2010 DOE Annual Merit Review

Hydrogen Program & Vehicle Technologies

Hydrogen Safety Sensors

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Project ID# SCS004

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Overview

- **Timeline**
  - Start: Summer FY2008
  - Finish: FY 2012
  - 60% Complete

- **Budget**
  - Total project funding
    - DOE share: $2,600k
    - Equal budgets for LANL and LLNL
  - Funding received FY09: $800k
  - Funding for FY10: $700k

- **MYPP Barriers**
  - Low-cost sensors for hydrogen leakage needed for vehicles and pipeline
  - Potential liability issues and lack of insurability affecting the commercialization of hydrogen technologies: Need for reliable H_2 safety sensor
  - Variation in standard practice of H_2 safety assessments: The requirement to calibrate and commercialize safety sensors

- **Partners**
  - Project lead: Fernando Garzon, LANL
  - Project lead: Robert Glass, LLNL
  - Commercial Industry Partner: ElectroScience Laboratories (ESL) Corp.
    - Commercial prototype engineering

Relevance – Objectives

- Develop a low cost, low power, durable, and reliable Hydrogen safety sensor for vehicle and infrastructure applications.
- Demonstrate working technology through application of commercial and reproducible manufacturing methods and rigorous life testing results guided by materials selection, sensor design, and electrochemical R&D investigation.
- Recommend sensor technologies and instrumentation approaches for engineering design.
- Disseminate packaged prototypes to DOE Laboratories and commercial parties interested in testing and fielding advanced commercial prototypes while transferring technology to industry.

Relevance – Technical Performance Requirements

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_2S, CH_4, CO, and VOCs

Major Milestones and Go/No-go for Fiscal year FY09 and FY10/11

- **FY 2009**
  - Develop a sensor fabrication process and perform long term testing (minimum of 500 hrs) of pre-commercial hydrogen safety sensor prototypes and initiate discussions with fuel cell manufacturers and potential end users to strategize the eventual transfer of the technology to a supplier for commercialization.
  - Completed early commercial prototype platform.
  - Exceeded 500 hr goal: Over 2000 hrs combined life testing achieved.
  - Industry input obtained.
- **FY 2010 to FY11**
  - Fabrication and lifetime performance evaluation (minimum 5000 hours) of advanced prototypes (Aug. '10-Feb. '11)
  - Cross-sensitivity studies, stability evaluation using LSM electrodes in advanced prototypes (Sep. '10-Dec. '10)
  - Characterize and understand sensing mechanism(s) in various modalities and apply to future devices and optimize next generation of pre-commercial prototypes (Sept. '10)
  - Go/no-go for mode of operation and fabrication processes with critical evaluation of mass manufacturing potential (Sept. '10)
  - Investigate and identify packaging schemes for field and laboratory testing (Nov. '10-Jan. '11)

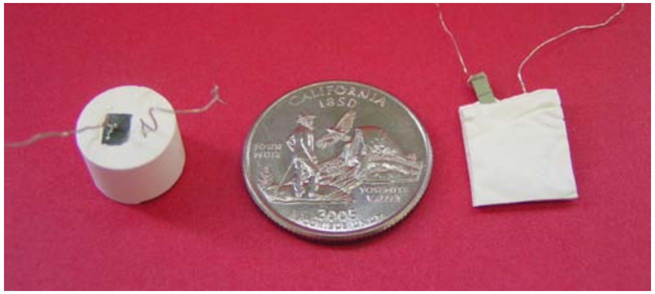
Approach: Positive Aspects of Collaborative National Lab Synergy

- Focus on long-term testing, packaging and manufacturing protocol for commercialization.
- On-going/parallel review of sensor materials and alternative designs, measurement strategy.
- Joint durability, sensitivity, and selectivity testing in partnership with industry (ElectroScience Laboratories).
- LLNL and LANL have a long history of the development of solid-state electrochemical sensors bringing unique and complimentary expertise:
  - Previous experience in detecting various gases, e.g., hydrocarbons and NO_x.
  - Full suite of gas handling equipment and test stands for characterizing electrochemical properties and performance.
  - Unique patents in mixed potential sensor technology.
  - Methods of electrochemical sensor fabrication.
- Solid-state electrochemical sensors, compared with other technologies, offer potential advantages including longer lifetime, lower cost, increased sensitivity, and better performance (i.e., selectivity and response time).

Approach: Controlled Interfaces for Sensor Design and Development

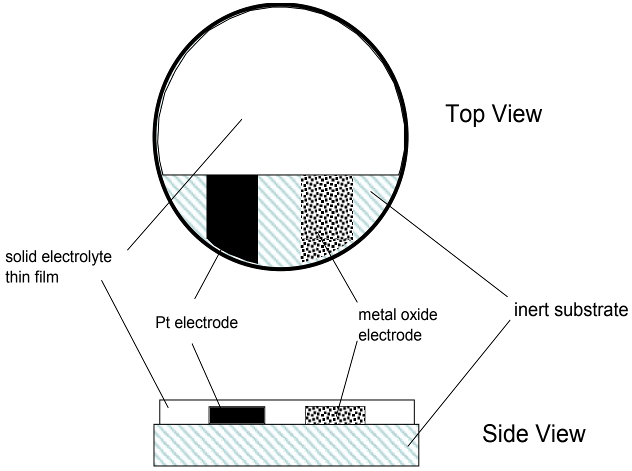
- Mixed-potential sensors generate a non-equilibrium potential in the presence of oxygen and a reducing/ oxidizing gas.
- The magnitude of this potential is determined by the relative rates of the oxidation and reduction reactions occurring at each electrode.
- Unique class of sensors have been developed 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).

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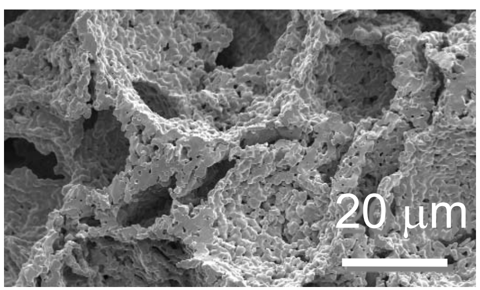
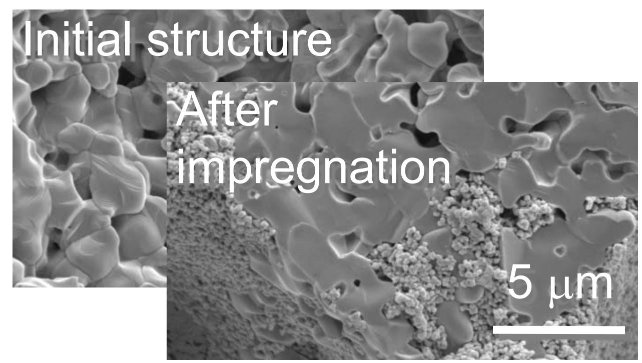
Approach: Evaluate alternative measurement and electrode processing methods to further improve sensor stability

- **ac impedance:** Similar to electrical resistance, which measures opposition to electrical current; measures opposition to **time-varying** or alternating current (ac), and is a complex quantity (magnitude and phase angle information).
  - Phase angle at a specified frequency and excitation amplitude can be correlated with changes in gas concentration where measurements at different frequencies may be used to compensate for cross-sensitivity to interfering gases.
  - Low-amplitude ac signal (phase angle in degrees), compared to open circuit potential signal (V), may prevent aging associated with reactions that slowly proceed in a preferred direction as a result of dc voltage operation.
- **Impregnation:** Prevent aging associated with changes in microstructure and/or porosity.



High-temperature processing to stabilize microstructure and porosity.



Separate low-temperature impregnation steps to introduce electronically conducting oxides or other components.

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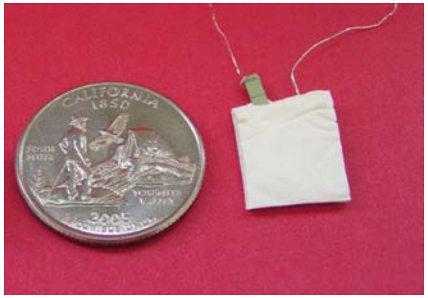
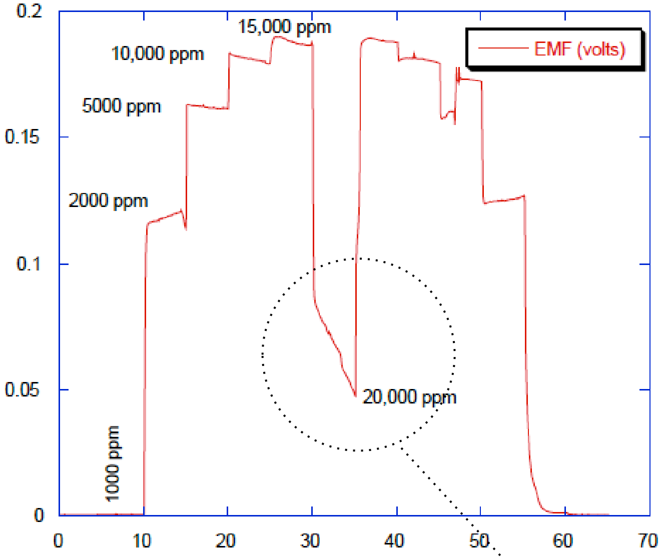
Technical Accomplishments and Progress

Previous Significant Accomplishments – entry into FY'10…

- New zirconia-based sensor with 0-4 vol% hydrogen sensitivity demonstrated [6].
- Durability testing of over 1700 hrs accomplished on pre-commercial, Nat'l Lab prototypes.
- Potential manufacturing platform demonstrated for early prototypes.
- Mixed potential sensors utilizing a machined, dense indium-tin oxide (ITO) working electrode (In_2O_3:SnO_2; 90%:10%), a Pt wire counter electrode, and porous yttria-stabilized zirconia (YSZ) electrolyte were prepared using ceramic tape casting methods [7]. The response of these devices to hydrogen concentrations up to 2% in air were studied from 600 to 740 °C.



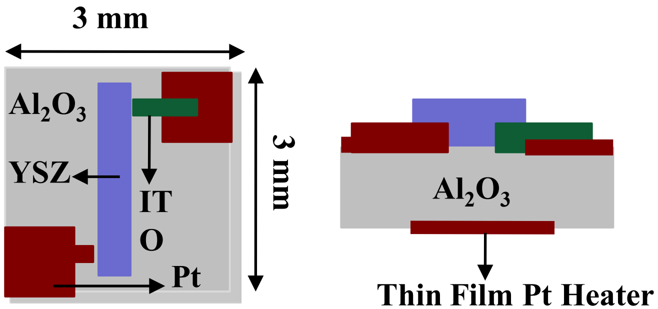
1st Gen device – tape cast using ITO electrode and controlled interface approach. **Externally-heated** with tube furnace (30lbs): **120V, 8A**. A quarter illustrates size of sensor.



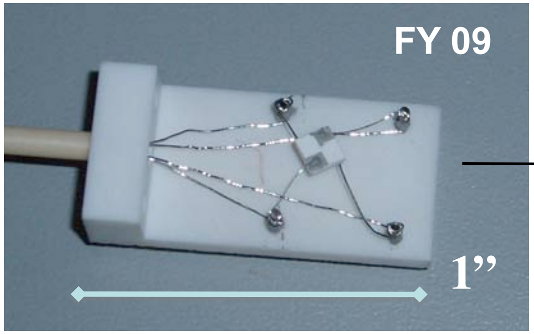
behavior caused by heterogeneous catalysis

Response of a tape cast ITO/YSZ/Pt sensor to step-wise increases in H_2 concentration in air. Sensor temp. was 640 °C.

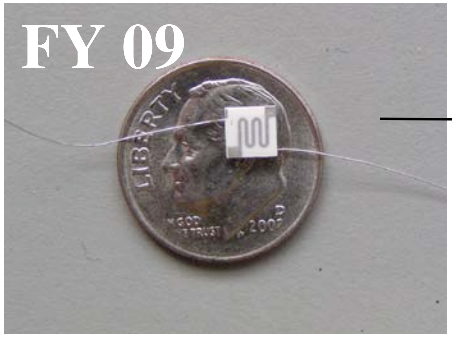
Technical Accomplishments: Milestone Completed for Development of a Miniaturized, Low Power, and Robust H_2 Sensor Prototype Conducive to Commercialization



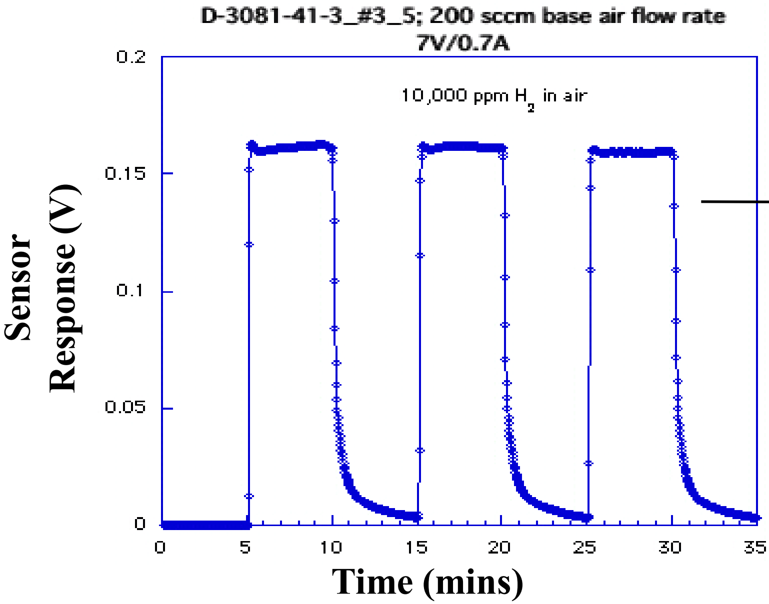
Top and cross-sectional view of the sensor prototype with ITO, Pt electrodes and YSZ electrolyte integrated with Pt heater.



Wire-wrapped from the electrodes and heater into the test wand.
Power requirements: 6.5V, 0.75A
Presently designing self-contained fixture so that sensors may be distributed to testing partners in FY10.

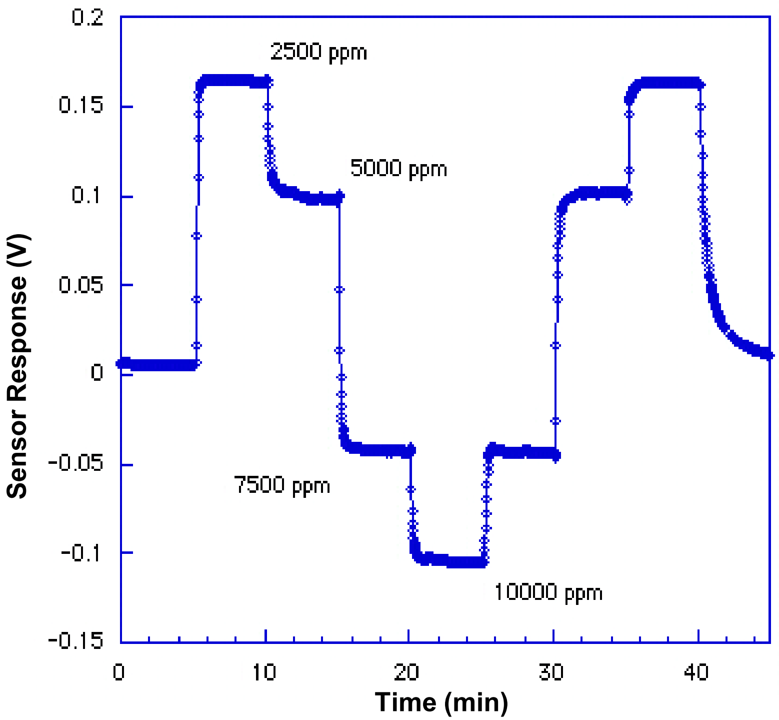


3rd Gen ESL Prepared Sensor. Resistive heater Side Shown. Sensor weight about 1gram. Size: 3 mm Square

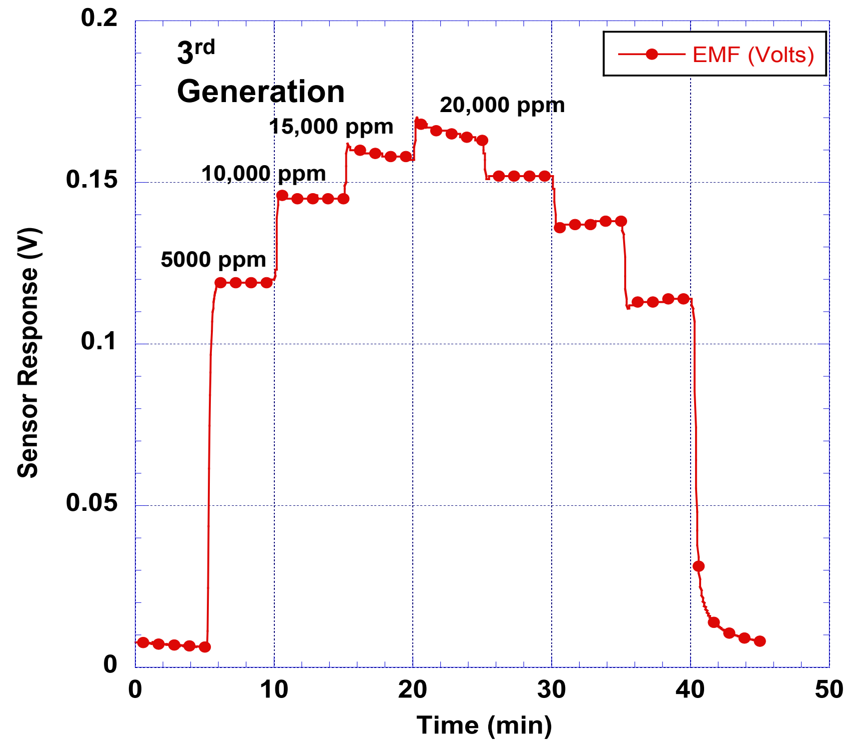


Stable sensor response shown after 13 days of testing.

Technical Accomplishments: Achievement of Milestone for a Stable Sensor Response over Time by Modifying the Pt Electrode Morphology



Improved counter electrode developed



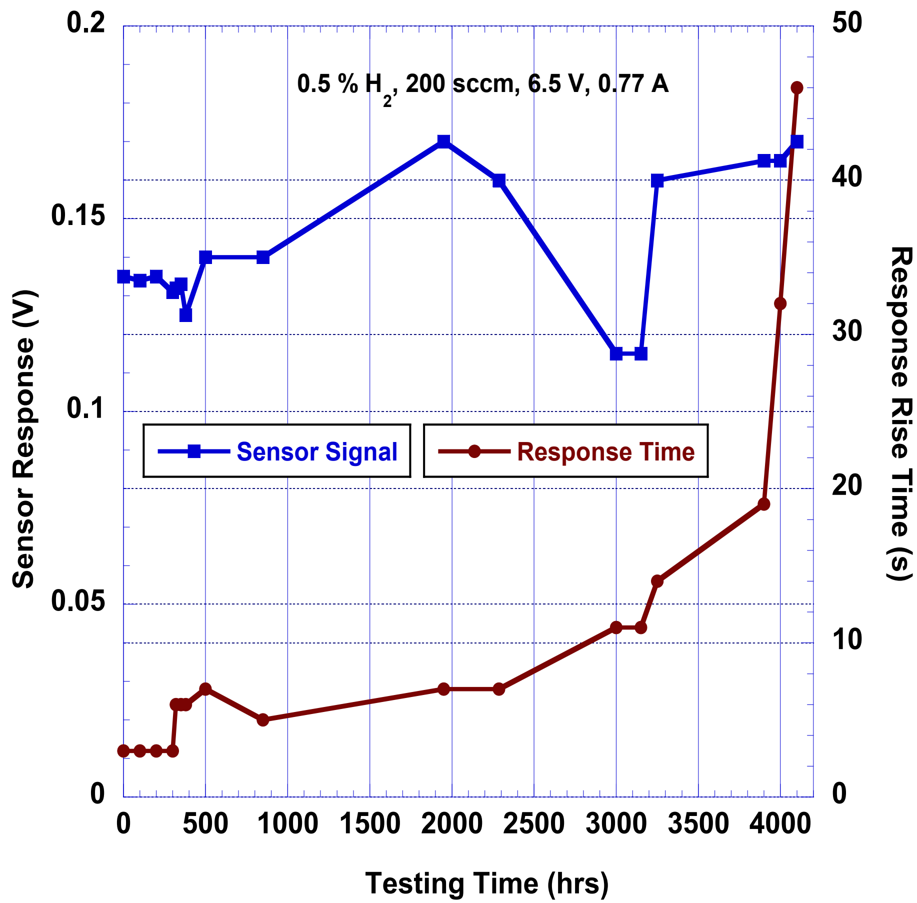
Inverted, unstable sensor response observed after 13 weeks of testing caused by interfacial changes and not heterogeneous catalysis.

Stable sensor response observed after electrode optimization (13 weeks testing).

Technical Accomplishments: Completed Milestone for Long-term Testing (~4000 hrs, LT) Including 100 hrs of Accelerated Stress Testing (AST)

LT and AST Protocols

Time (hrs)	Conditions
0 - 300	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
301 - 390	Temperature Cycling 6.5 V to 0 to 6.5 V, Three Cycles, Maintaining Humidity Level and Base Gas
391 - 822	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
823 - 894	Operating Temperature Variations – 6.5 to 5.75 V, Maintaining Humidity Level and Base Gas
895 - 1900	Static Conditions – No humidity, No Base Gas, Set Voltage – 6.5 V
1901 - 2296	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
2297 - 3249	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
3250 - 4000	Stress Testing – Temperature Cycling 6.5 V to 0: 100, 500, 1000, and 10000 Cycles, Sensor Response Measurement Before and After Each Cycle



Stable and Reliable Sensor Response to 0.5% H_2 after 4000 hrs and AST; Sluggish Response Observed after AST.

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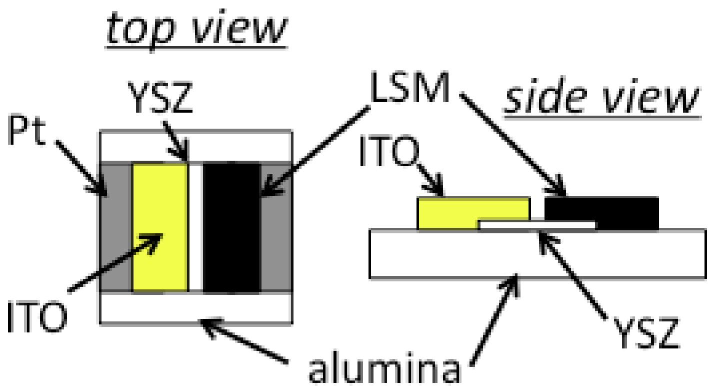
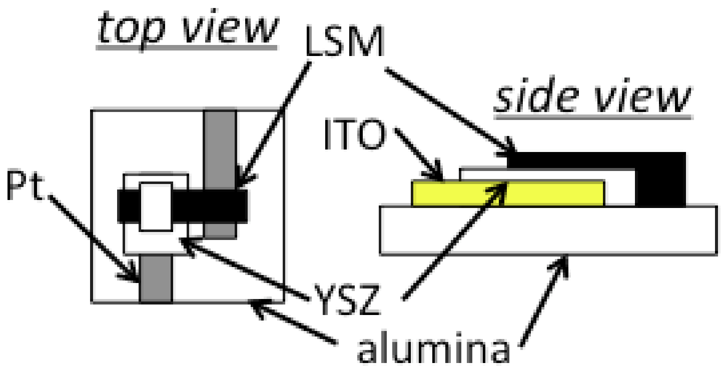
Technical Accomplishments: Completed Milestone for Evaluating Electrode Materials and Sensor Design to Further Improve Long-term Stability and Prevent Sensor Aging Effects

- Completed task to evaluate electrode materials and sensing mechanisms: Materials and design changes have led to improved long-term stability.
  - Composition: Poor performance linked to deleterious changes in platinum electrode.
    - In addition to previous efforts to modify platinum morphology, also investigated replacing platinum with an electronically conducting oxide material: strontium-doped lanthanum manganite (LSM).
  - Microstructure: Dense LSM electrode showed better long-term stability than porous LSM electrode.
- Geometry: Perpendicular ion conduction path had better signal-to-noise than parallel.

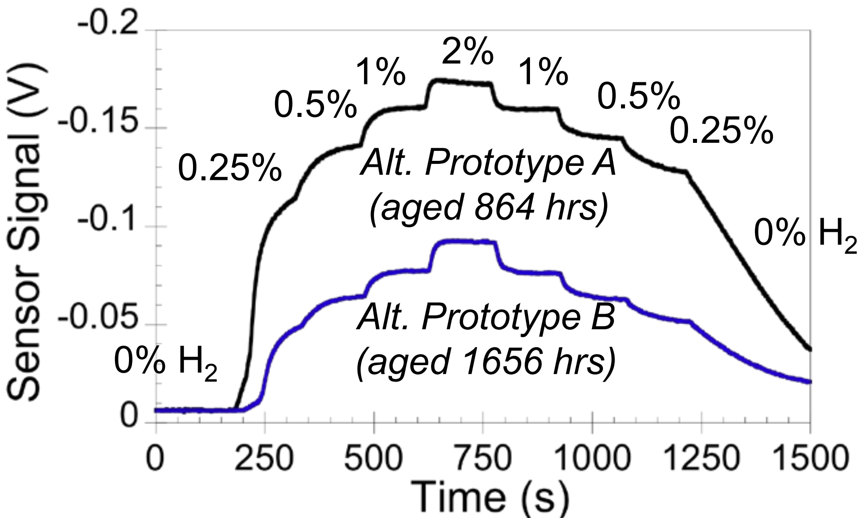


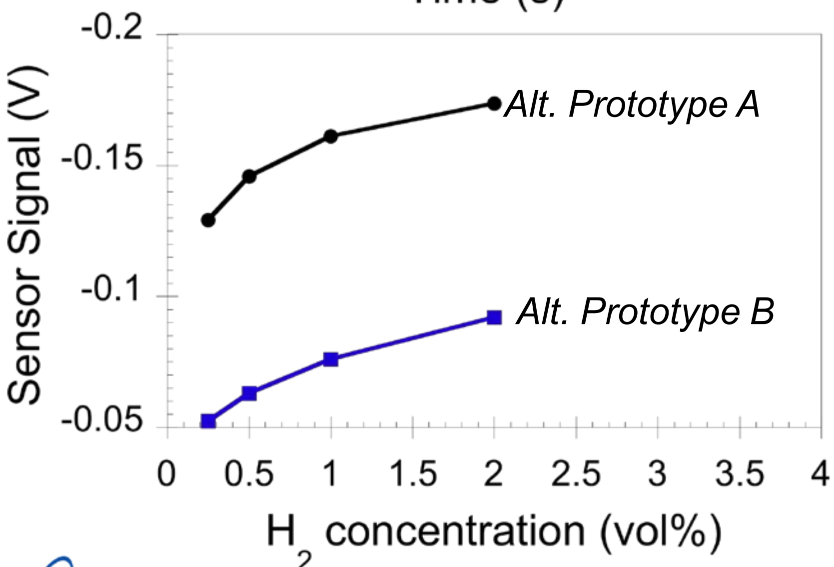
Alt. Prototype A: Porous LSM with parallel conduction path



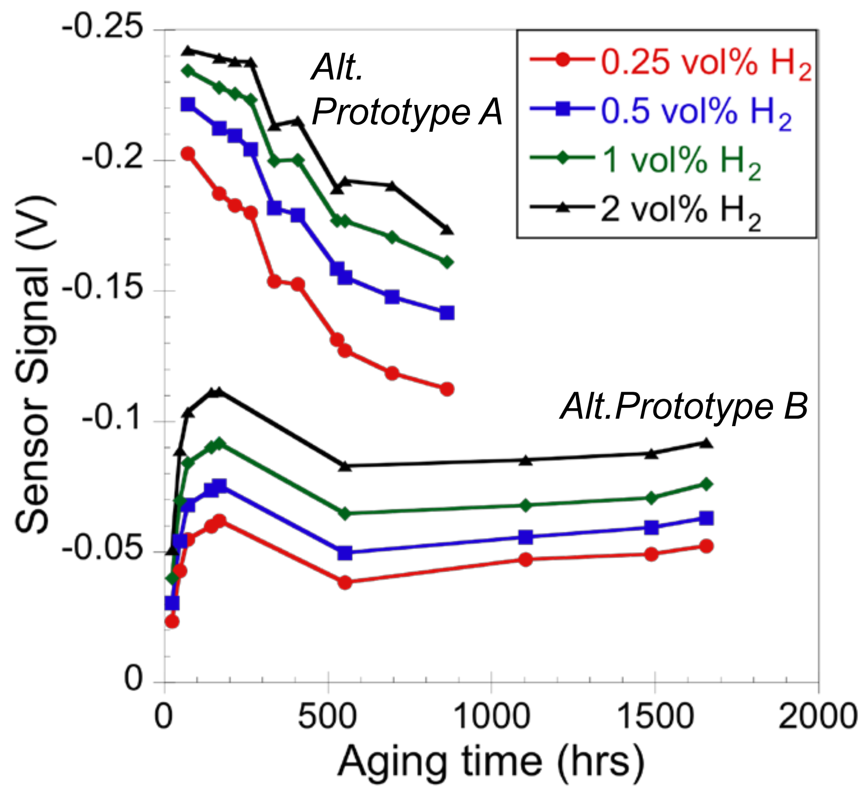
Alt. Prototype B: Dense LSM with perpendicular conduction path

Technical Accomplishments: Completed Milestone for Long-term Testing (>1500 hrs) of Improved Prototype Sensor Platforms Replacing Platinum Electrode with Conducting Oxide (LSM)





- Comparing Alt. Prototype A and B:
  - Similar sensitivity toward changes in H_2 concentration.
  - Alt. Prototype B (dense LSM electrode, perpendicular conduction path) demonstrated better longer term stability.



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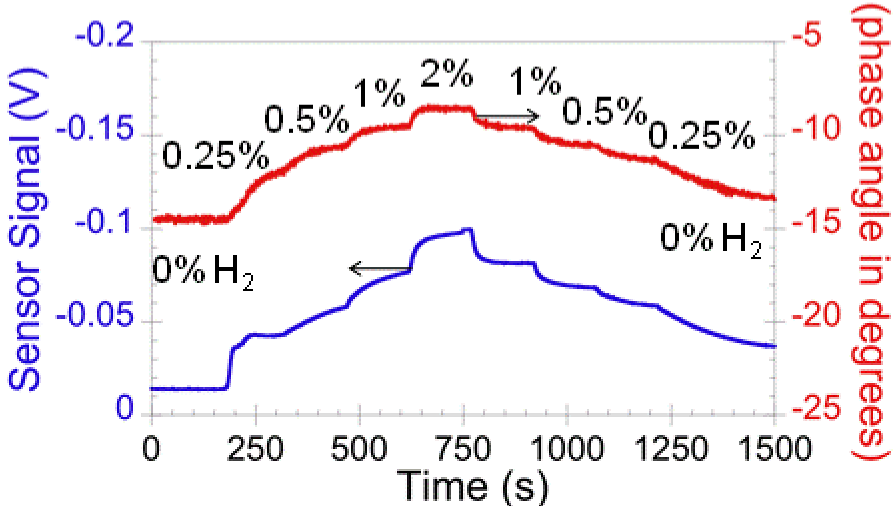
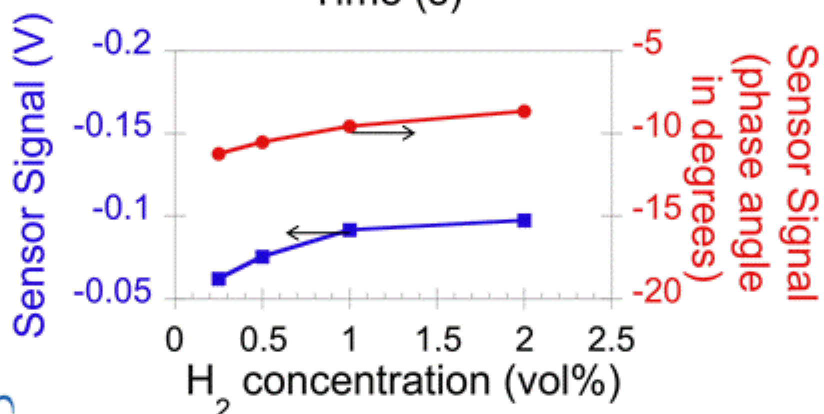
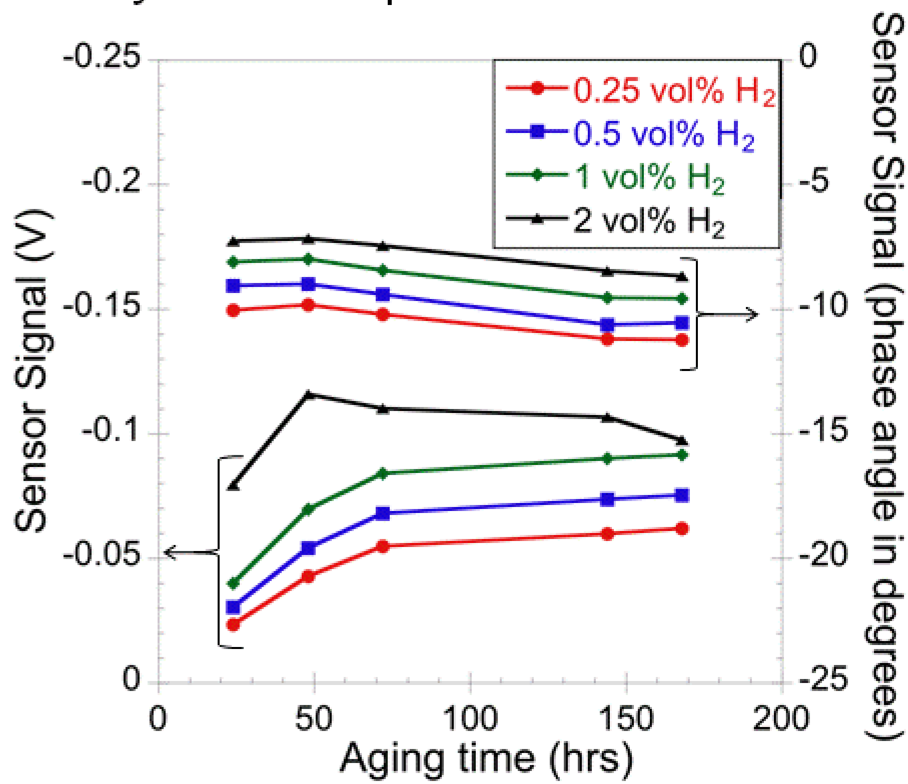
Technical Accomplishments: Completed Milestone to Characterize Alternative Modalities (Potentiometric and Impedancemetric): Open circuit potential (V) and phase angle (degrees)

Alt. Prototype B (dense LSM electrode, perpendicular conduction path) was used to evaluate alternative solid-state electrochemical sensing modality using ac-impedance based signal (i.e., phase angle in degrees) for improving long-term stability and sensor performance.







Initial testing to >150 hrs demonstrated similar behavior for alternative modalities: continuing long-term testing.

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Collaborations

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

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

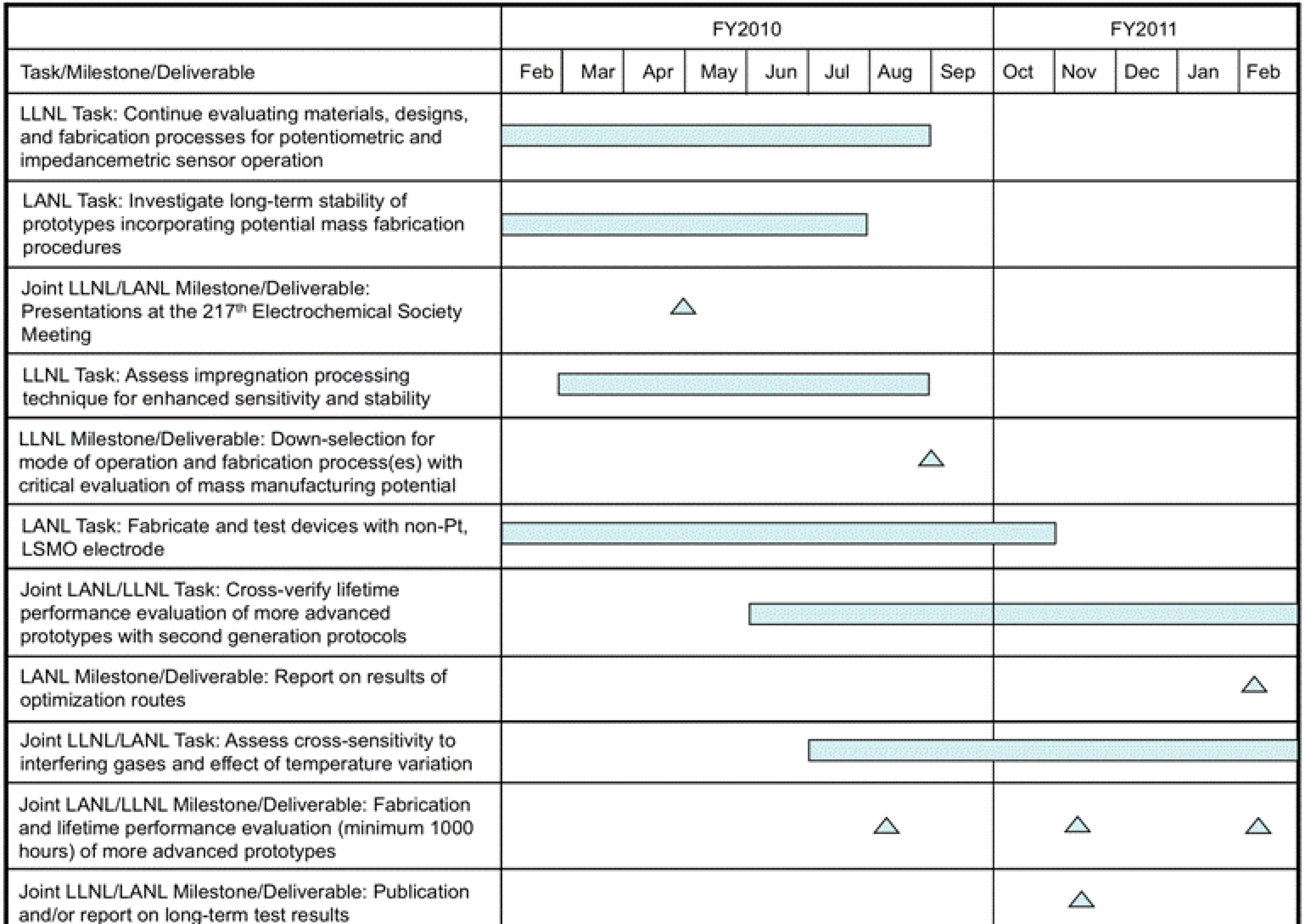
ESL

ESL ElectroScience

Industrial Partner

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

Proposed Future Work: From FY'10 AOP



Proposed Future Work: From FY'10 AOP

- Remainder of FY2010:
  - Continue evaluating materials, designs, and fabrication processes for potentiometric and impedancemetric sensor operation
  - Fabricate and test devices with non-Pt, LSMO electrode
  - Investigate long-term stability of prototypes incorporating potential mass fabrication procedures
  - Assess impregnation processing technique for enhanced sensitivity and stability: potential for stabilizing microstructure and porosity to mitigate deleterious aging

- Begin towards end of FY2010 and continue into FY2011:
  - Cross-verify lifetime performance evaluation of more advanced prototypes with second generation protocols
  - Assess cross-sensitivity to interfering gases and effect of temperature variation

Summary: FY'09 to present

- Improved electrode materials with potentially better performance were investigated where dense electronically conducting oxide (LSM) counter electrode showed better long-term stability.
- An alternate impedancemetric sensing modality was explored to evaluate improvements in long-term performance and stability.
- A pre-commercial H_2 sensor prototype was fabricated on an alumina substrate with ITO and Pt electrodes and YSZ electrolyte with an integrated Pt heater to achieve precise operating temperature and minimize heterogeneous catalysis.
- During the initial 2000 hrs of long-term testing for the prototype with optimized platinum electrode, the sensor response to 5000 ppm of H_2 varied at a maximum of ca. $\pm$10% from its original value of 0.135 V (0 hrs). The response rise time fluctuated between 3 to 8 s.
- The extended sensor response stability over time may be attributed to a stable, engineered three-phase interface.
- The salient features of the investigated H_2 sensor prototype include (a) conducive to commercialization, (b) low power consumption, (c) compactness to fit into critical areas, (d) simple transduction mechanism, and (e) fast response.

References

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2. P.K. Sekhar, E.L. Brosha, R. Mukundan, W. Li, M.A. Nelson, P. Palanisamy, and F.H. Garzon, “Application of Commercial Automotive Sensor Manufacturing Methods for NOx/NH3 Mixed Potential Sensors for On-Board Emissions Control”, Sensors and Actuators B: Chemical, 144, 112 (2010).
3. R. Mukundan, E. L. Brosha, and F. H. Garzon, J.Electrochem. Soc. 150 (12) H2799-H284 (2003).
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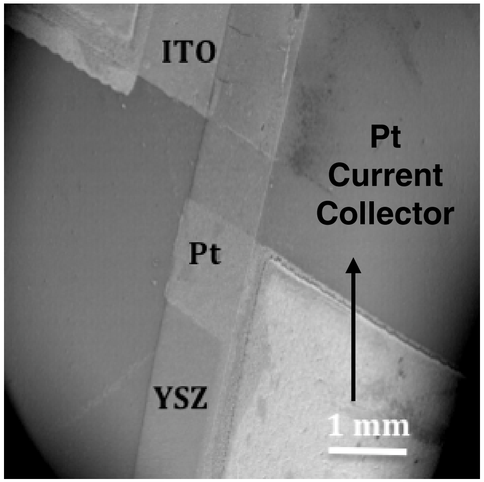
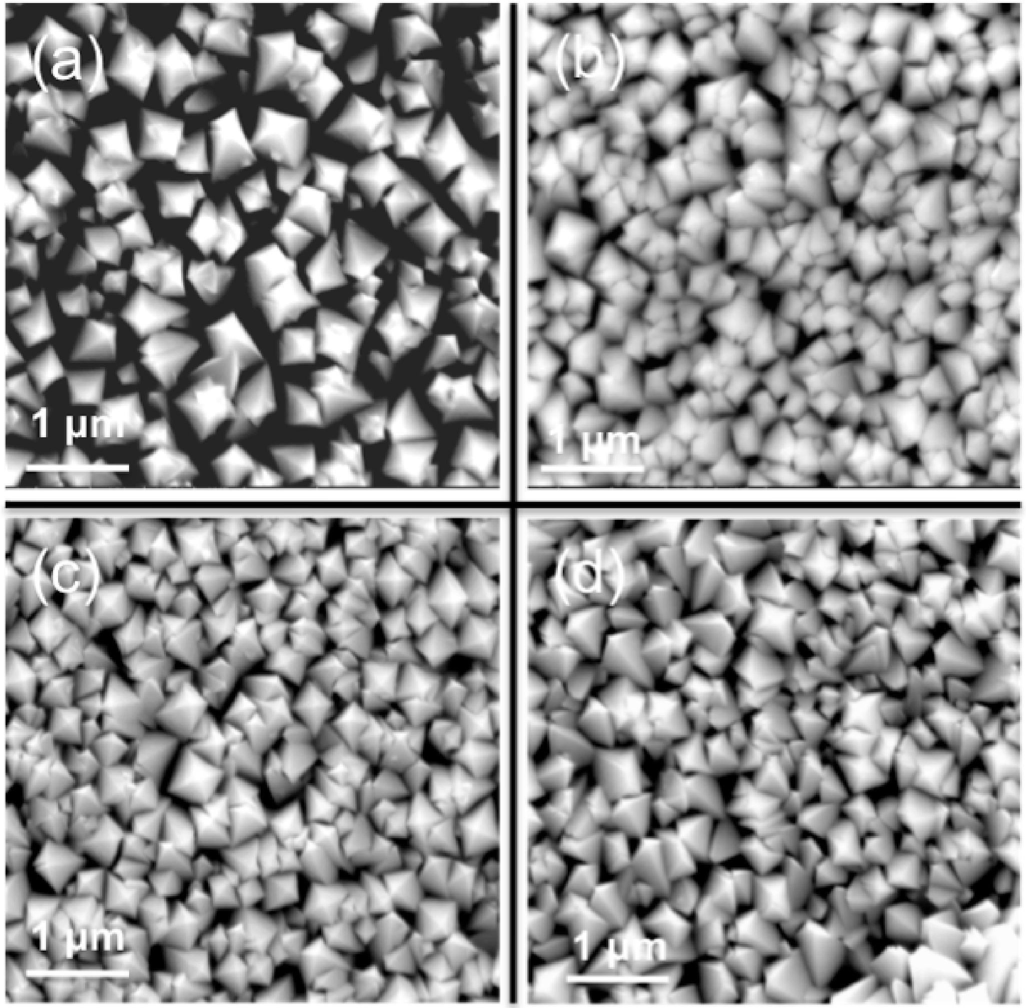
6. L.P. Martin and R.S. Glass, “Hydrogen Sensor Based on YSZ Electrolyte and Tin-Doped Indium Oxide Electrode”, J. Electrochem. Soc. 152 (4) H43-H47 (2005).
7. E.L. Brosha, R. Mukundan, R. Lujan, and F.H. Garzon, “Development of a Zirconia-Based Electrochemical Sensor for the Detection of H_2 in air”, ECS Transactions, 16 (11), 265 (2008).

Supplemental Slides

SEM Micrograph the of H_2 Sensor Prototype

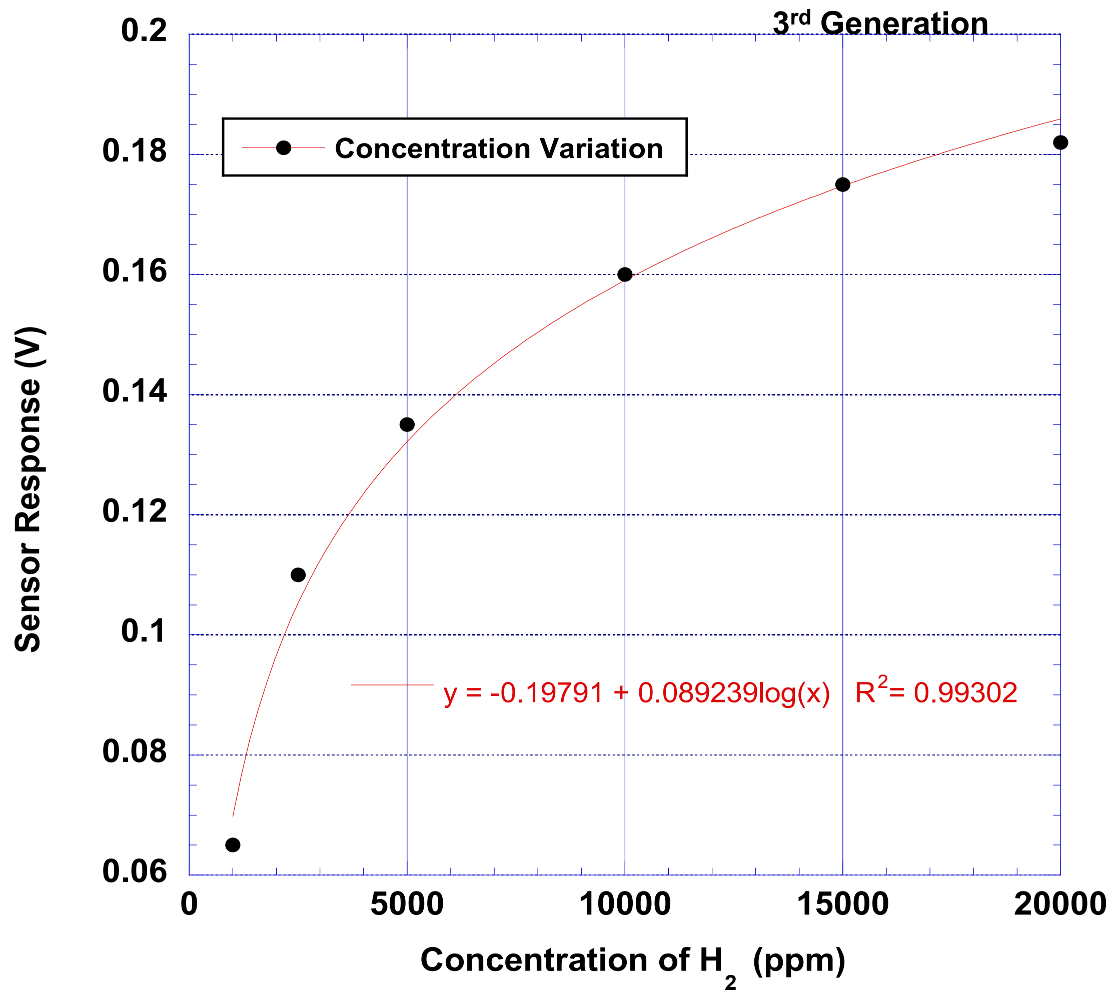


SEM micrograph showing ITO and Pt electrodes along with YSZ Electrolyte



SEM composite micrograph showing ITO morphology annealed at different temperatures.

Concentration Dependence of H_2 Sensor Prototype



Concentration Dependence Curve of the H_2 Sensor Prototype with a Logarithmic Fit (6.5 V~535^0 C, 200 SCCM, H_2 in air, y- Sensor Response, x Concentration of H_2)

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Customized LabView Program to Aid FY'10-FY'11 AST