# 2014 U.S. DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office Annual Merit Review and Peer Evaluation Meeting

## Hydrogen Safety, Codes and Standards: Sensors


P.I. & Presenter : Eric L. Brosha

**Project Team Members**: Eric L. Brosha[1], William Penrose[3], Leta Woo[2] Robert S. Glass[2], and Rangachary Mukundan[1]

*[1]Los Alamos National Laboratory, Los Alamos, New Mexico*
*[2]Lawrence Livermore National Laboratory, Livermore, California*
*[3]Custom Sensor Solutions, Oro Valley, Arizona*


June 18, 2014

Project ID# SCS004

# Overview

- **Timeline**
  - Start: Summer FY 2008
  - Finish: 9/2014*

  *Project continuation and direction determined annually by DOE

- **Budget**
  - Total DOE project Value (Combined LANL/LLNL)
    - $4676K
  - Funding for FY13:
    - $150K LANL
    - $ 50K LLNL
  - Planned FY14 Funding: $225K
    - $150K LANL
    - $ 75K LLNL

- **MYRD&D Barriers**

✧ 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)

(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: LANL and LLNL
  - NREL: Codes & Standards field performance evaluation/validation team member
  - ESL ElectroScience
  - Custom Sensor Solutions, LLC – Commercial electronics developer
  - Zircoa Inc. and Agile Engineering, Software development

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# Relevance – Objectives

- Develop a low-cost, durable, and reliable **hydrogen safety sensor** for stationary and infrastructure applications, extendable to vehicle protection, 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, 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 commercialization of the new sensor technology through industry partnerships.

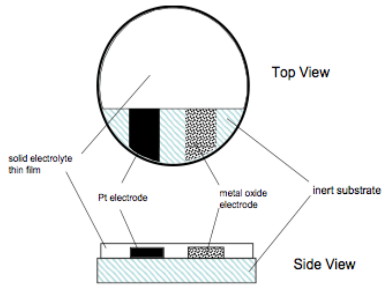
# Relevance – Technical Performance Requirements
# Why does the hydrogen community need better $H_2$ Safety Sensors?

- **Major Problem**: sensor drift leading to false positives and false negatives.
  - **Frequent calibration requirements and present technologies drive up costs substantially!**
- Lack of $H_2$ sensor technology that address accuracy and sensitivity in the concentration range where alarm points and actions are required by codes and standards.
  - **Good technology for ppm and high percent levels but there is a performance gap around the LFL**.
- 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 (reaffirmed findings of Hydrogen Safety Sensor Workshop, Washington DC, April 3-4, 2007).
- **LANL/LLNL technology produces a high signal-to-noise with maximum sensitivity in the 1-4 vol% $H_2$ range based on a voltage generated by sensing electrochemical oxidation of hydrogen on a robust ceramic platform**.

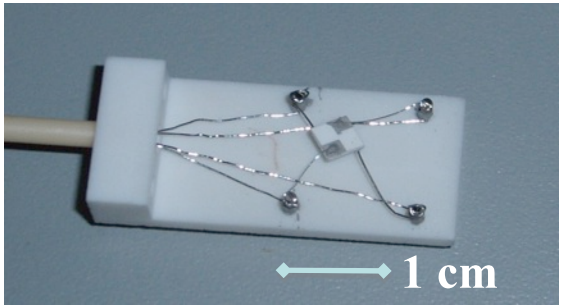
# Approach: Controlled Interfaces for Sensor Design and Development

## Sensor Technology Selection

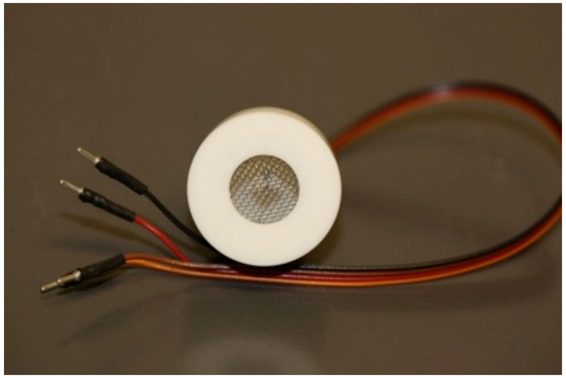
- **Derivative of the hugely successful automotive Lambda, potentiometric $O_2$ sensor.**
- Mixed-potential sensors generate a voltage in the presence of oxygen and a reducing/oxidizing gas.
- Unique class of sensors have been developed that are based on dense electrodes and porous electrolyte structures.
- 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

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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…

✓ Sensor aging

✓ Reproducibility problems

✓ Selectivity

4. Technology Commercialization

LANL/LLNL R&D has addressed these impediments in ***laboratory devices*** and has developed commercial prototypes that exhibit desirable sensor characteristics.

Tail end of this R&D project is to tackle remaining engineering and development challenges identified by LANL – LLNL – NREL work.

- ESL ElectroScience, Inc. – lay groundwork for mass fabrication of the sensor element using commercial High Temperature Co-fire Ceramic (HTCC) methods presently used for automotive sensors. Low cost and practical.
- Custom Sensor Solutions, LLC and LANL have developed electronics to control the sensor and interface the sensor element to the outside world.

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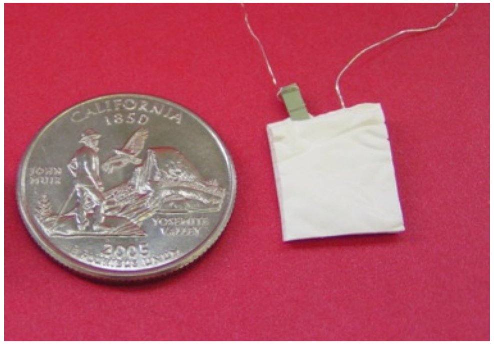
Custom Sensor Solutions, Inc.

ESL

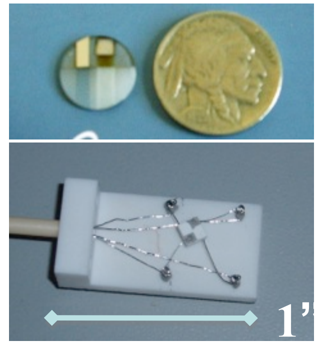
# Overview of Project Timeline

## 2008



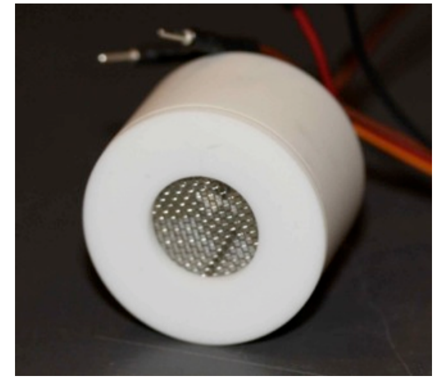
1st Generation device – tape cast using ITO electrode and controlled interface approach. **Externally-heated** with tube furnace (30lbs): **120V, 8A**.

## 2009-2010



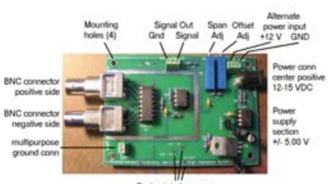

Pre-commercial mixed potential sensor in thick film version on ESL fabricated platform (LANL specs). **Power requirements**: **6.5V, 0.75A.**

## 2011



Pre-commercial ceramic packaging/sensor supported by 4 posts. **Power requirements**: **5.0V, 0.65A**. Pre- commercial prototype easily handled. 1st devices sent to NREL for **Round 1** testing.

## 2012




**Round 2** NREL testing. Begin developing sensor electronics with commercial partner.

## 2013


Round 3 NREL testing. Prototype sensor heater control board developed and tested.

## 2014

Sensor and signal / heater electronics integrated into a single unit with wireless communications. Field trials preparation begins.
**THIS PRESENTATION.**

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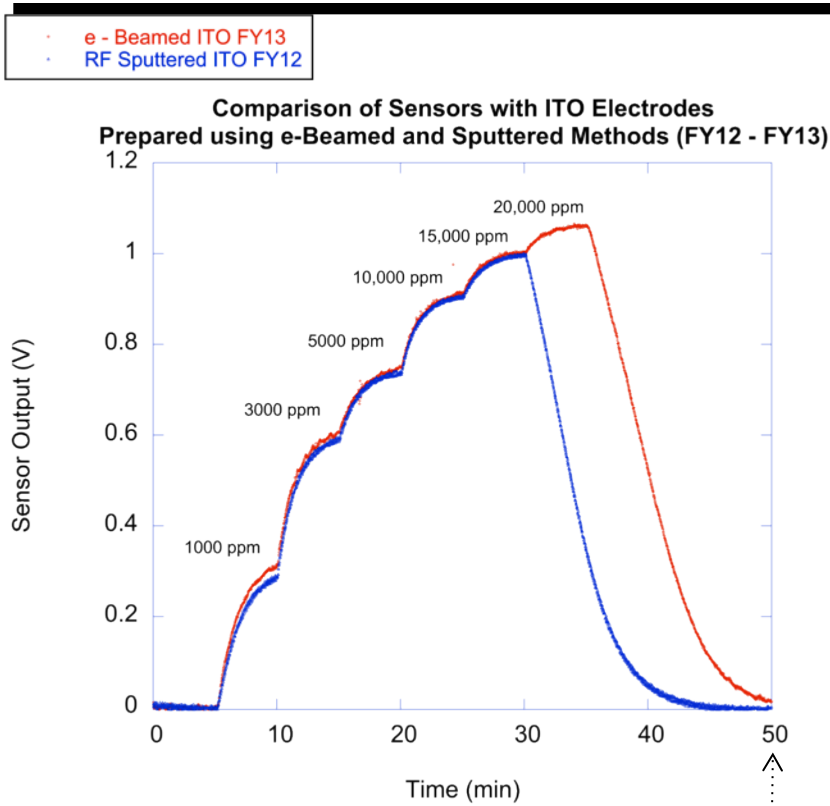
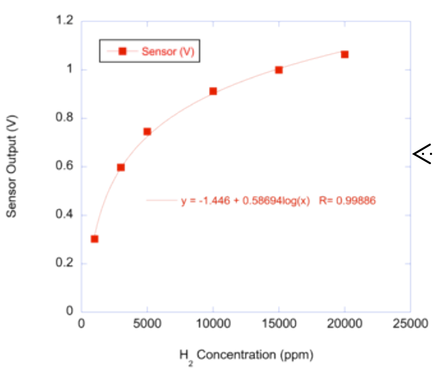
# Summary of Technical Accomplishments & Milestones in FY13

- Completed 3rd round of NREL testing.
  - Tested Custom Sensor Solutions (CSS) constant resistance power supplies at NREL.
  - Heater power / sensor operating point maintained during changes in ambient T simulated in NREL test chamber.
  - Performance of CSS high impedance buffer (HIB) validated again. Testing with, without HIBs.
  - Reported new results on NREL 2nd round testing for $PO_2$ (including anaerobic conditions) , interference gases, and temperature.
- Identified a more robust working electrode: $La_{1-x}Sr_xCrO_3$.
  - Stable and chemically robust material that can withstand oxygen starved conditions.
  - Compatible with Electroscience Laboratories (ESL) HTCC manufacturing process.
- Demonstrated exceptional sensor reproducibility in a prototype system.
  - 2 different $H_2$ sensors fabricated using different PVD approaches on ESL platforms.
  - Custom Sensor Solutions HIB's and power supplies together with LANL/LLNL device construct produced nearly identical $H_2$ responses.
  - Exceptional result that validates National Laboratory sensor approach and research path taken.
- Project recognized by DOE EERE FCTO "Pathways to Commercial Success."
- Photograph of packaged LANL/LLNL $H_2$ sensor on cover of 2013 AMR Report.

# Technical Accomplishments FY13: Sensor and System coming together / enabling successes for FY14 start of Field Trial work

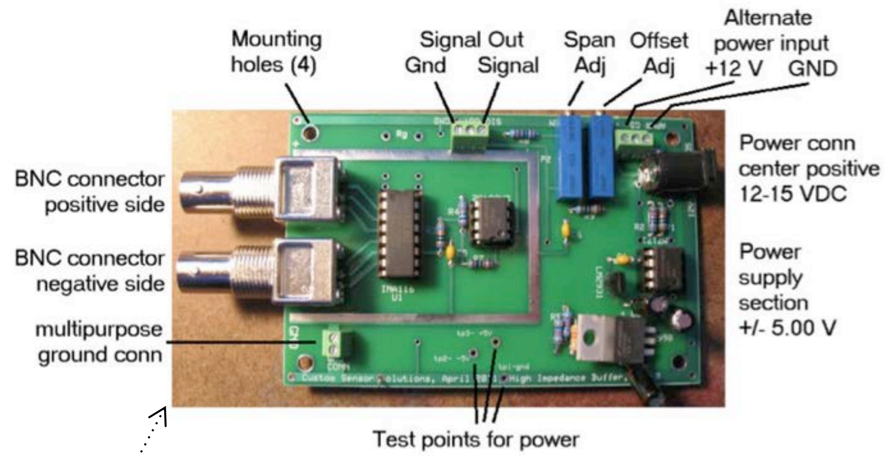


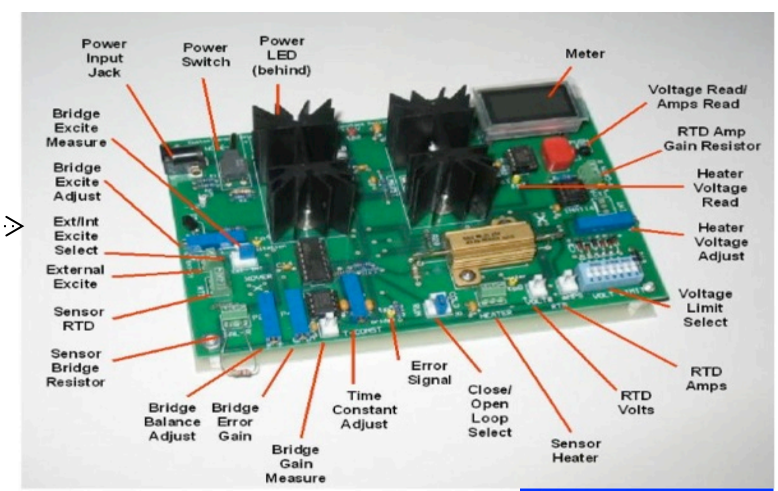

3 Rounds of Testing

## Electronics tested as independent circuits

High Impedance Buffer; model # HIB




Constant resistance power supply; model # CRPS



# Technical Accomplishments FY14: Preparations for field testing

- Sensors have been validated in as "real" laboratory testing as possible (LLNL, LANL, NREL); we are ready to go to the field.
- Permits refinement of electronics and data transmittal package.
- Necessary to prove viability.
- Builds data base necessary for industrial entity to commercialize.
- Addresses program technical barriers:
  - ➢ Safety Data and Information: Limited Access and Availability.
  - ➢ Safety is Not Always Treated as a Continuous Process.
  - ➢ No Consistent Codification Plan and Process for Synchronization of R&D and Code Development.
  - ➢ Usage and Access Restrictions.

# Technical Accomplishments FY14: Safety Document for Commercial $H_2$ Partner – A Learning Tool for SCS Projects

## Elements:

- Background/reason for testing
- Benefit to commercial partner of participation
- Overview of hydrogen sensors and needs
- LLNL/LANL technology description
- Testing locations and procedure
- Testing risks and mitigation strategies, detailing design features for safety enhancement
- Insurance/indemnity issues
- Experimental results demonstrating sensor safety under ignition conditions in the range up to 20% hydrogen in air in laboratory testing
- Compliance

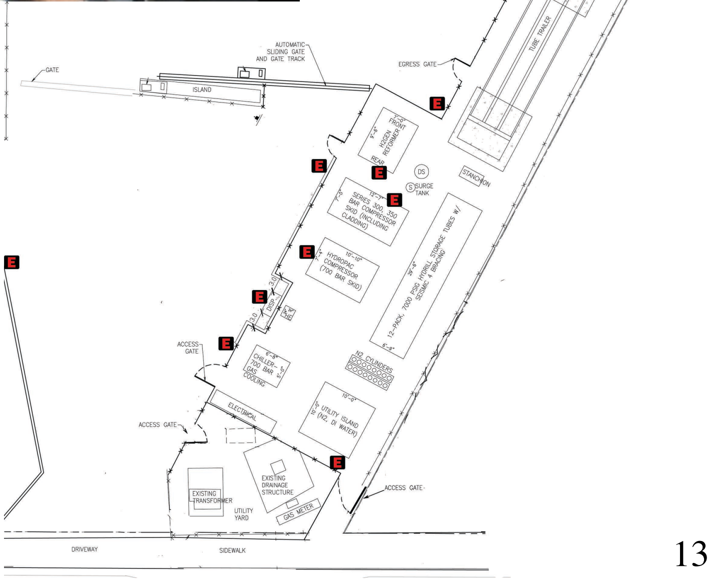
# Technical Accomplishments FY14: Linde site identified at Livermore and designated as a parallel test facility


- LLNL site is convenient.
- Permits comparison against expensive commercial device that must undergo frequent, periodic calibration.
- Enclosed areas offer field trials units protection from direct exposure to sun, rain, wind, wildlife, etc.
- Good preparation before testing at primary site.

# Technical Accomplishments FY14: Hydrogen Frontier Inc. identified and designated as the primary testing site

HYDROGEN FRONTIER INC




- Discussions with Dan Poppe and planning began summer 2013.
- Location: Burbank within a mile of the airport.
- Pallet locations identified, need to prioritize deployment strategy based on resources.
- Outdoor facility largely does not require sensors. Hydrogen Frontiers would like to study/monitor areas where hydrogen accumulation is believed to occur.

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HYDROGEN FRONTIER INC

# Technical Accomplishments FY14: Hydrogen Frontier Inc. identified and designated as the primary testing site

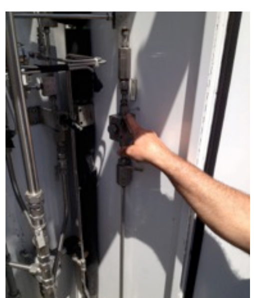
- LANL research staff visited Burbank site on April 16, 2014.
- Survey of facility identified 4 locations for sensor placement. All sites are either exposed directly to the weather with minimal shielding from elements, or exposed to high heat (e.g. inside reformer encl.)
  - **Identified :** high heat (up to 140°F for the electronics bay), vibration, insects, spiders, wind, water, and birds as an example of real-world conditions
  - **Best locations :** #1) $H_2$ dispenser enclosure[1]
    #2) HydroPAC compressor skid
    #3) and possibly, inside the Reformer enclosure itself [1,2]

1. Location of commercial sensor
2. Known methane leaks

This is space available for data logging electronics.

Enclosure is in sunlight and can get as hot as 140°F or more in summer.

**No Laptop!**



Bus for 24VDC


Compressor for 700 bar delivery

Reformer



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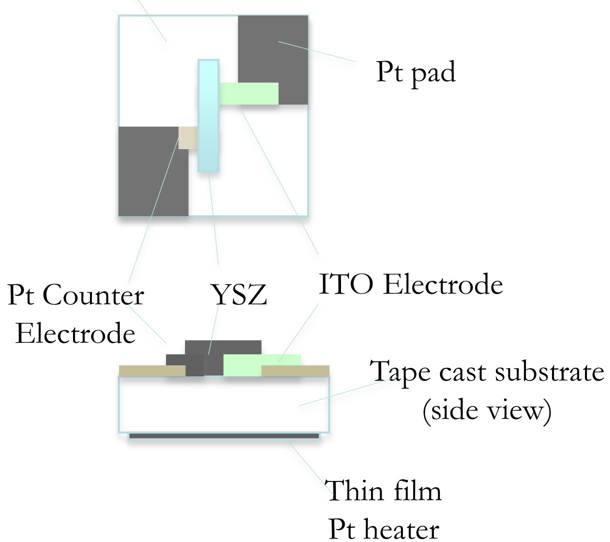
HYDROGEN FRONTIER INC

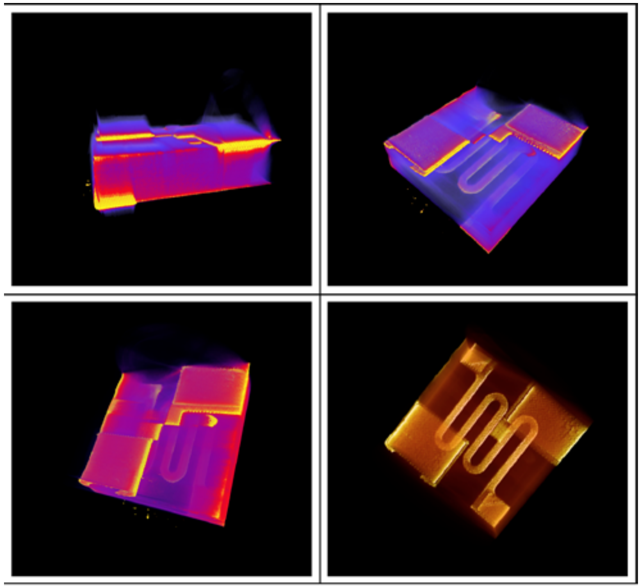
# Technical Accomplishments FY14: Indemnity Issues - Ignition probability experiments

- Pre-commercial prototype devices were designed using LANL-LLNL approaches.
- ESL fabricated sensor platforms for LANL and LLNL.
- Incorporates a resistive Pt heater to provide sufficient ionic mobility in the YSZ solid electrolyte to permit electrochemical reactions.
- Flame arrestor is incorporated into LANL-developed packaging
- Previous concern raised as possible ignition source.

Pre-commercial $H_2$ sensor proposed to ESL

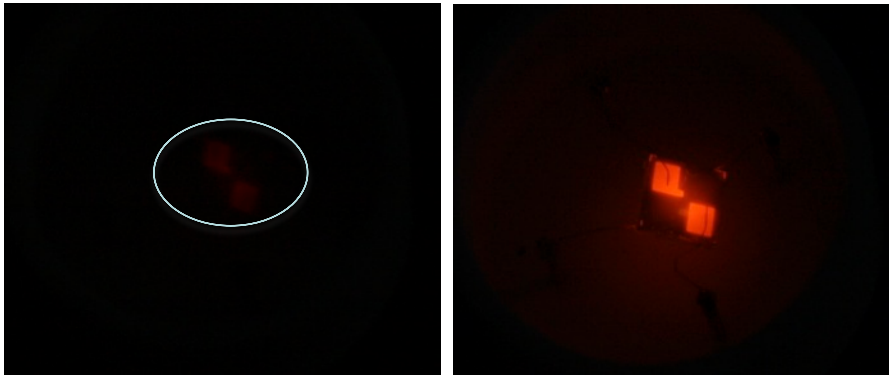



3D X-ray Tomography of 1st ESL devices.



Normal operating point

Sensor driven well above (3W) normal operating power.



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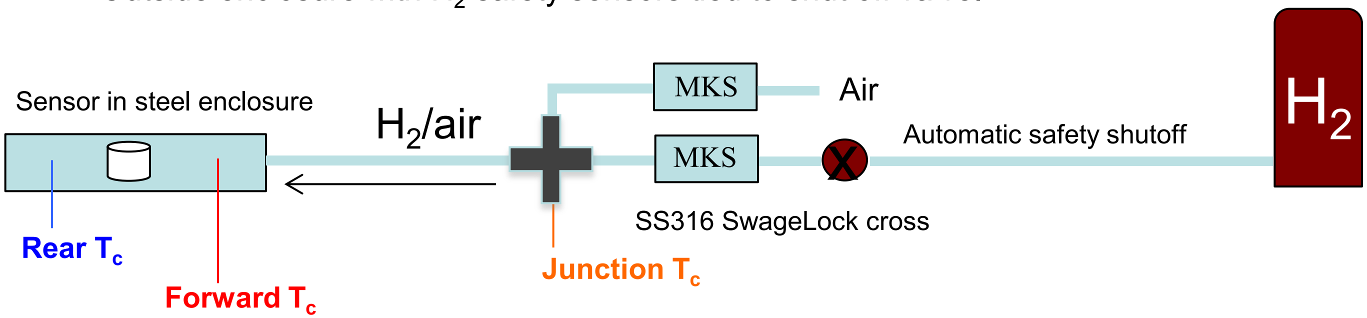
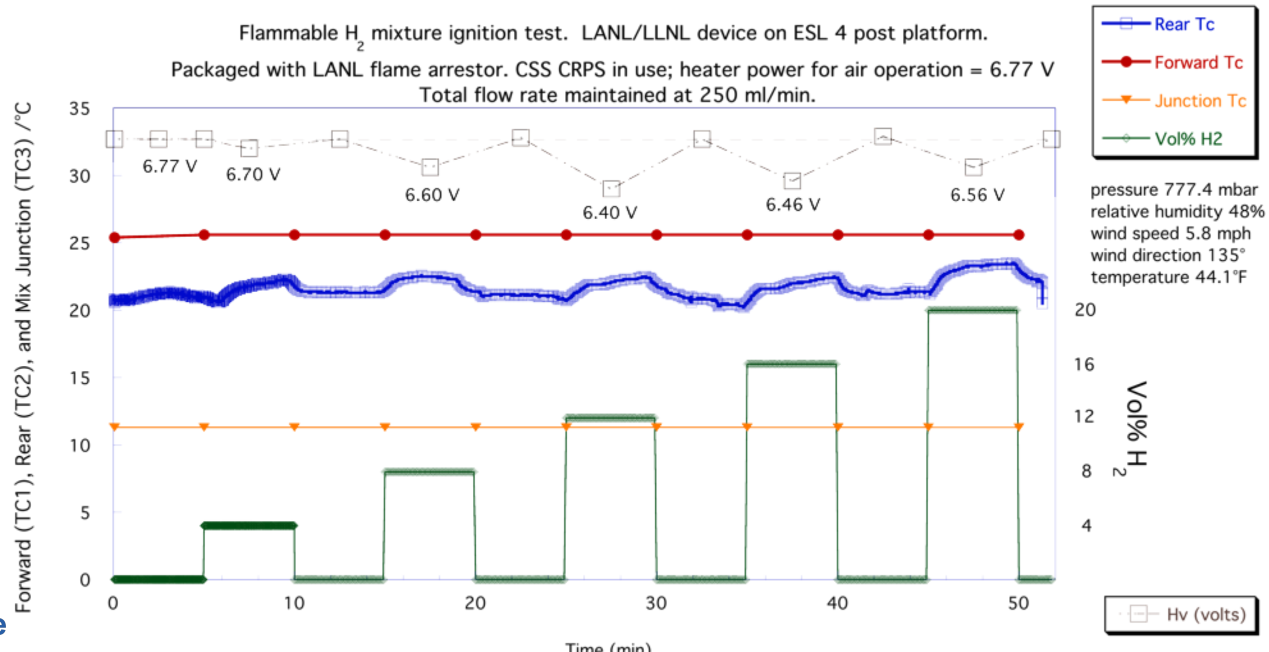
# Technical Accomplishments FY14: Ignition probability experiments at LANL

- LANL safety documentation for sensor testing "Form 4" expanded. And approval obtained to mix and deliver up to 20% $H_2$ in air to experiments.
  - Initial experiments conducted using flowing mixtures
  - Concentrations well above %'s of LFL
  - Outside enclosure with $H_2$ safety sensors tied to shut off valve.




- Tests were repeated using higher concentrations of hydrogen in air.
- No spike in T was observed any of the thermocouples.
- Heater power supplied by CSS CRPS-H power supply maintaining desired sensor operating T.
- Multiple runs were performed with and without flame arrestor on sensor.
- Data indicate that the sensor **did not ignite the hydrogen/air mixture at any point during experiments**.

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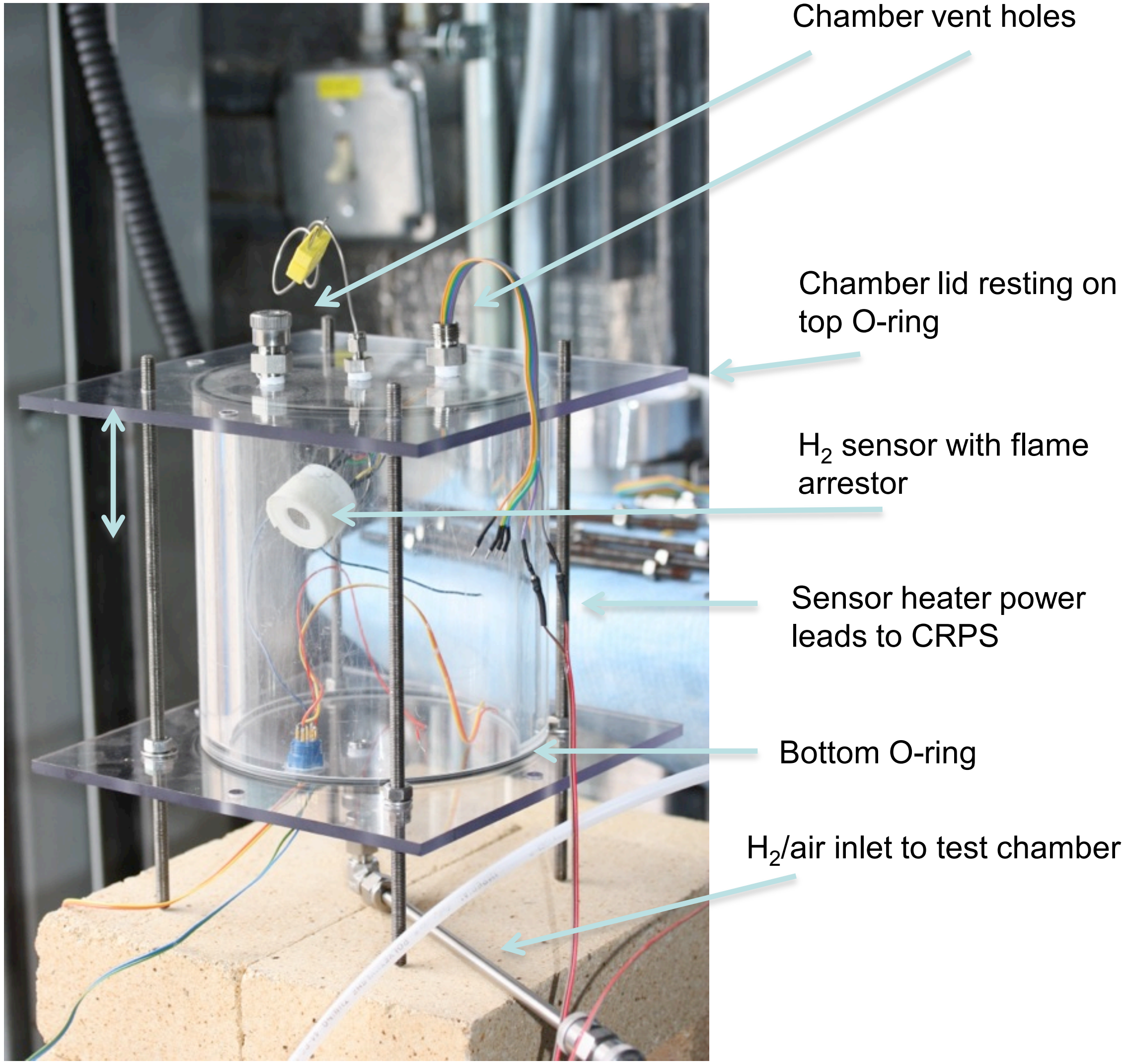
# Technical Accomplishments FY14: Ignition probability experiments (static chamber $H_2$ exposure)




## Summary

- Static release experiments performed next up to 10 vol% $H_2$/air mixtures
- Normal $H_2$ sensor test chamber was transferred to outdoor building.
- Chamber lid was NOT secured but simply rested on top of O-ring on central cylinder.
- Flammable $H_2$/air mixtures were introduced at the bottom of the chamber for 15 minute durations while sensor was at operating T.
- No ignition observed in any experiments.
- Did not have permission to deliberately ignite these mixtures.

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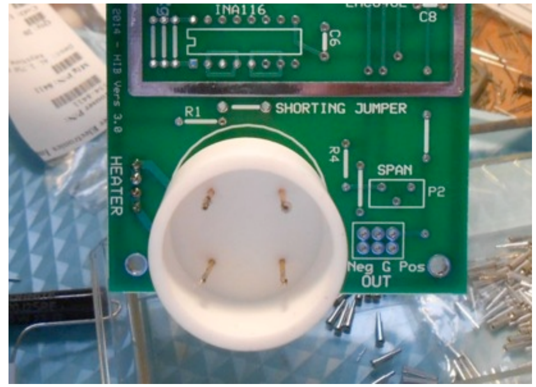
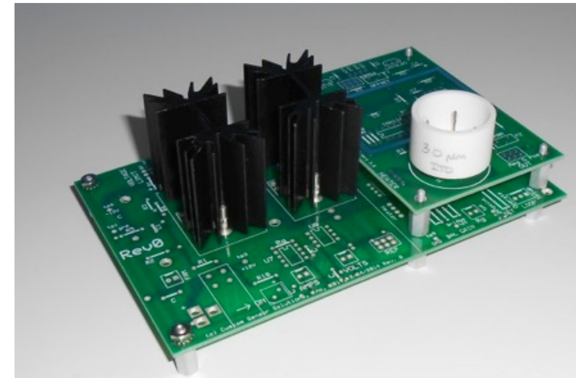
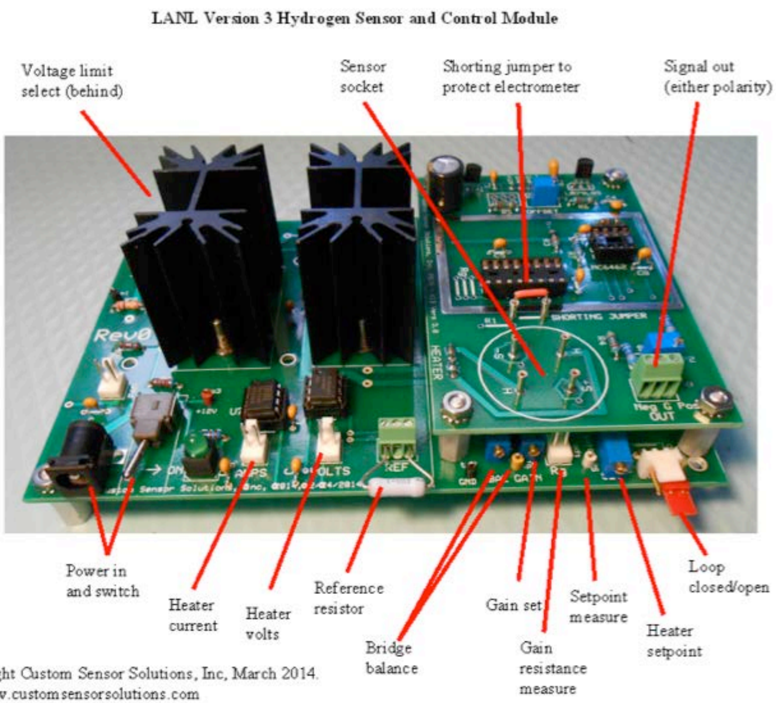
# Technical Accomplishments FY14: New field trials electronics designed and built by Custom Sensor Solutions

- Combines and simplifies CRPS and HIB boards previously tested.
- Designed around LANL sensor packaging.
- Sensor plugs into HIB.
- Easy to replace sensor element.
- Accommodations for cooling fan or convection cooling of heater circuit.
- Enclosure will be selected and entire unit will fit into LANL test chamber for one-time, initial calibration and testing.

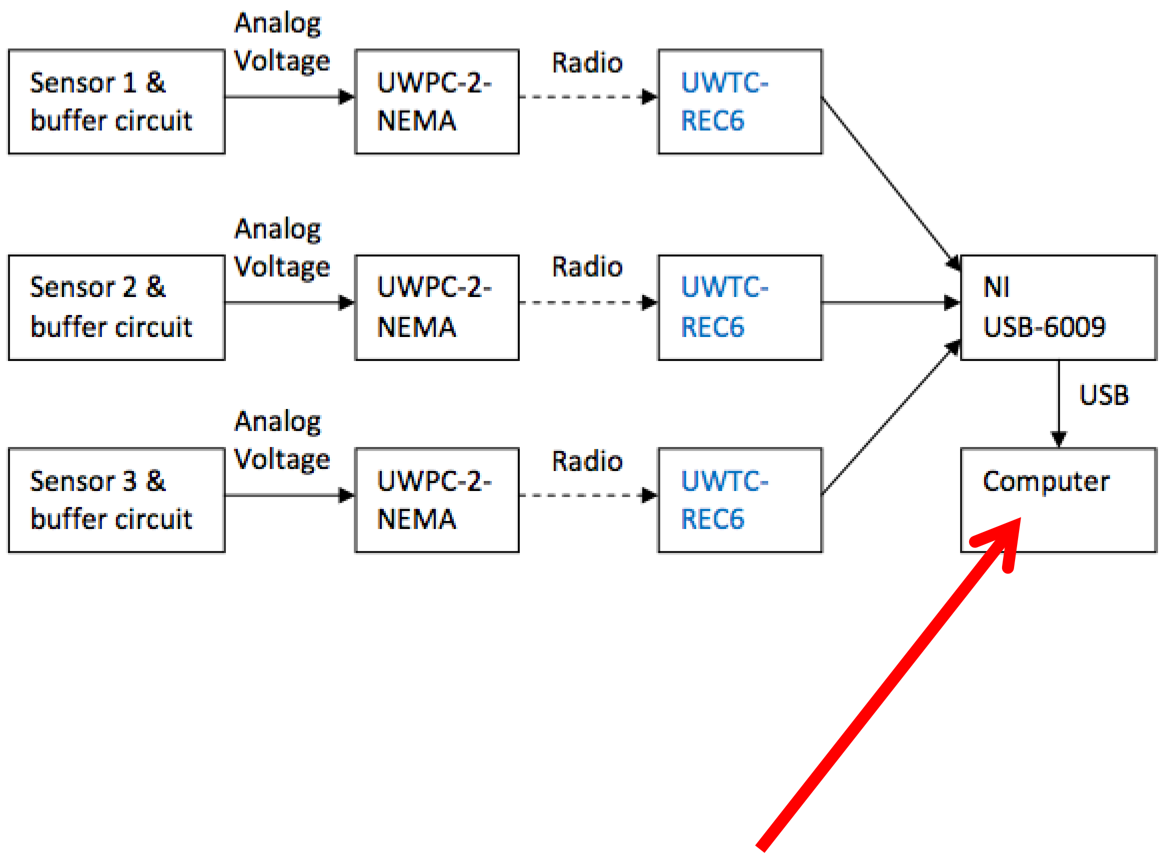


# Technical Accomplishments FY14: New field trials electronics will use commercial wireless communications

- Simplifies field trials.
- No need for running long sensor leads through explosion proof conduits at testing site.
- Cheap – COTS technology from Omega Engineering.
- Accommodations for operating up to 3 independent sensors at 3 different placement points at a test facility.




**Laptop with executable Labview™ code written by Agile Engineering and integrated with wireless components and validated at Zircoa Inc.**
**Logs up to 3 sensors at once.**
**Accepts calibration curve to convert raw voltages to %$H_2$.**
**User selectable alarm points.**
**User selectable logging rates / averaging / file write rates.**

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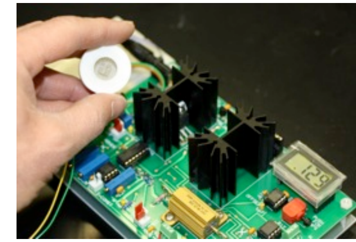
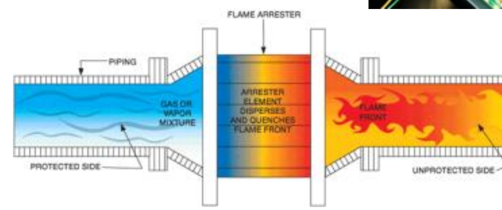
# Codes Must Be Met – No Exemptions for Research Purposes



**Requirements: Design for electrical enclosures to meet Class 1, Div 1 (most restrictive) and Class 1, Div 2 codes**




**<u>ANSI/NFPA areas description</u>**

**Class I, Div. 1 - Where ignitable concentrations of flammable gases, vapors or liquids are present continuously or frequently within the atmosphere under normal operation conditions.**

**Class I, Div. 2 - Where ignitable concentrations of flammable gases, vapors, or liquids are present within the atmosphere under abnormal operating conditions.**

# Response to Previous Year Reviewers' Comments (Extended reply in Reviewer Only section)

- The results demonstrated are worthy of praise. In terms of value it appears that DOE contribution of ~$5M will produce a substantial benefit to not only the hydrogen and fuel cell industry but has "backward compatibility" with the overall hydrogen and flammable gas safety market (a substantially larger commercial market in the near term). This "backward compatibility" is critical to the survival of sensor manufacturers ahead of vehicle deployments in 2015-2020. This project team has clearly identified that need and delivered a result that encompasses that critical aspect.

  ✓ We agree with the reviewer's comments and would like to give two real examples of how this technology is poised to positively impact overall hydrogen industry. #1) H2 crossover safety sensor in anode electrolyzer systems call for unique sensor properties. #2) Robust sensors for vehicle safety where re-calibration is undesirable.

- The collaboration is good. Unfortunately there seems to be a continued miscommunication between the project team and the NREL test lab.

  ✓ By NREL Sensor Testing Lab charter, we do not guide NREL in their sensor testing or in any way ask for special testing conditions when they carry out the tests. We have found NREL's independent evaluation and feedback very valuable and we feel we have advanced the technology further and faster with NREL than would have been the case without their help.

- With regard to sensors, I think we have had multiple issues moving towards an approach that can be adopted by industry for various reasons. The lack of sensor manufacturers at the table for discussion within the working group and coming forward to address potential standards issues that need to be addressed hampers the work needed to role out a solution for industry. The manufacturer's of sensors need to be involved.

  ✓ We agree, and although a specific manufacturer has not come forward with an expressed desire to take over and bring this technology to market, the participation of ESL does bring to the table a high degree of credibility for the potential of our technology to be successfully commercialized. The electronics have been prototyped by Custom Sensor Solutions and are now a commercially available item. What remains: collecting real-world database on performance, applications, and durability; is what we are doing now. This is a market driven problem however, we have largely tackled most of the show-stopping, commercialization. Any partner will no doubt wish to wait to see the field trials performance data from the test sites and from mock field trials testing planned at the NREL ESIF building and this is where we are now and into next year.

# Collaborations

Fundamental electrochemical sensor R&D, establish prototype designs, packaging, field testing, off-site safety protocols development

Materials selection, field testing, partner and off-site protocols development

Codes & Standards field performance evaluation/validation team member

*Federal Laboratories within DOE Hydrogen and Fuel Cells Programs*

## *Commercial Partners:*

Agile Engineering through Zircoa: field trials software development and testing

Hardware for sensor control electronics

Manufacturing, scale-up, engineering processes

# Future Work

- Build and test sensor test units (to extent resources permit).
  - Site sensor units at Hydrogen Frontier and Livermore.
  - Collate and analyze data from California locations.
  - Set up mock field trials experiments at NREL.
- Perform limited field testing (to extent resources permit).
- Collect and analyze data from deployed sensors.
- Seek out partners for sensor commercialization / parties interested in infrastructure safety sensor development & deployment.
- Seek out parties interested in vehicle safety sensor development & deployment.

## Summary

- ✓ All FY14 experimental Milestones have been completed.
- ✓ A commercial California Hydrogen Partner was identified and preparations to begin field trials development and testing commenced.
- ✓ Codes and Standards guided planning for field trials work.
  - ✓ LLNL Indemnity agreement work
  - ✓ Class 1 / Div 2 standards as guidance
- ✓ Custom Sensor Solutions developed electronics for field trials work.
- ✓ A certified Labview™ developer identified to provide data logging software.
  - ✓ Substantial cost savings compared to in-house coding
- ✓ Site location survey at Hydrogen Frontier, LLC / Burbank filling station
- ✓ Mock field trials work planned at NREL $H_2$ Sensor Testing Facility in collaboration with Dr. William Buttner