Robust Nitrogen oxide/Ammonia Sensors for Vehicle on-board Emissions Control

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Los Alamos National Laboratory

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Project ID : ACE079

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Project Overview

Timeline

- Project Start Date
  - **August 2010**
- Project Duration
  - **≈ 2 Years**
- ≈ 95% complete

Budget

- Total project funding
  - 2 Years : $504,000
  - DOE Cost : $504,000
  - Cost Share : None
- Funding for LANL

FY 10 $ 154k

FY 11 $ 350k

Barriers

B. *Lack of cost-effective emission control*

C. *Lack of modeling capability for combustion and emission control*

D. *Lack of effective engine controls*

E. *Durability.*

By 2013, develop NO_x sensor materials and prototypic NO_x sensors that meet the sensitivity requirements identified by industry for emissions control in light duty diesel engines.

Partners

- LANL – Project Lead, Design, Testing
- ESL ElectroScience – Sensor prototype manufacturer
- Custom Sensor Solutions, Inc – Sensor electronics developer
- Caterpillar Inc. - Potential Test Site

Relevance

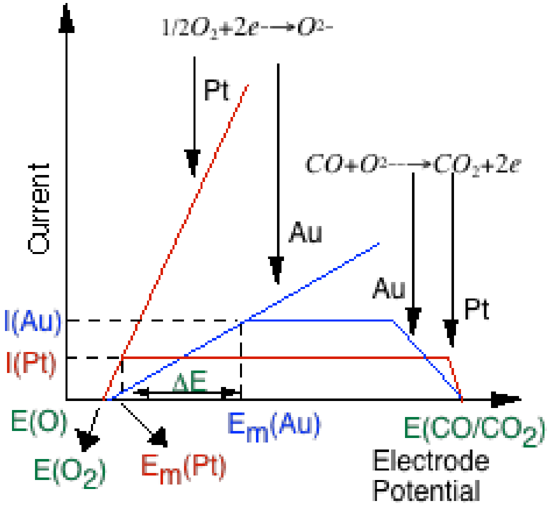
- From VT Program MYPP 2011-2015
  - Table 2.3-3 Tasks for Combustion and Emission Control R&D
  - Task 3. *Engine Technologies R&D (fuel systems, sensors and controls, integrated systems, etc.)*
    - Develop and validate NO_X and PM sensors for engine and after-treatment control and diagnostics
- Objective of the project is to develop low cost robust nitrogen oxide/ammonia sensors
- Accurate fast and reliable sensors can:
  - Improve efficiency of emissions system
  - Verification of emissions–system efficiency
  - Help validate models for the degradation of exhaust after treatment system
  - Potential feedback for effective engine control

Milestones

- M1 (May 2011): Report on the results of 4-electrode testing of a NO_x sensor. (Complete)
- M2 (August 2011): Demonstrate ±5ppm NH_3 sensitivity (Complete)
- G1 (Sept 2011): Demonstrate ±5 ppm NO_x sensitivity in a thin film NO_x sensor platform(Complete)
- Go: Continue development of thin film technology to demonstrate long-term stability (FY12)

Approach (Background)

Mixed Potential Sensors



Other Research:

Kyushu University	University of Florida	ORNL
University of Rome	Nagoya University	LLNL
National Industrial Research Institute of Nagoya		

LANL : 15 peer reviewed publications and 5 patents

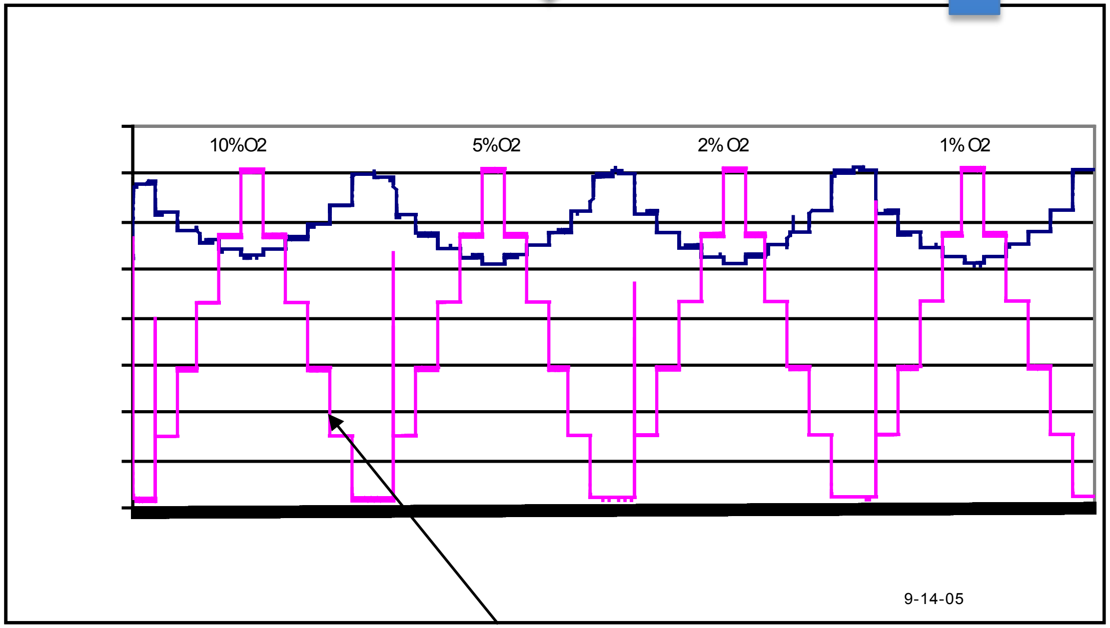
LANL UNIQUENESS

Dense Electrodes, Porous/thin film electrolyte, Controlled interface

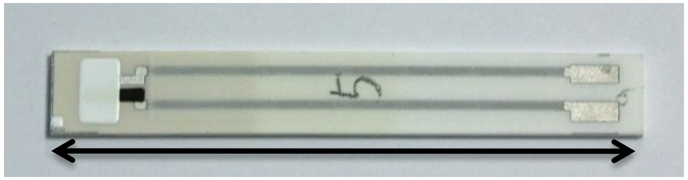
- Minimize heterogeneous catalysis (maximize sensor sensitivity)
  - Avoid gas diffusion through a catalytic material
  - Minimize diffusion path to 3-phase interface
- Avoid changes in morphology: Control interface (Robustness)
  - Fixed and reproducible interface
  - Need not have ability to sustain high currents (large 3-phase boundary length)

Approach (Background)

Excellent performance of bulk sensor achieved



NO Mass flow controller



50 mm

Need to retain performance in a commercially manufacturable device, validate, and transfer technology to industry

Data obtained by FORD Motor Co.
R. Novak, R. Soltis, D. Kubinski, E. Murray and J. Visser
September 2005

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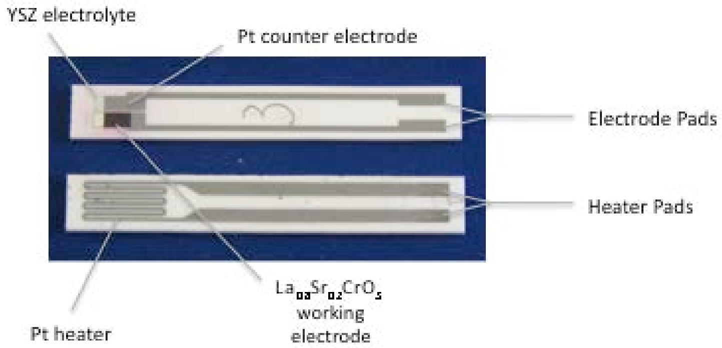
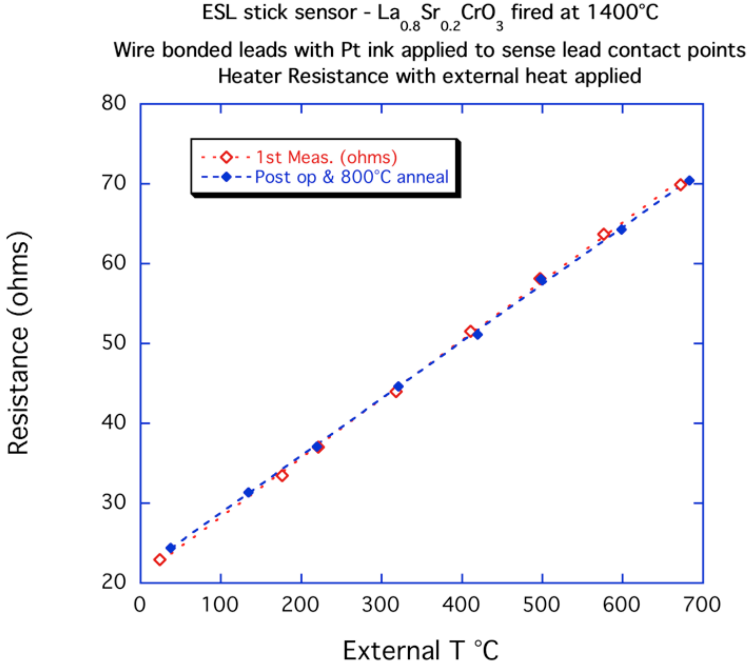
Technical Accomplishments

Heater



Serial No.	Peak firing Temp. °C	Length mm	Width mm	Thickness mm	Heater resistance (Ω)
A1	1450	51.5	7.5	1.3	13.8
A2	1450	51.5	7.5	1.3	13.9
A3	1450	51.5	7.5	1.3	13.7
A4	1450	51.5	7.5	1.3	13.4
A5	1450	51.5	7.5	1.3	13.3
A6	1500	51.3	7.4	1.3	11.5
A7	1500	51.3	7.4	1.3	11.6
A8	1500	51.4	7.5	1.3	11.3
A9	1500	51.4	7.4	1.3	11.6
A10	1500	51.3	7.3	1.3	11.5

Table 1.: Properties of Type 1 Sensor Parts, Part No. 42523, Lot No. D-3094-64A

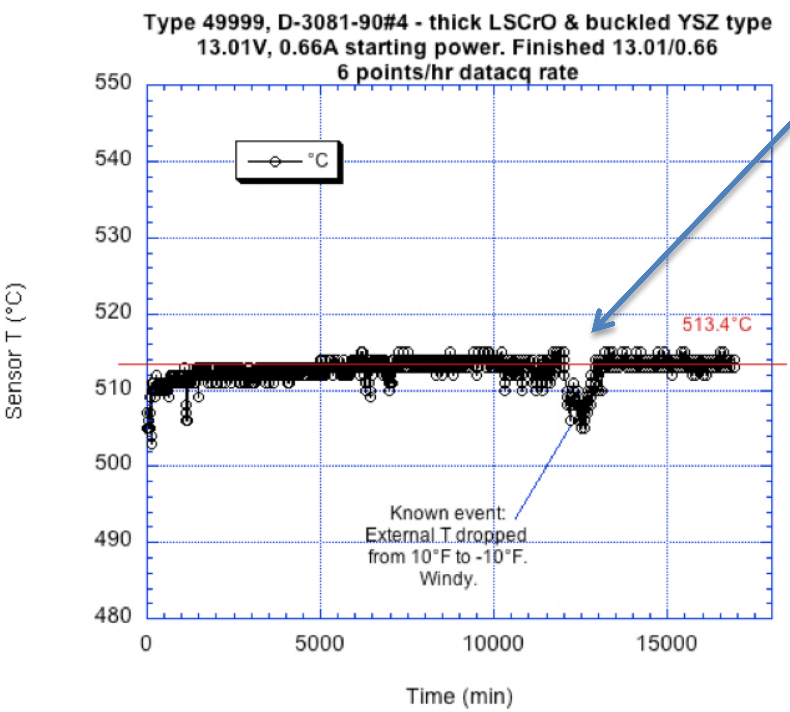


- Heater design typical of automotive sensors
- Easy to manufacture reliably
  - Excellent sample reproducibility within one batch (<2% variation in resistance)
  - Control of heater power can be achieved by changing firing temperature and Pt ink formulation
- Accelerated tests (extended anneal at 800 °C) indicate good heater stability

Highlight : Good heater stability

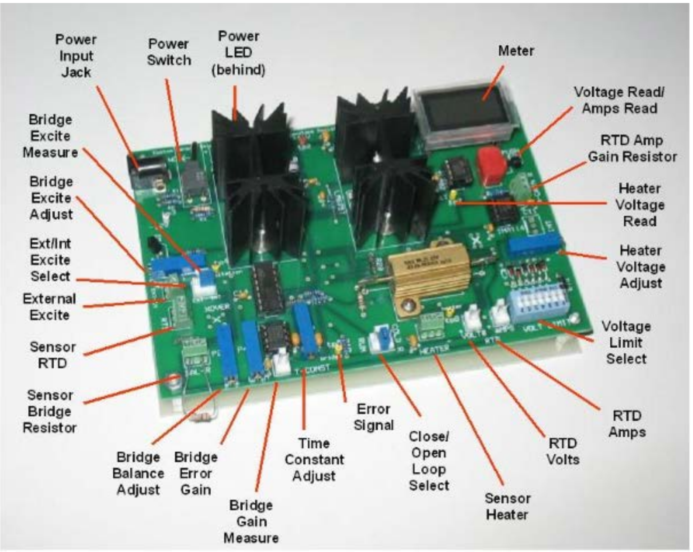
Technical Accomplishments

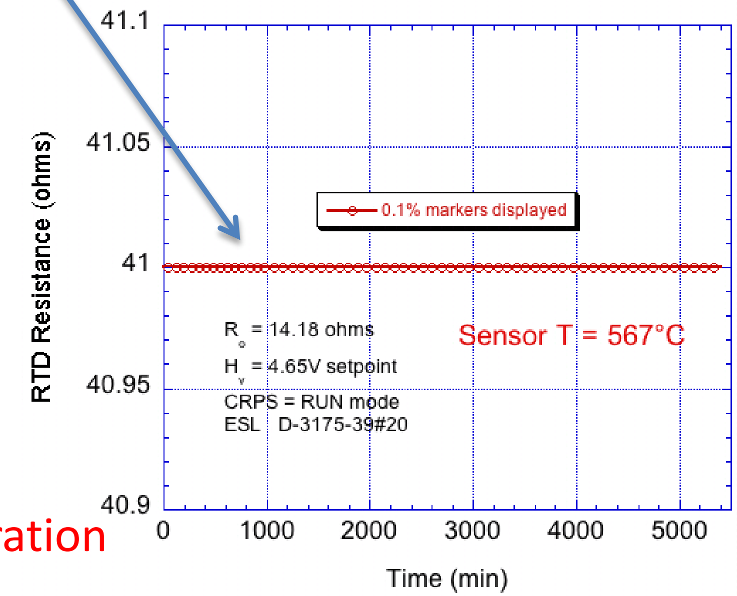
Heater Development: Internal sensor feedback and control electronics



Without feedback: stable T but susceptible to transients.

With RTD feedback and active heater control: stable T, less noise.





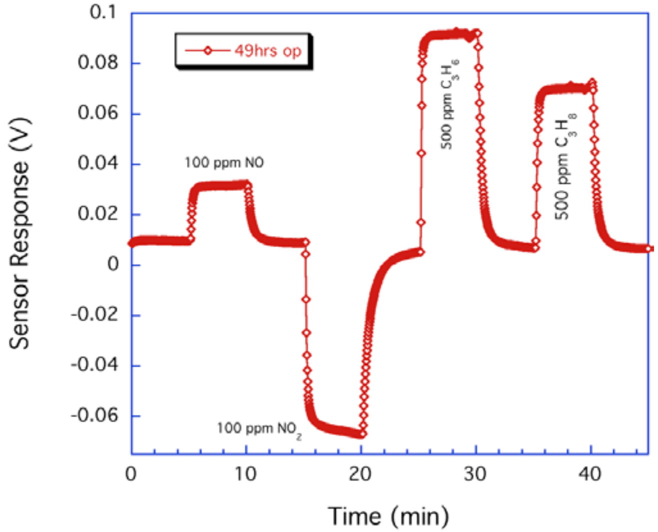
- Heater feedback control essential for mixed potential sensor
- Board designed/built with collaborator Custom Sensor Solutions, Inc.
- Synergy with DOE funded H_2 Safety sensor project (joint project with LLNL)

Highlight : Heater control board ready for incorporation

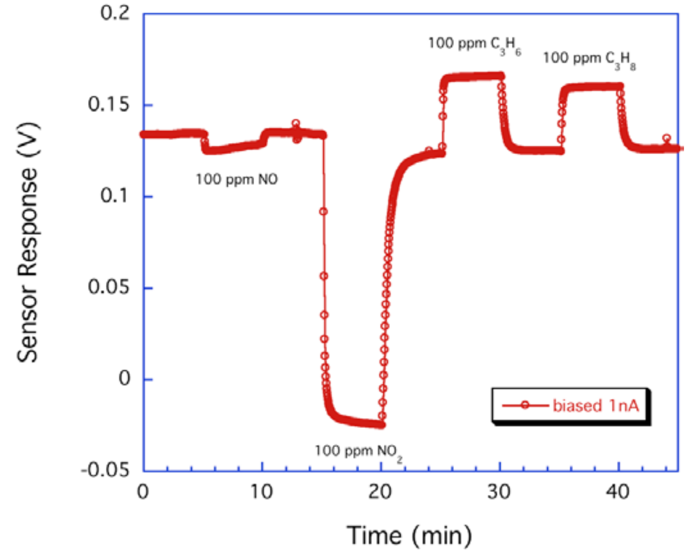
Technical Accomplishments

Sensor Performance

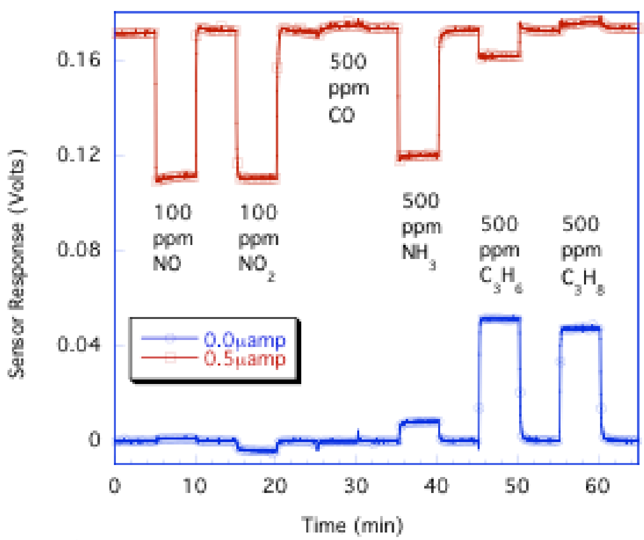
ESL made Sensor (un-biased response)



ESL made Sensor (biased response)



Hand made Sensor (optimal response)



- Quality of sensor responses maintained under un-biased conditions
  - Good hydrocarbon response
  - High NO_2 response under un-biased condition (can be mitigated by higher temperature operation
- Sensor response under bias needs improvement
  - NO/NO_2 response not equivalent under bias
  - Current bias not effective in enhancing the NO response or mitigating the hydrocarbon response
- Conclusion: **Need to improve the Interface**

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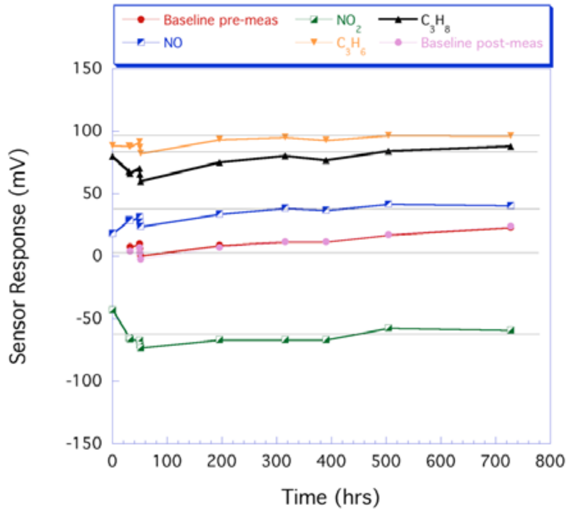
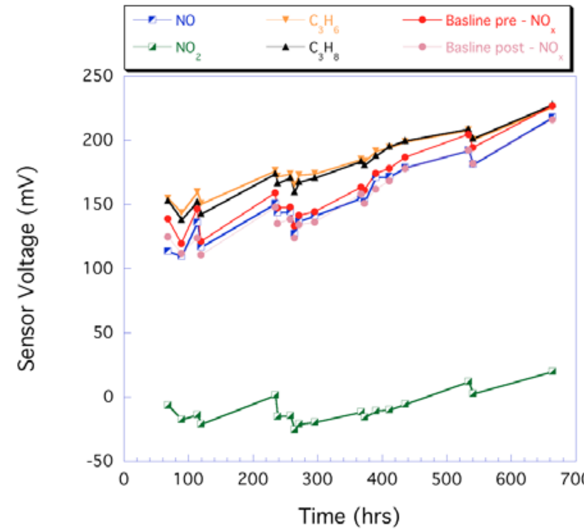
Technical Accomplishments

Sensor Stability

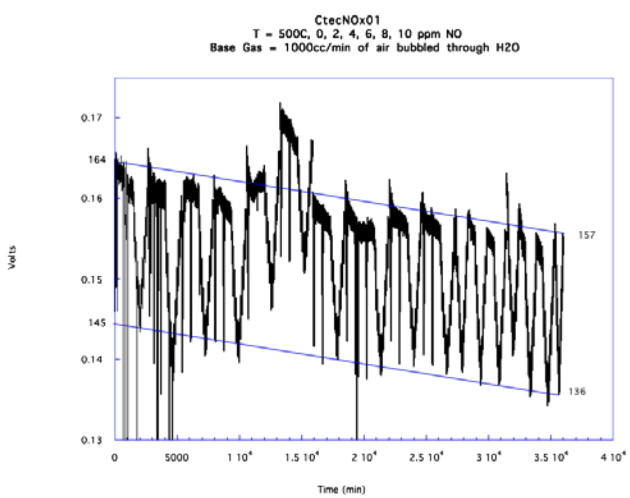
ESL made Sensor (un-biased stability)



ESL made Sensor (Stability under bias)



Hand Made Sensor (Stability under bias)



- Stability of hand made sensor :
  - Over 600 hours 10 ppm NOx = 20 ± 1mV
  - Baseline drift of 7 mV needs to be addressed
- Interfacial stability of ESL devices lacking
  - Over 100 mV drift in baseline
  - Over 50 mV drift in response
  - Conclusion: **Need to improve the Interface**

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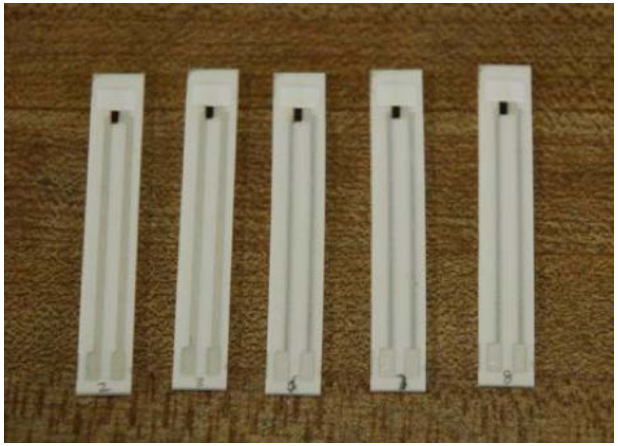
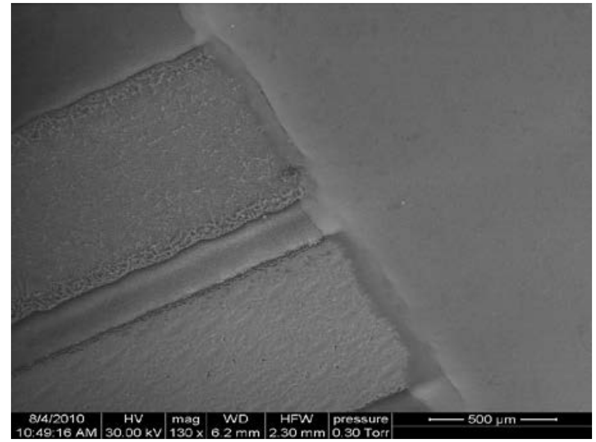
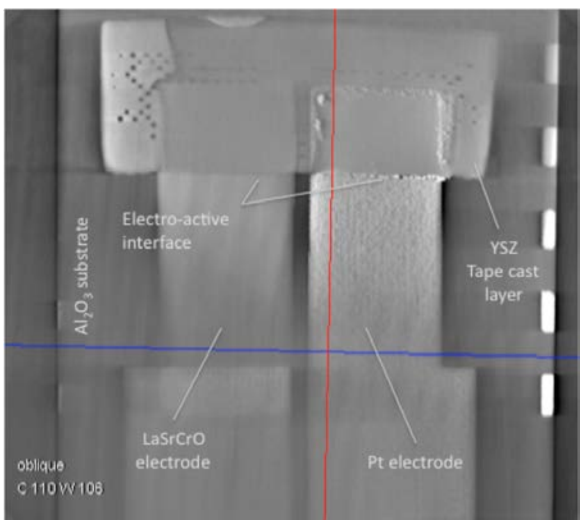
Technical Accomplishments

Sensor Interface



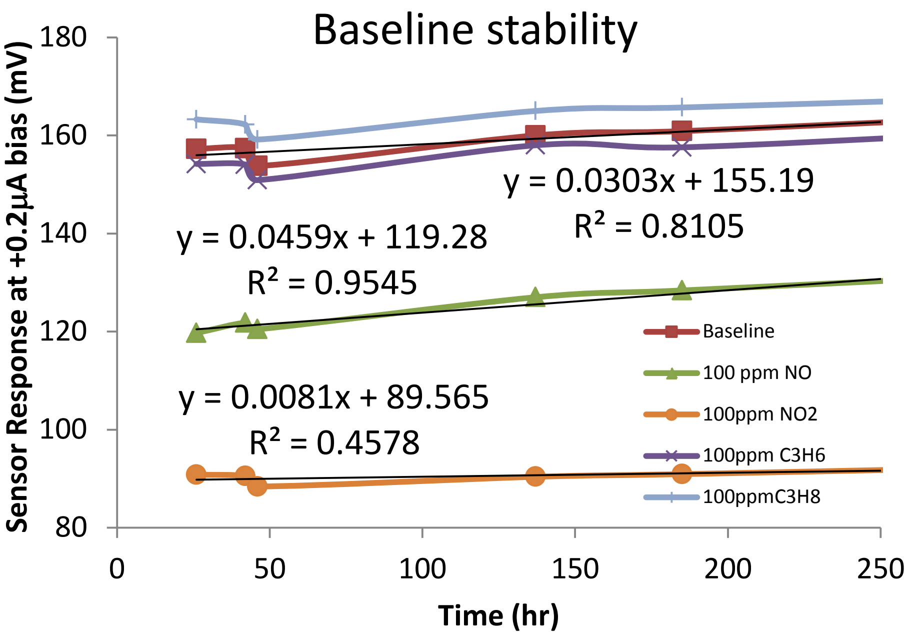


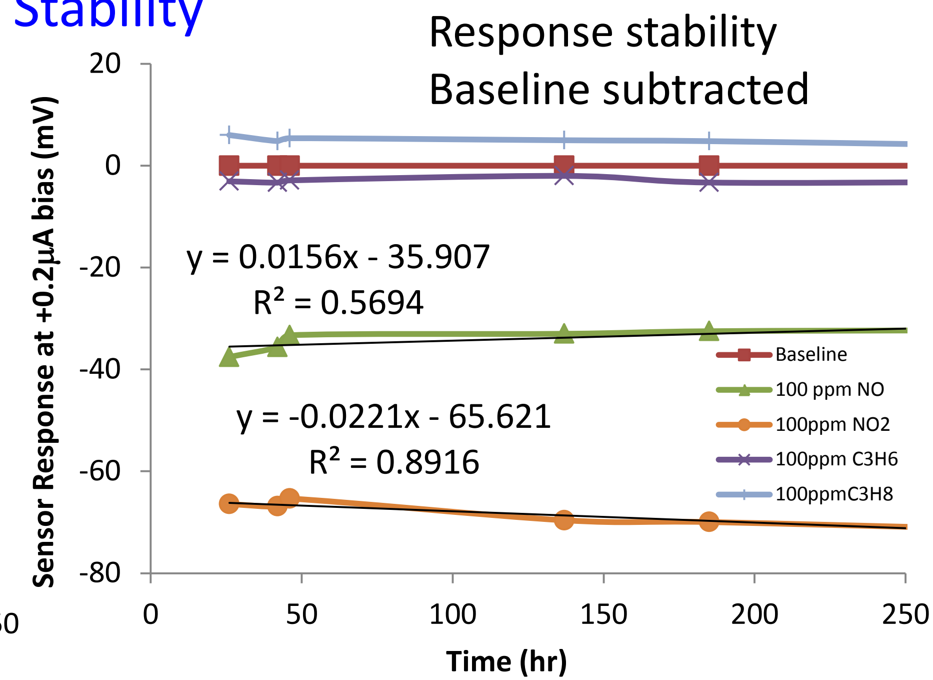


- Extensive sensor characterization
  - Optical, SEM, X-ray micro tomography, XRD, and EDAX
- Identified interfacial issues and worked with ESL to address these issues
  - Formulated better inks
  - Altered platform composition and experimented with ceramic doping to better match thermal expansion coefficients (CTEs)
  - Tuned firing temperatures (single co-fire)
  - Optimized insulating layer composition

Technical Accomplishments

Sensor Stability





- Interface Stabilization successful
  - Remarkable improvement over first generation
  - Need more development to get performance/stability comparable to hand made sensors
- Need to incorporate heater feedback to control sensor temperature
  - Introduction of RTD (or use of heater resistance to control and monitor temperature)
  - Heater control board obtained
- Study sensor conditioning to improve sensitivity
  - High voltage/current applied to sensor @ 280 hours
  - Improvement in sensor response observed

5 – 30 mV variation in 600 hours

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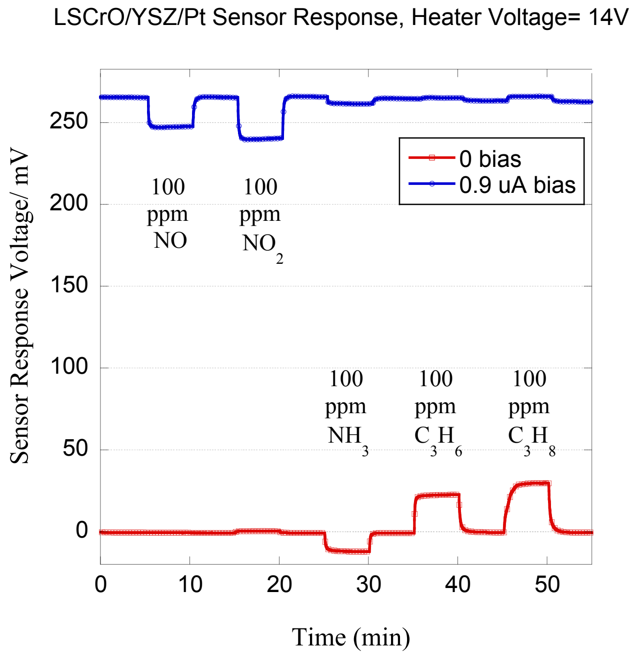
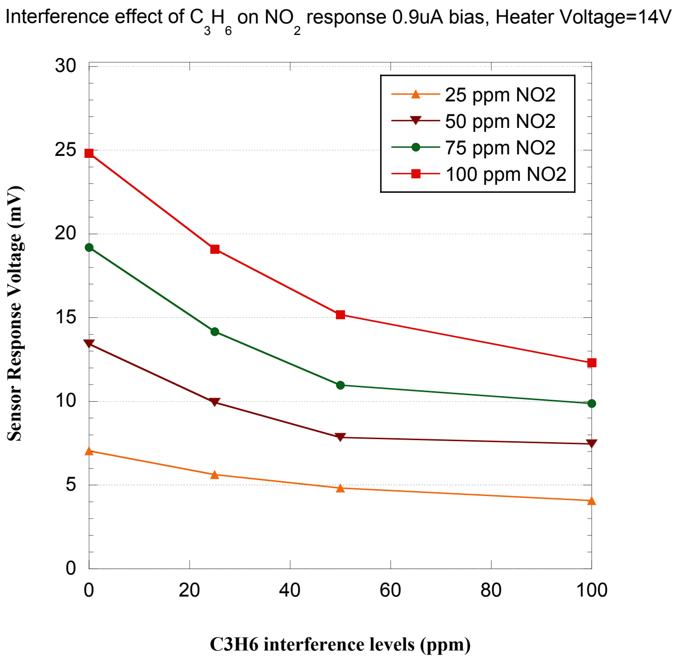
Technical Accomplishments

Interference Testing



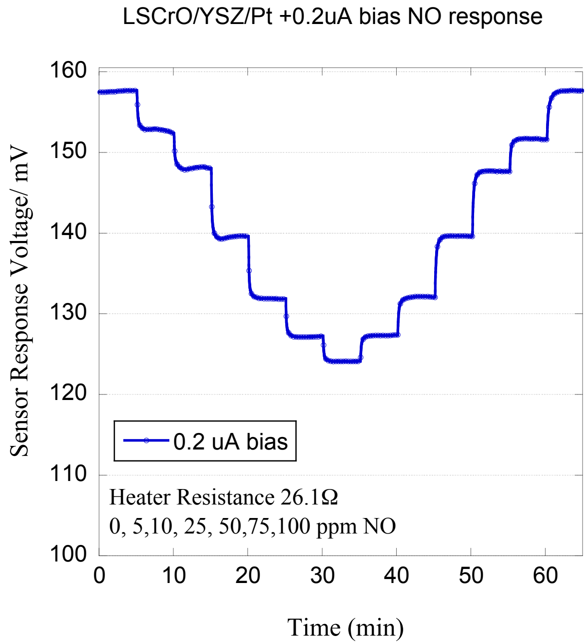


- Excellent selectivity to NO and NO_2 (Similar to hand-made devices)
- Bias can be used to tune selectivity (Sensitivity needs improvement)
- Mixed gas interference studies are more complicated and are required for validation of these sensors. Interference under bias with and without mixed gases is not identical
- Similar results obtained for both NO and NO_2 and interference gases C_3H_6 and C_3H_8

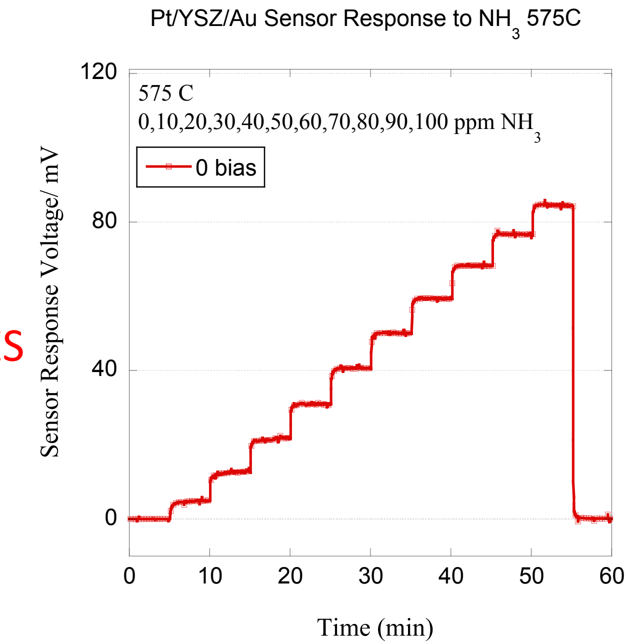
Mixed gas interference studies important

Technical Accomplishments

Sensor Sensitivity



MILESTONES



- LSCO/YSZ/Pt has ± 5ppm NO/NO_2 sensitivity
- Au/YSZ/Pt device has ± 5ppm NH_3 sensitivity
  - Temperature of operation is similar to that of NO_x sensor
  - Can be incorporated into a single sensor package
    - Will require multiple firing temperatures for the various layers

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Collaboration / Future work

Rangachary Mukundan, Eric Brosha, Praveen Sekhar, Cortney Kreller, and Fernando Garzon
Fundamental mixed potential sensor R&D
Sensor design, materials selection, laboratory testing

Wenxia Li, and Ponnusamy Palanisamy
Manufacturing, scale-up, valuable feed back in sensor design

Bill Penrose
Custom sensor control electronics: Heater control and High impedance boards

Svetlana Zemskova
Potential Sensor test site.
Joint proposal to continue sensor development.
Future work will be to identify funding mechanisms to validate technology at end user site and commercialize

Summary

- Unique LANL mixed potential sensor has been adapted to low cost robust NO_x and NH_3 sensors.
- Technology compatible with commercial prototype manufacturing. First generation NO_x sensors manufactured by ESL using LANL sensor designs
  - Interfacial stability issues identified
  - Morphological instability identified
- Changes made to processing in iterative fashion result in dramatically improved sensor response
  - ± 5ppm NOx sensitivity obtained
  - Improvement needed in stability
- Heater electronics developed and heater stability confirmed
- Pathway identified for future development of this technology for transfer to industry. Awaiting DOE funding.

Technical Back-Up Slides

NO_x Sensor (Background)

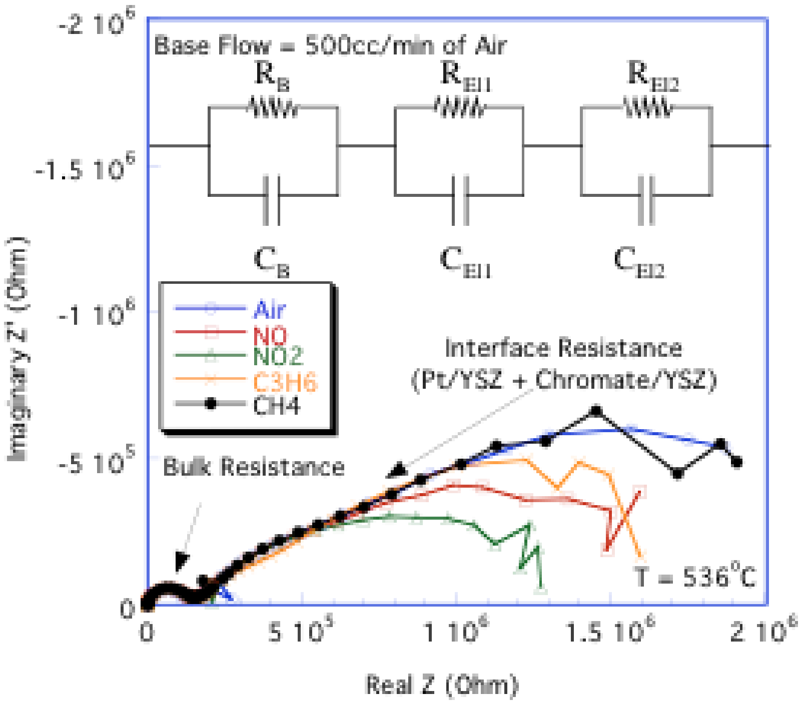
- Resistance decreases in the presence of NO, NO_2, NMHCs
- Resistance is unaffected by CO, CH_4
- Bulk resistance (pF capacitance) is unaffected
- Interface resistance (μF capacitance) decreases
- The oxygen incorporation into the lattice (O_2 dissociation) is probably being affected by the presence of NOx and NMHCs

$$\mathrm{NO} + O_2 \rightarrow NO_2 + O_{ads}$$

$$NO_2 \rightarrow \mathrm{NO} + O_{ads}$$

The resistance of the sensor needs to be dominated by interface resistances

AC IMPEDANCE

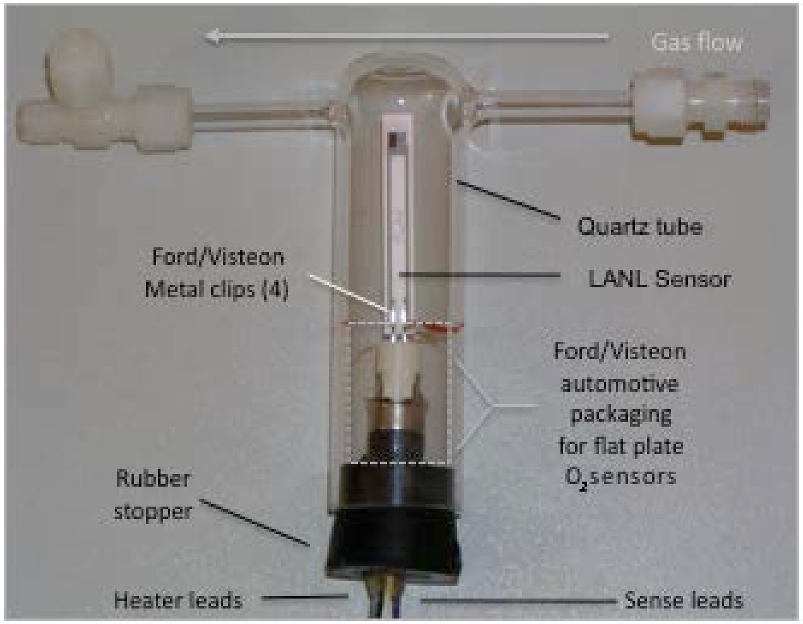


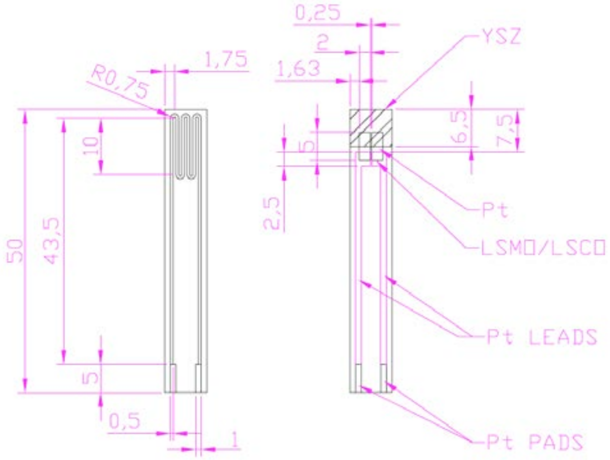
Kyushu University

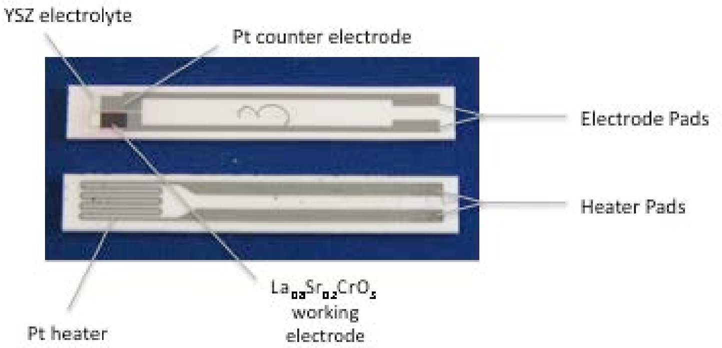
R. Mukundan, K. Teranishi, E. L. Brosha, and F. H. Garzon, "Nitrogen oxide sensors based on Yttria-stabilized zirconia electrolyte and oxide electrodes". *Electrochemical and Solid-State Letters*, **10(2)**, J26-J29 (2007)

Sensor Platform/Test setup

- LANL sensor design
- LANL materials
- ESL manufacturing of automotive stick sensor
- New LANL test setup







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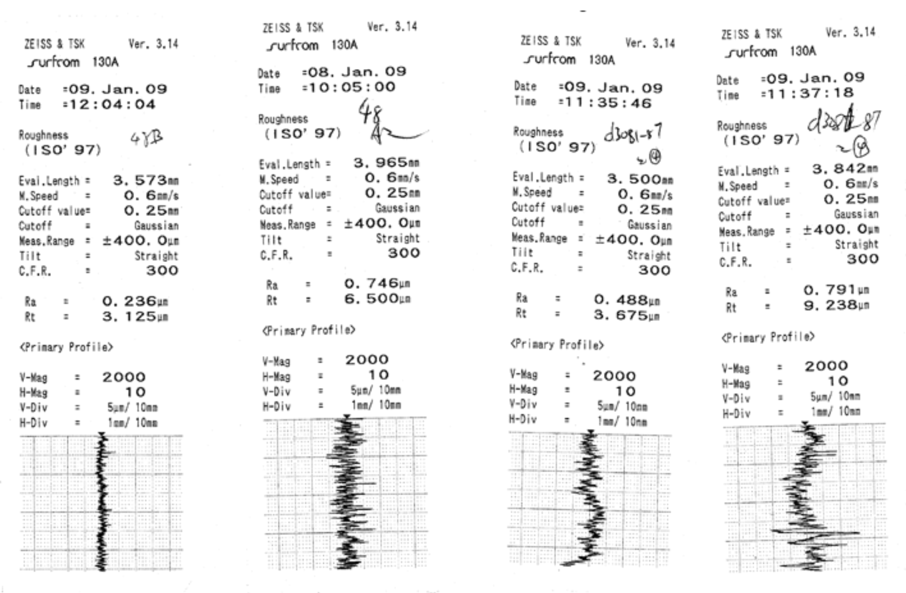
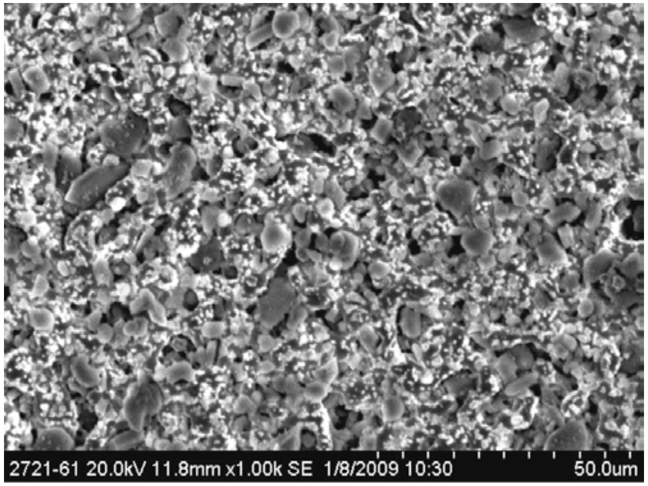
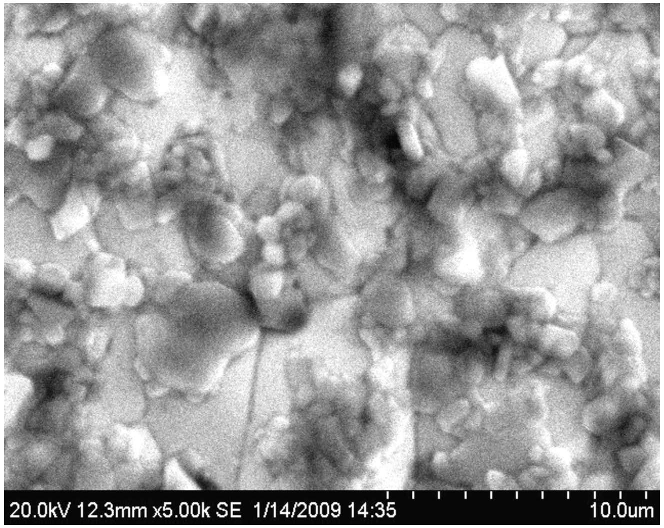
SEM Analysis

- ESL has experimented with a new Pt formulation to create smoother, more uniform counter electrodes
- Higher firing temperature (1510°C) and new inks provide for a smoother electrode surface (see left most profilometer trace in figure below)

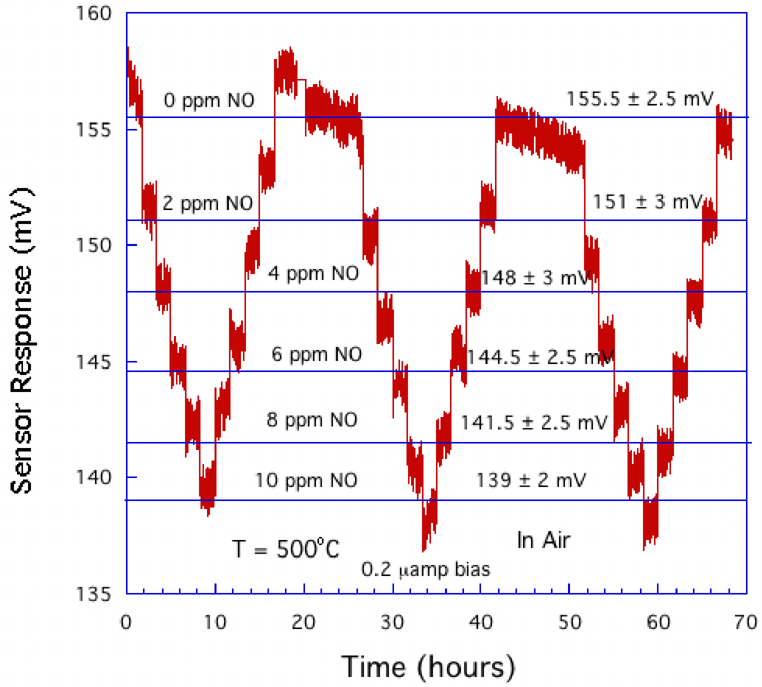






NO_x Sensitivity

- Can detect < 2 ppm of NO in air at 500°C and 14%H_2O
- Baseline voltage exhibits some drift
  - 175mV to 155mV over a period of 1 month
  - A function of the water and oxygen content in the test gas



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