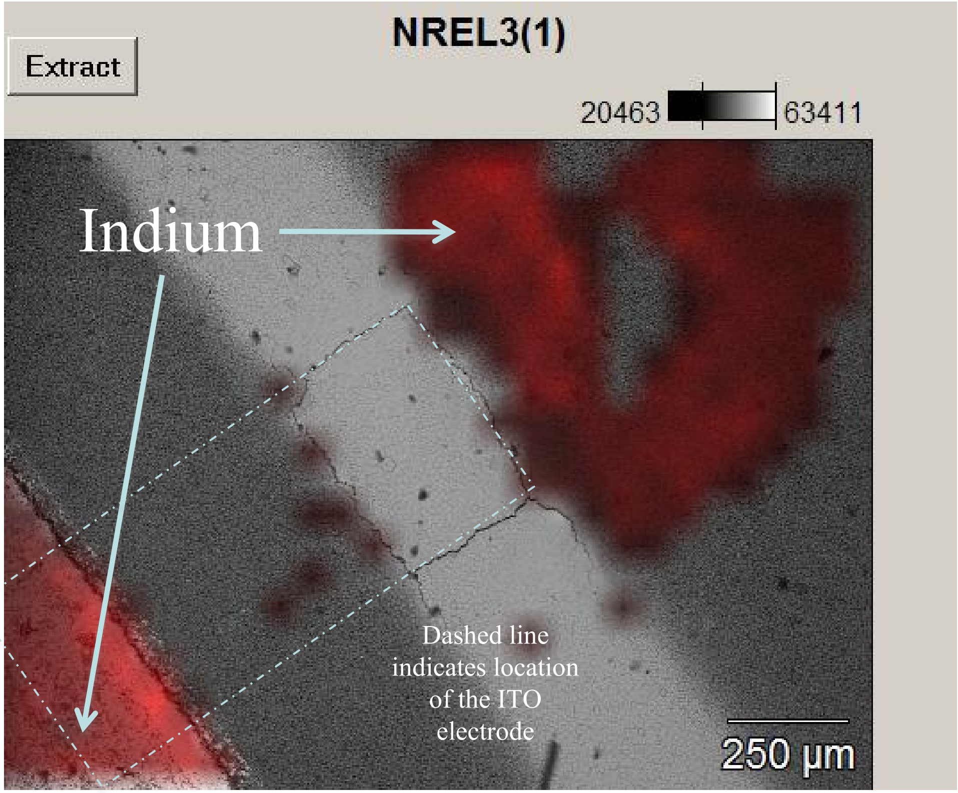
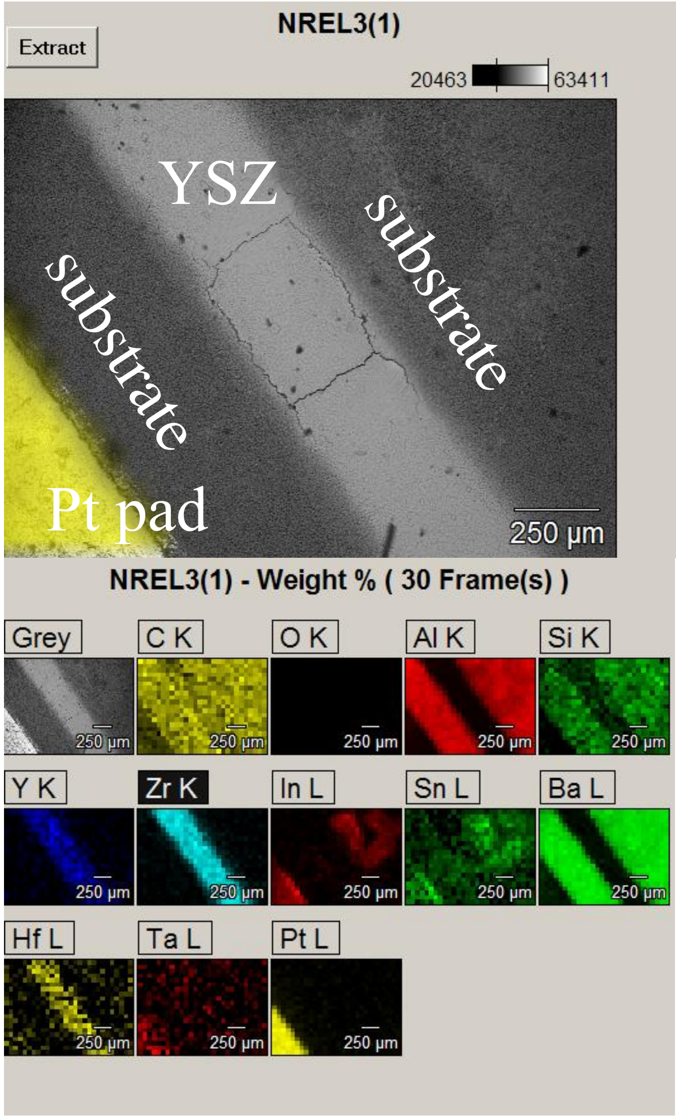
Technical Accomplishments: NREL Round 2 – results of anaerobic testing and postmortem analysis of LANL#3 device (New Results)





- EDAX analysis (image taken in backscatter mode) clearly show In diffusion into substrate and alloyed with Pt pad. Residual In traces on portions of alumina substrate.
- YSZ electrolyte only shows degradation in region where material covered ITO working electrode.
- All other parts of the device appear nominal and unaffected by exposure to severe operating conditions.

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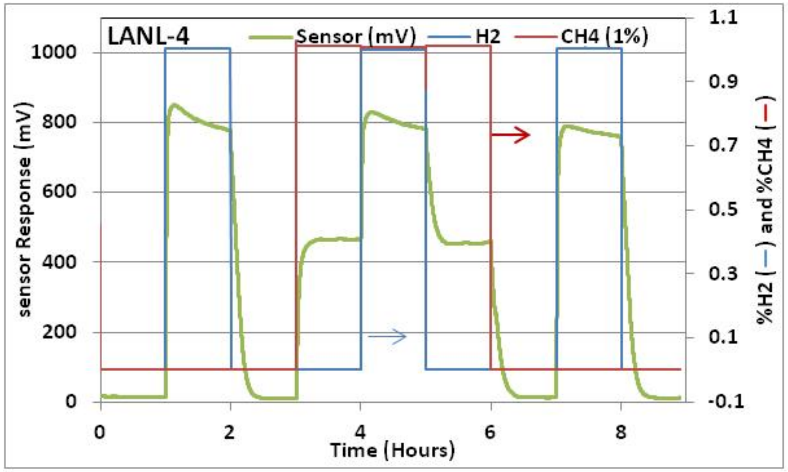
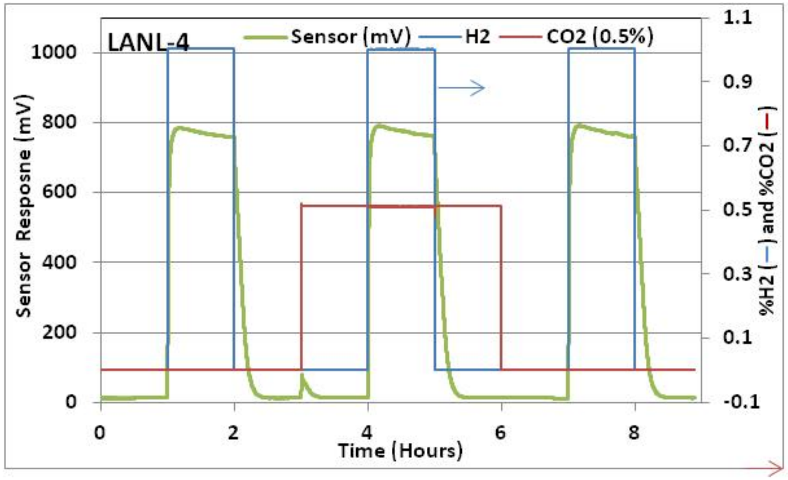
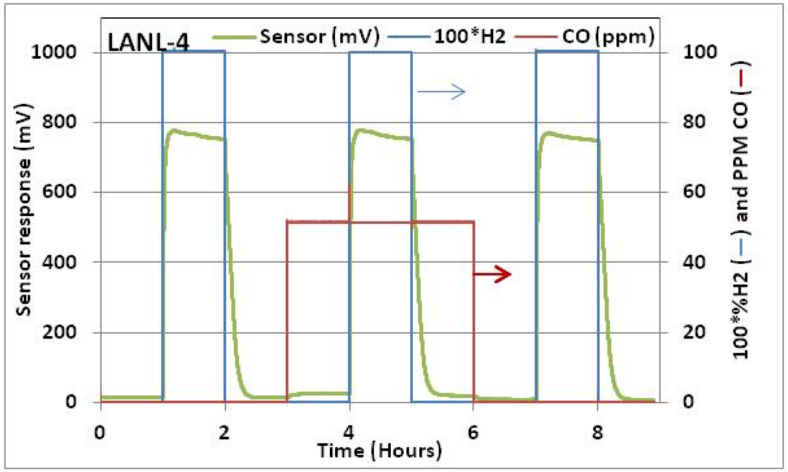
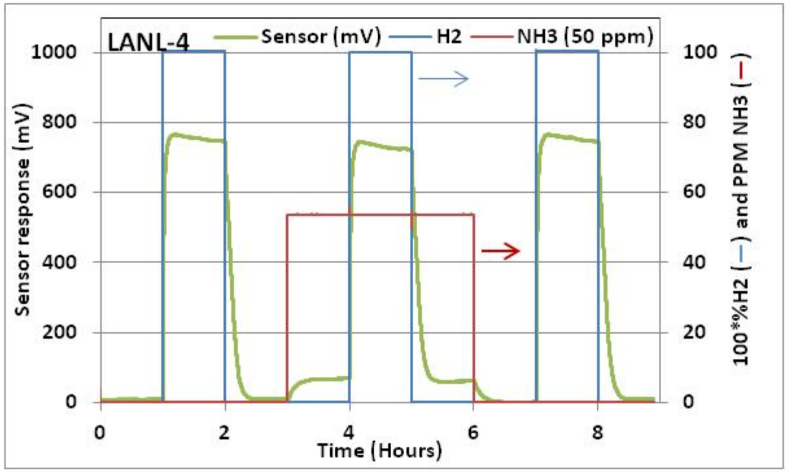
Technical Accomplishments: NREL Round 2 –interference testing LANL#4 (New Results)

- Standard interference test: 1% H_2, interferent, interferent + 1% H_2, interferent, 1% H_2
- 0.5% CO_2, 1% CH_4, 50 ppm CO, 50 ppm NH_3 interference species tested in Round 2
- NREL noted interesting methane/hydrogen response









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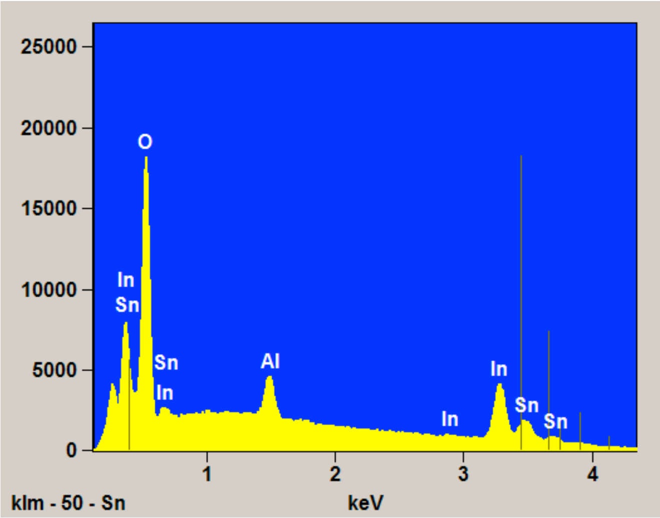
Technical Accomplishments: FY13 results and lead-up to Round #3 NREL testing

- ✓ Electron beam evaporation deposition of both ITO working electrode and YSZ electrolyte.
  - ITO electrode grown more than an order of magnitude faster than using RF magnetron sputtering.
  - E-beam evaporation common manufacturing technique
- ✓ ESL prepared new platforms for FY13 work.
  - Unitary design with RTD and heater combined into one circuit
  - Simplifies design and lowers manufacturing costs.
- ✓ In response to NREL anaerobic testing, a new working electrode material was tested on an ESL prepared platform for H_2 response.
  - La-Sr-Cr-O perovskite is a well known SOFC interconnect material, ultra-stable
  - Would permit, in principle, non-PVD fabrication of sensor.
  - Another opportunity to reduce manufacturing costs.
- ✓ Modification and testing of sensor temperature control electronics to automatically change sensor heater power with changes in ambient temperature.
  - Eliminates temperature response reported by NREL after Rounds 1 & 2 of validation testing.

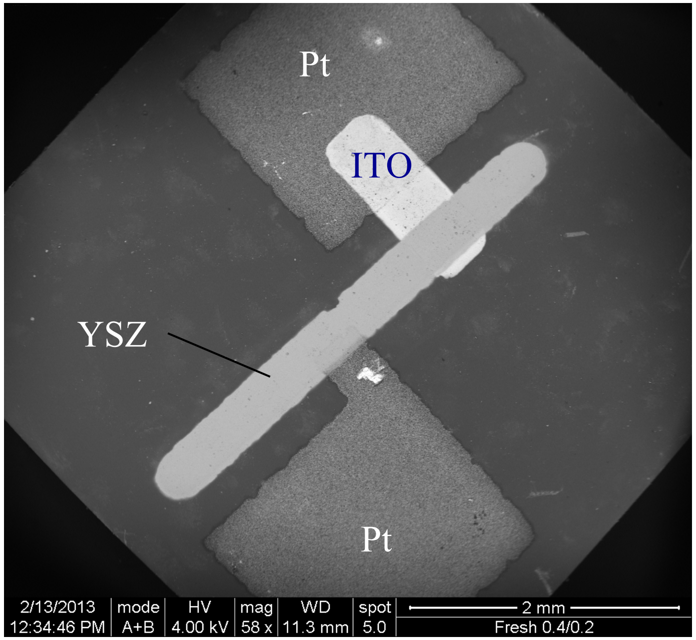
Technical Accomplishments FY13: e-Beam evaporation of ITO and YSZ components

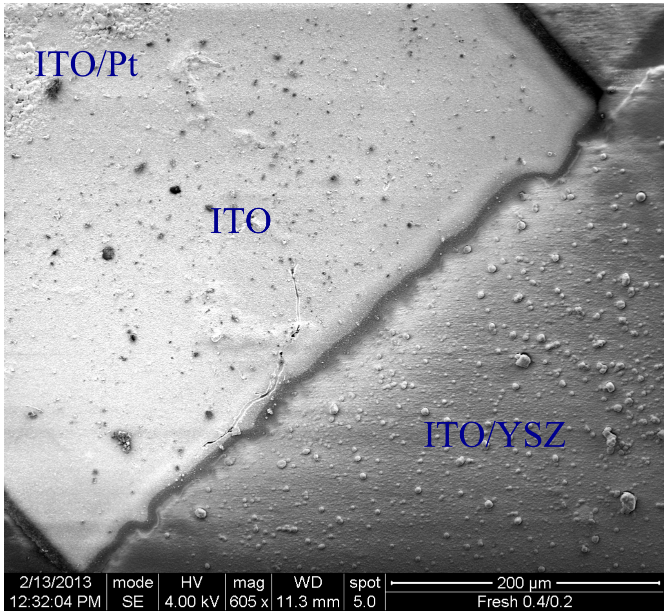
- New deposition method (ITO) and system used.
- New masks were fabricated to improve positioning of films.
- Relative thicknesses of films were reduced (up to 70-80%) to study effects on sensor performance.
- Higher deposition rates introduces small boulders (predominately in the YSZ) otherwise devices look acceptable. Possible sources of defects!

Presence of indium and tin confirmed using EDS.



SEM of sensor using backscatter detector.





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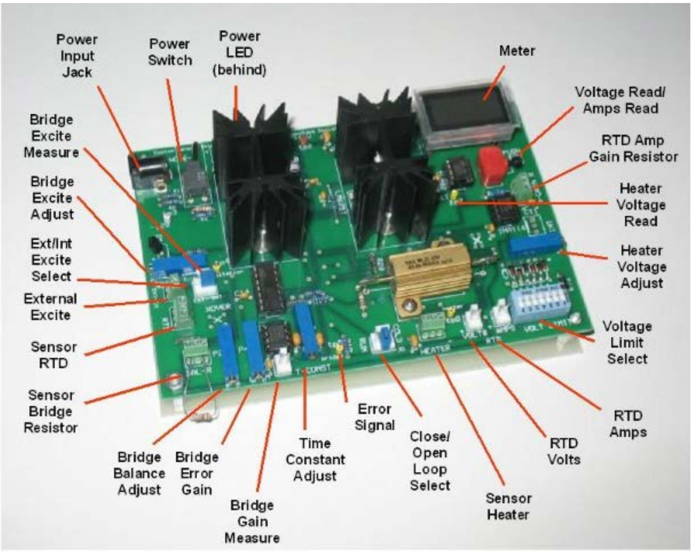
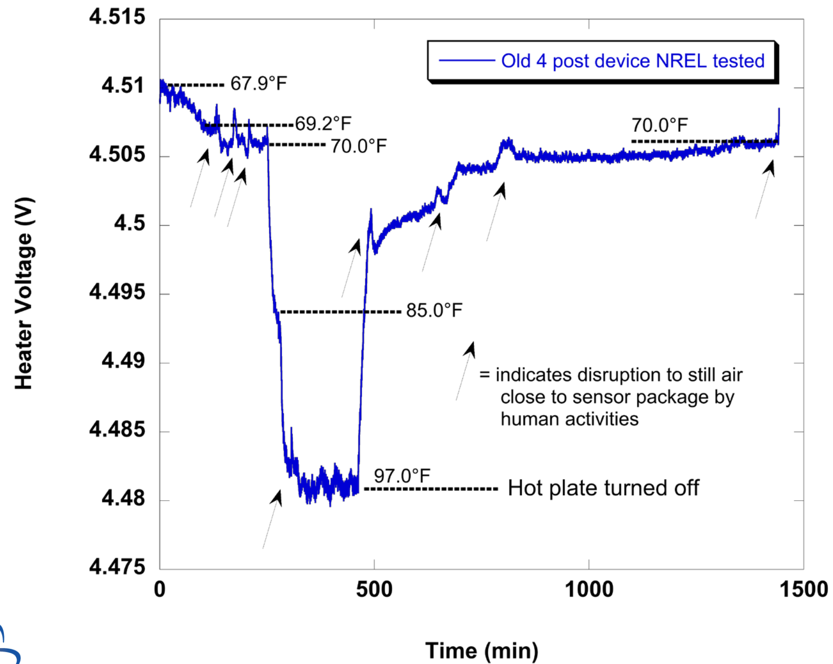
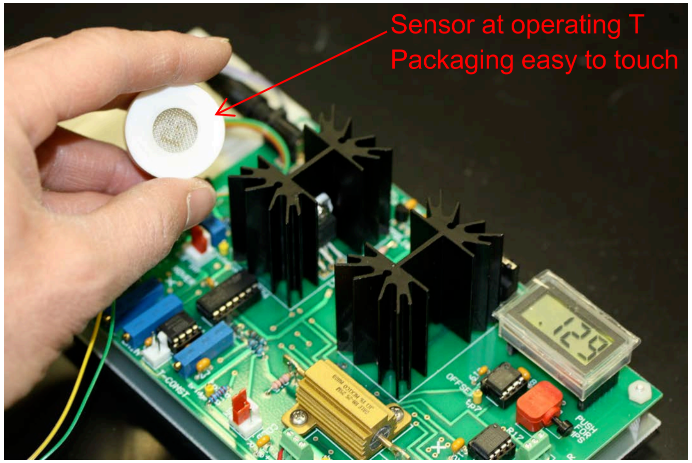
Technical Accomplishments FY13: Improved heater control prototype electronics

- Constant Resistance Power Supply prototype designed by Custom Sensor Solutions.
- Designed to use unitary RTD/Heater construction of the ESL sensor platform.
- Designed to function with mixed potential electrochemical sensors.
- This model is now a CSS stock item available to researchers.

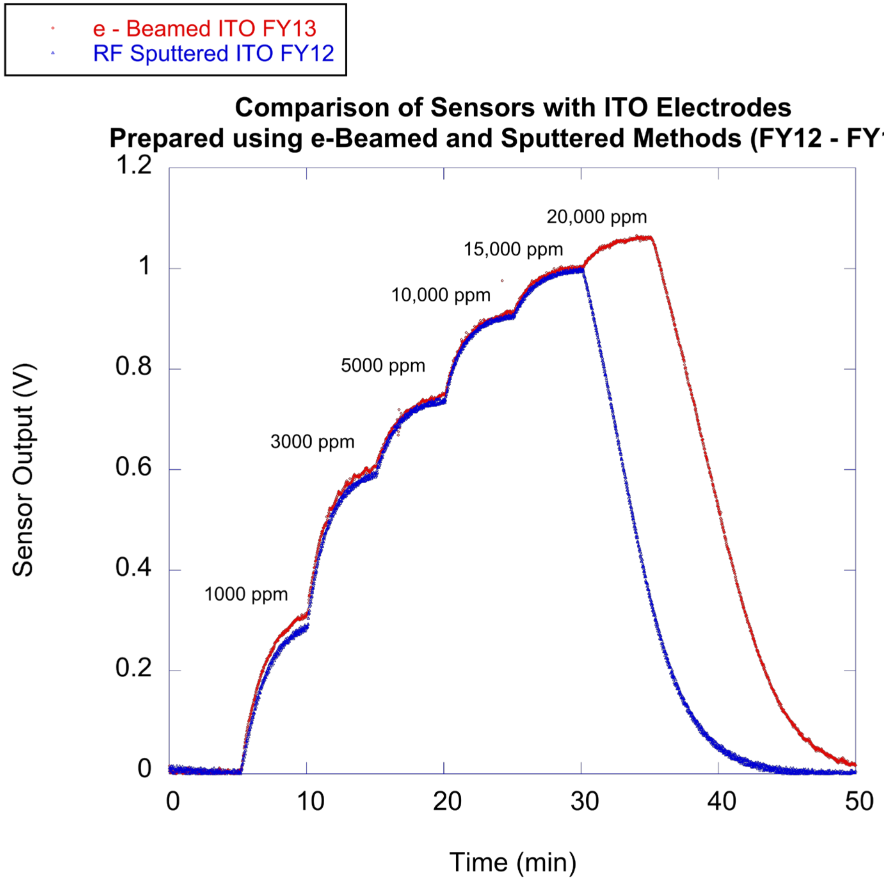


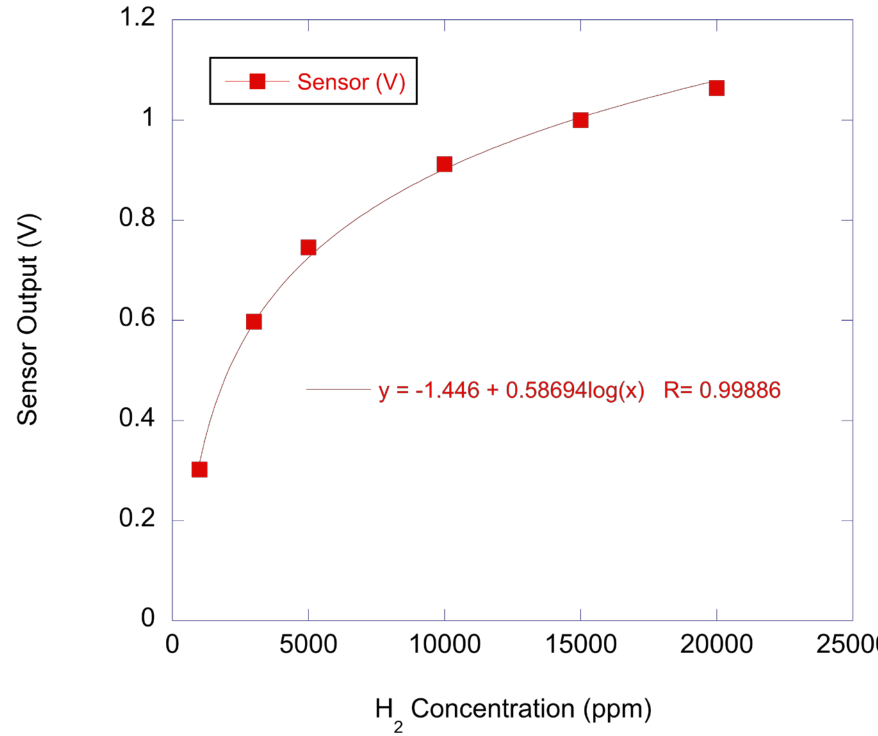
Heater/RTD Unitary operation - response to changes in abient temperature. Packaged sensor placed above hot-plate. Ambient T indicated measured by independent thermocouple.





Technical Accomplishments FY13: Faster, Better, and Cheaper





- Response of sensors with electron-beamed ITO have identical response despite 60x faster deposition rate.
- Sensor substrate from new ESL production run, different deposition systems/operator, etc.
- T feedback for heater control reveals true logarithmic device response.

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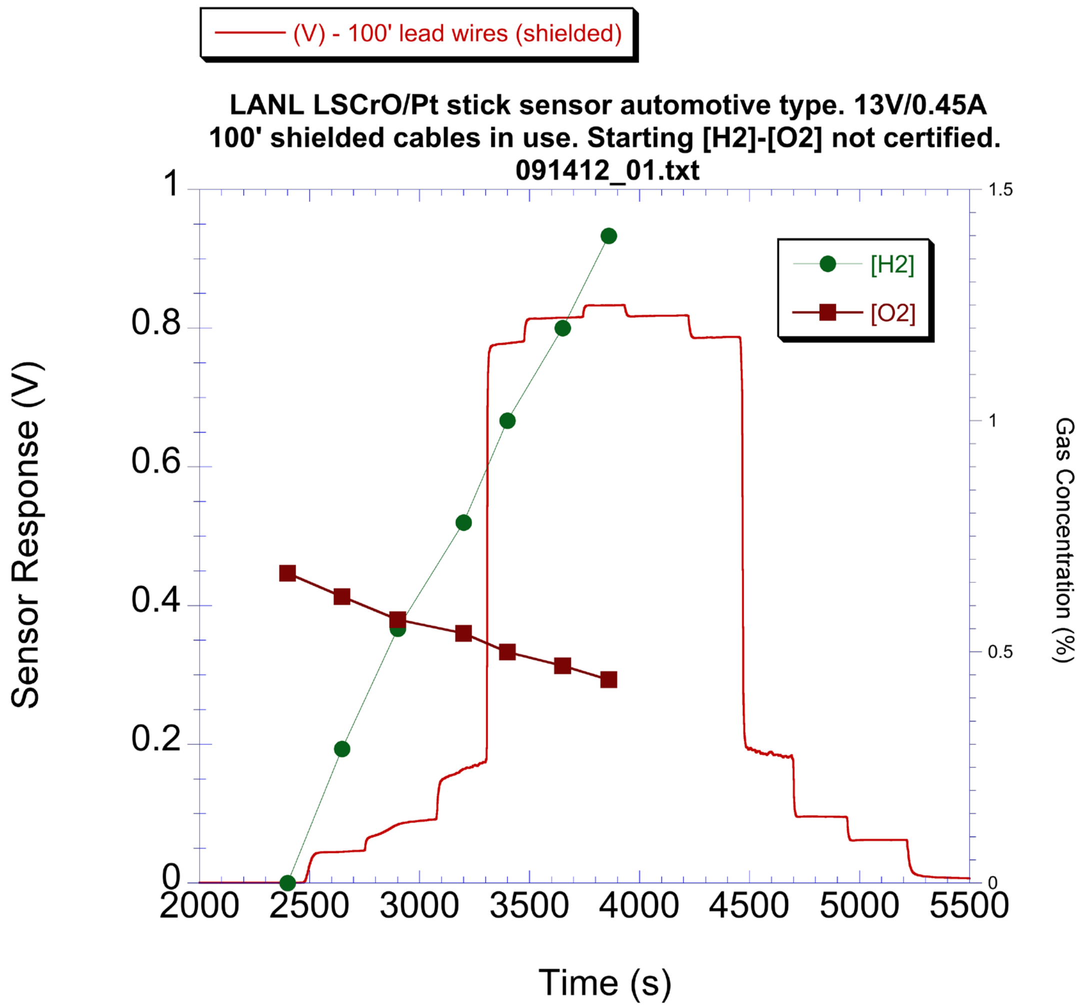
Technical Accomplishments FY13: Feedback work from NREL anaerobic testing – New working electrode for harsh environments

- A LANL mixed potential sensor using La-Sr-Cr-O perovskite working electrode was tested as "wide range" H_2 sensor. E.g. H_2/O_2 ratio was taken past stoichiometry.
- LSCrO will survive anaerobic conditions.
- Analogous behavior to oxygen lambda sensor with pseudo-reference electrode.
- H_2 level could be measured either side of stoichiometry.
- Demonstrates flexibility for technology to adapt and …. "there's still lots to be explored and done."



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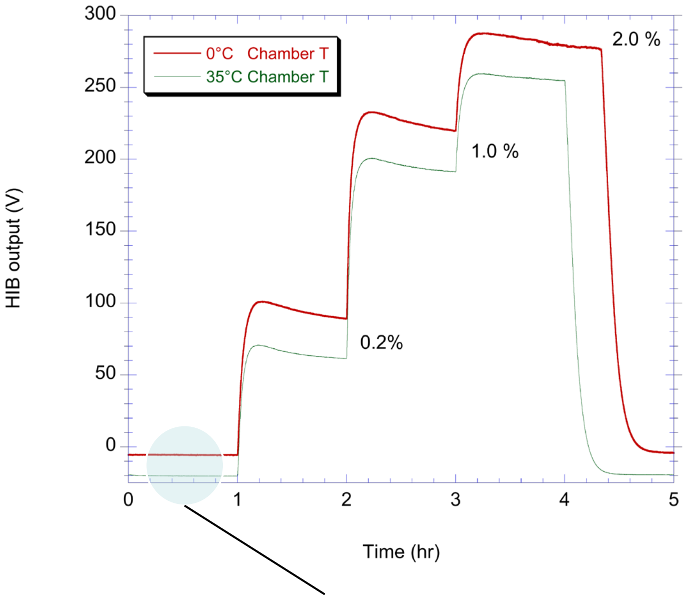
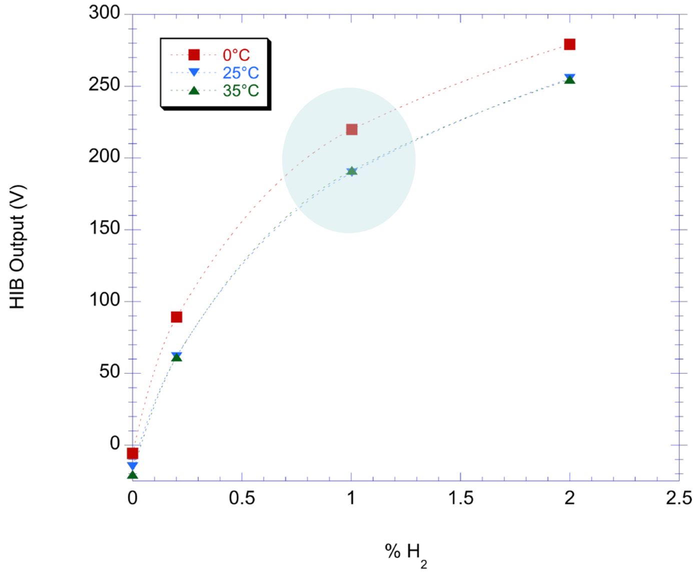
Technical Accomplishments FY13: Round 3 NREL testing results – Significant reduction in Temperature effect on H_2 response

FY13: 35°C change in T_{amb} led to 15% change in sensor level at 1% H_2 compared to a 136% change at 1% H_2 in FY12. Note, no change between 25°C and 35°C.





Packaged H_2 sensor, **and impedance buffer** placed into NREL test chamber.

- "Linear range test" to confirm proper functioning of sensor and data acquisition electronics.
- Heater control electronics located outside NREL test chambers.

Shift in baseline voltage can only be explained by a temperature-induced shift in offset dialed into HIB!

- A 35°C difference in ambient T was studied on day 2 of testing at NREL.
- Shift in H_2 response – primarily baseline driven- should have been anticipated. HIB electronics were placed inside test chamber with sensors and there is a clear temperature effect on the impedance buffer circuit . Good news: Predictable, repeatable, and can be calibrated out!
- Data collected during chamber T transition (T, P, RH, dew point) and H_2 level test.

Collaborations

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

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

NREL National Renewable Energy Laboratory

Codes & Standards field performance evaluation/validation team member

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 FY2013:
  - Collate and analyze data with NREL.
  - Prepare report on testing results and outline path forward.
  - Seek commercial development partners with commercialization achievements in hand.
  - Continue to work with NREL to develop testing protocols for mixed potential type electrochemical gas sensors.

- Future focus of safety sensor R&D:
  - Field testing/trials using present TRL mixed potential sensor technology in infrastructure applications in collaboration with NREL/commercial H_2 partners.

Future Work – Sensor technology can be improved even more:

- Great opportunity - TRL to conduct field trials (e.g. infrastructure applications)
- Large reduction in sensor size and mass possible.
  - Adapt LANL/LLNL mixed potential sensor technology to MEMS type platforms.
  - Drastically decrease sensor power requirements.
  - Incorporate sensor element on PC board with rest of control electronics.
  - More robust, compact sensor packaging
- Reduce size/optimize electronics for specific production spec.
- Add log-linear conversion for sensor-out of impedance buffer board.
  - Output for simple safety systems requiring linear sensor voltage signal.
- Develop $La_{1-x}Sr_xCrO_3$ working electrode with ESL for applications where substantially harsher environments may be experienced.

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Summary

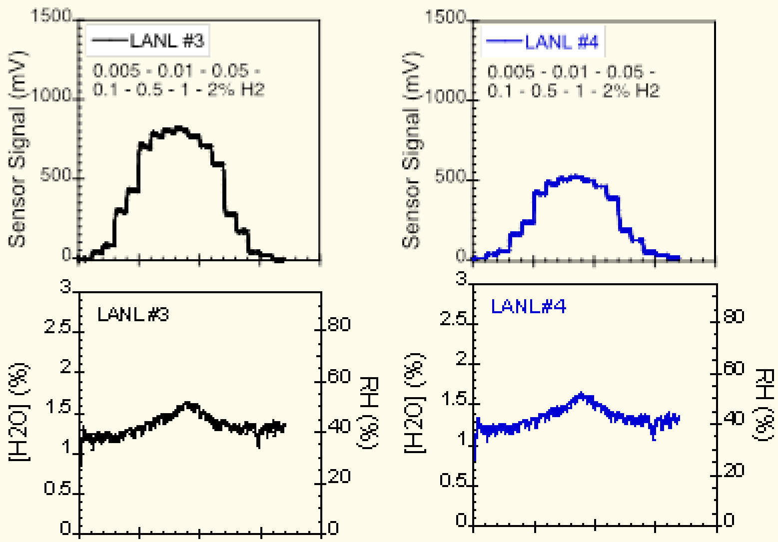
- ✓ All FY13 experimental Milestones in lead-up to NREL testing have been completed.
- ✓ Funding planned for outreach to commercial manufacturing partner will start after AMR date.
- ✓ Round 3 NREL testing conducted immediately before AMR presentation due date.
  - Focus on testing unitary heater/RTD/electronics operation and testing sensors made from lower cost fabrication protocol.
- ✓ Platform of prototype simplified for unitary operation with heater power supply/control.
- ✓ New faster film deposition methods (lower manufacturing cost) adopted in FY13.
- ✓ New sensor working electrode candidate identified that will protect sensor from extreme sensor environments better such as anaerobic events.

Technical Back-up Slides

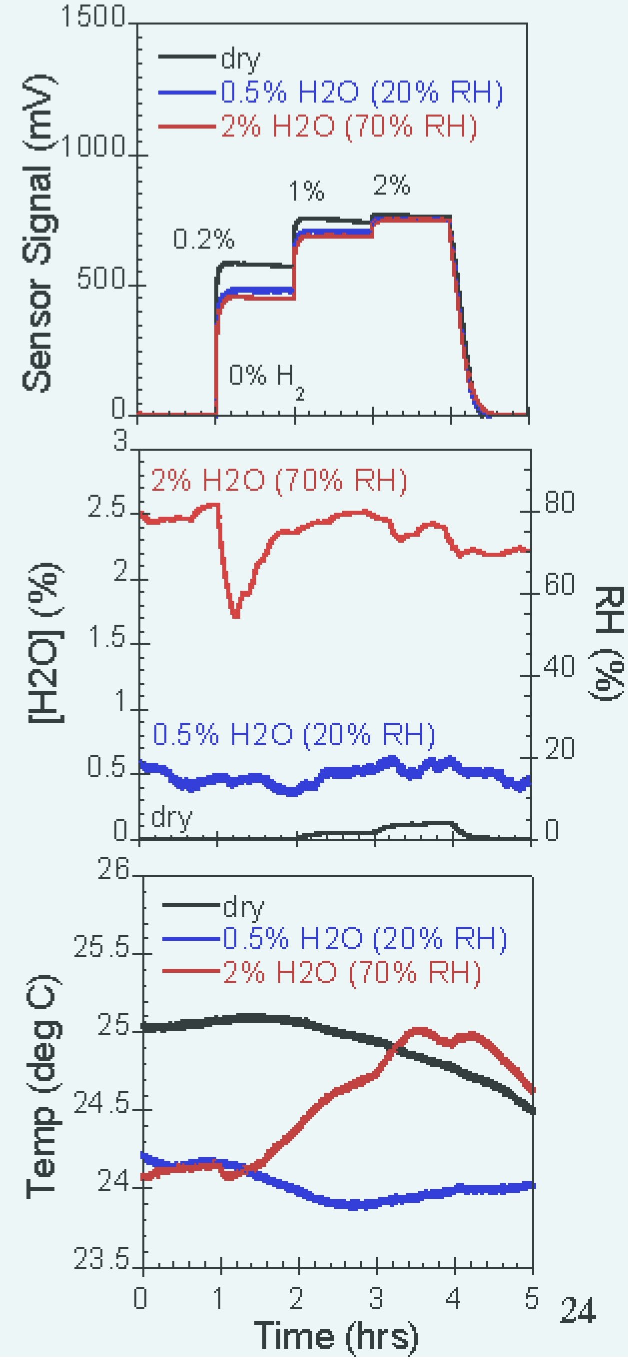
Technical Accomplishments: FY12 testing at NREL – results of humidity testing, LANL#3 device

- Lower H_2 levels added to test protocol (below)
  - 0.005, 0.1, and 0.05% levels added
- Normal changes in R.H. have little influence on hydrogen response.
  - LANL#3 shown on right.

LANL #3,4 device low level sensitivity at fixed R.H.



* Impedance buffers set at different gains



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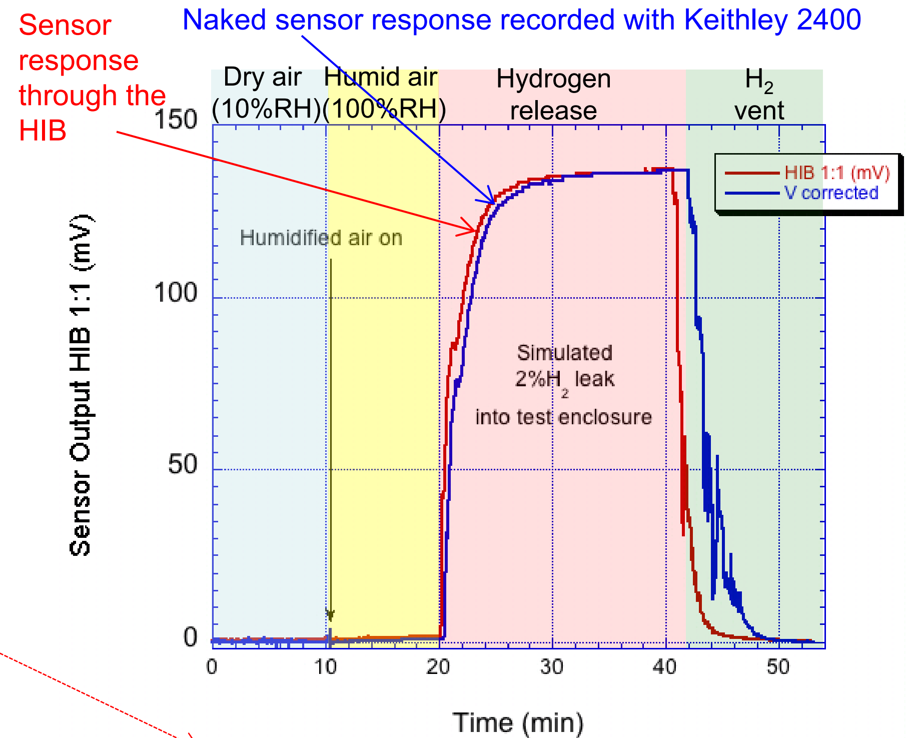
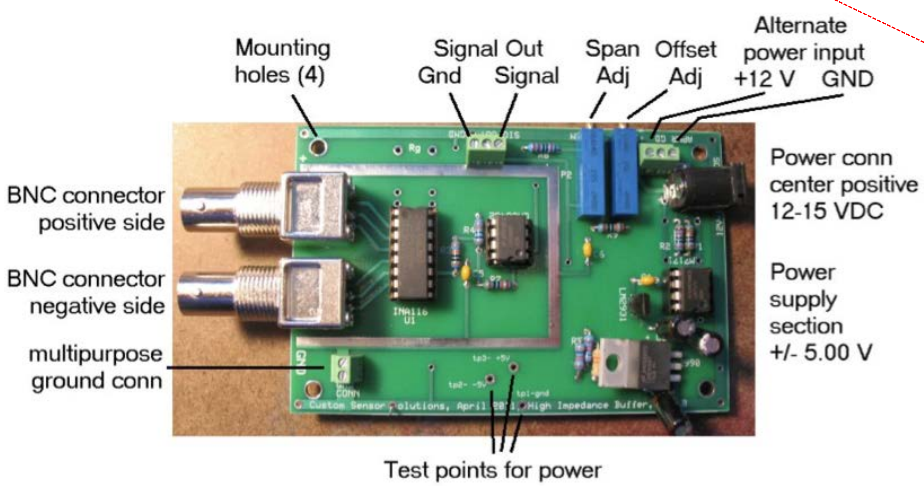
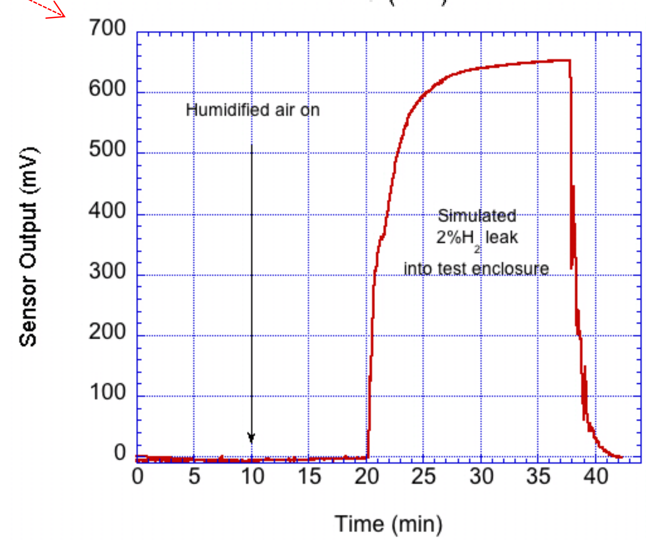
Technical Accomplishments FY12: High impedance buffer (HIB) board prototype electronics

- 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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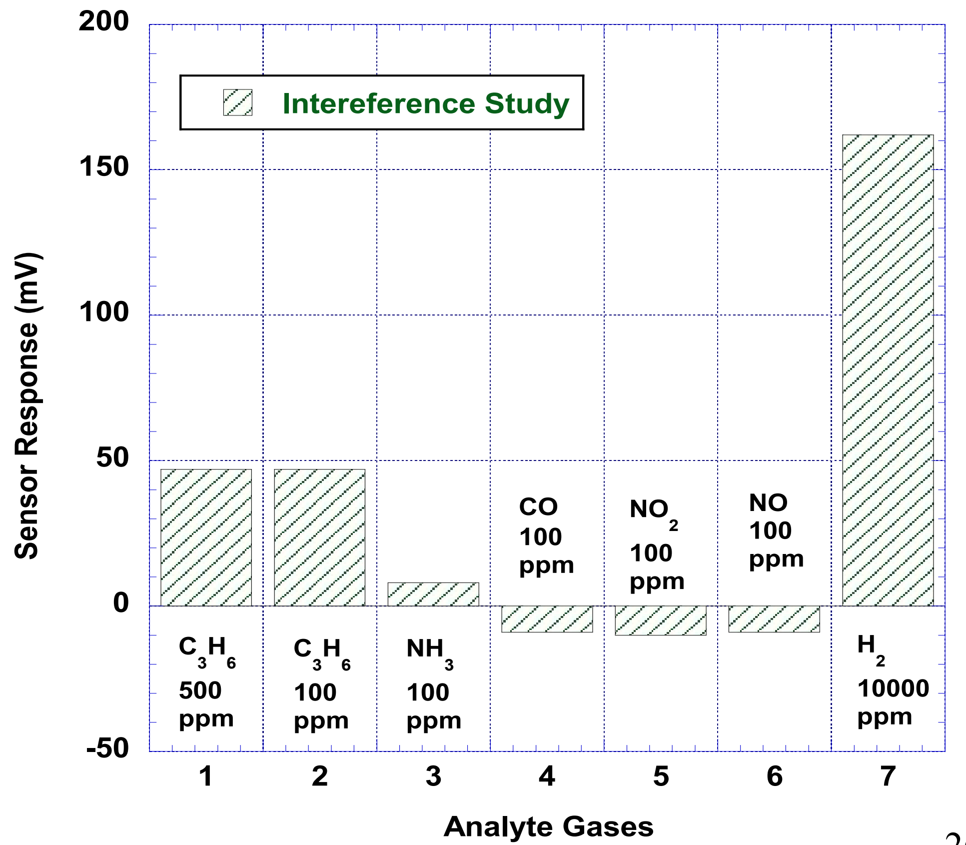
Technical Accomplishments: Milestone for Interference/cross sensitivity progress

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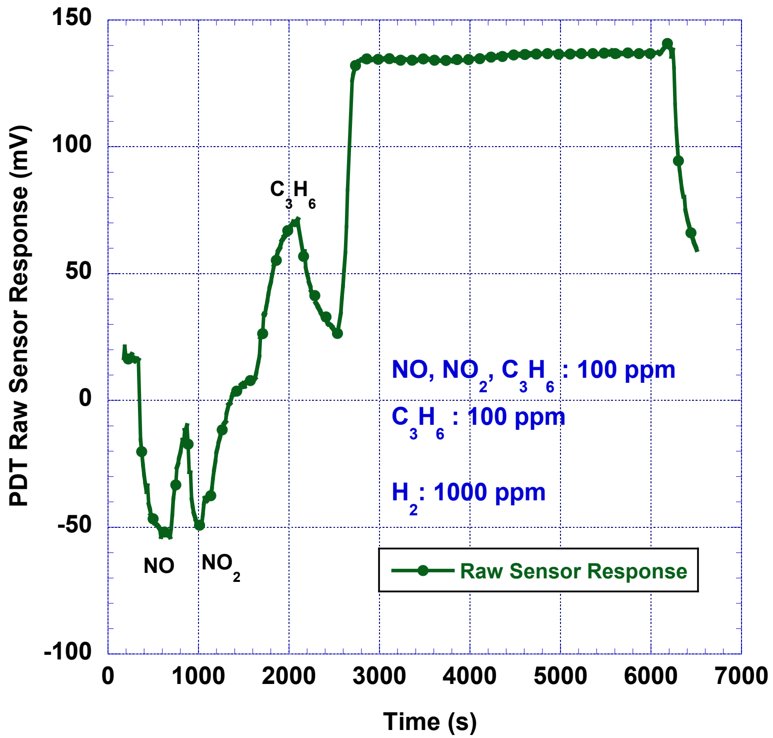
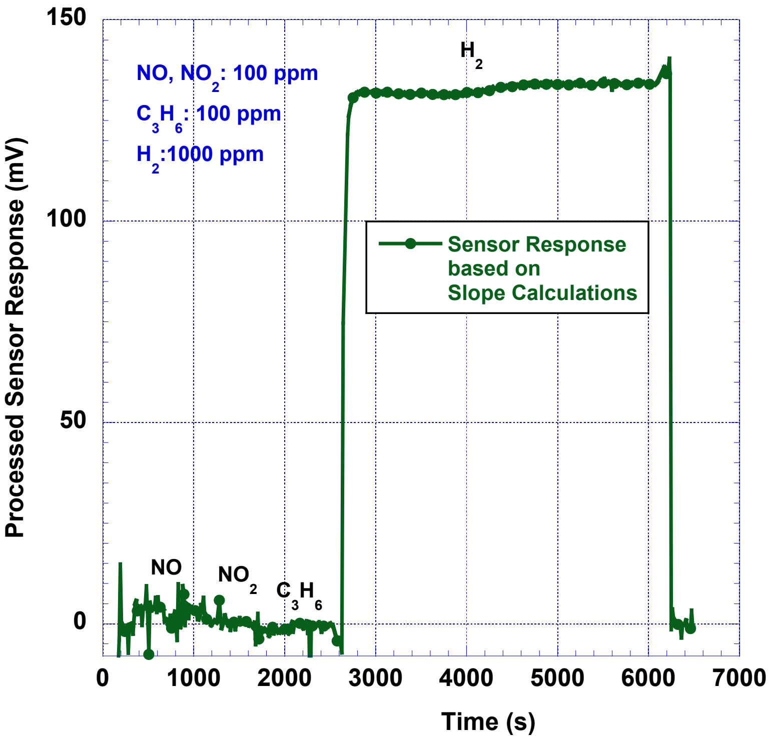
Technical Accomplishments: Collaboration BJR Sensors LLC utilizing Pulse Discharge Technique (PDT) combined with unique properties of the LANL/LLNL pre-commercial sensor prototype





- 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).

References

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