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
  - **October 2012**
- Project Duration
  - **≈ 3 Years**
- ≈ 17% complete

Barriers

NO_x sensors that meet stringent vehicle requirements are not available:

a) Cost (Complex sensors compared to the automotive λ sensor)
b) Sensitivity (Need ± 5ppm or better sensitivity)
c) Stability (Need ≈ 5000 hours)
d) Interference (P_{O2}, P_{H2O}, hydrocarbons)
e) Response time (< 1 sec)

Budget

- Total project funding
  - 3 Years : $1,050,000
  - DOE Cost : $1,050,000
  - Cost Share : None
- Funding for LANL
  FY 13 $ 350k

Partners

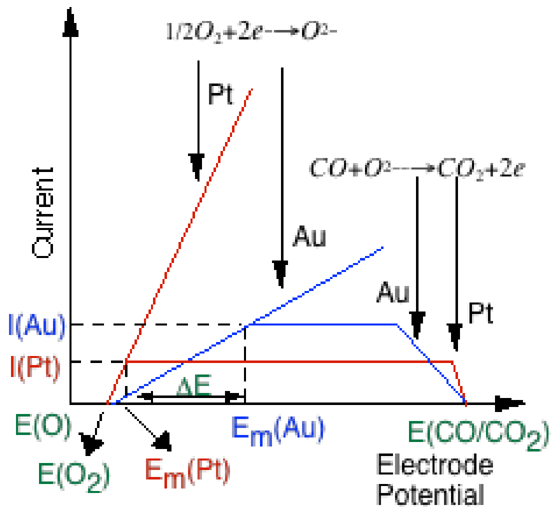
- LANL – Project Lead, Design, Testing
- ESL ElectroScience – Sensor prototype manufacturer
- Custom Sensor Solutions, Inc – Sensor electronics developer
- ORNL - National Transportation Research Center. No cost. Funded directly by VT.

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
    - GOAL: 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.
- 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

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

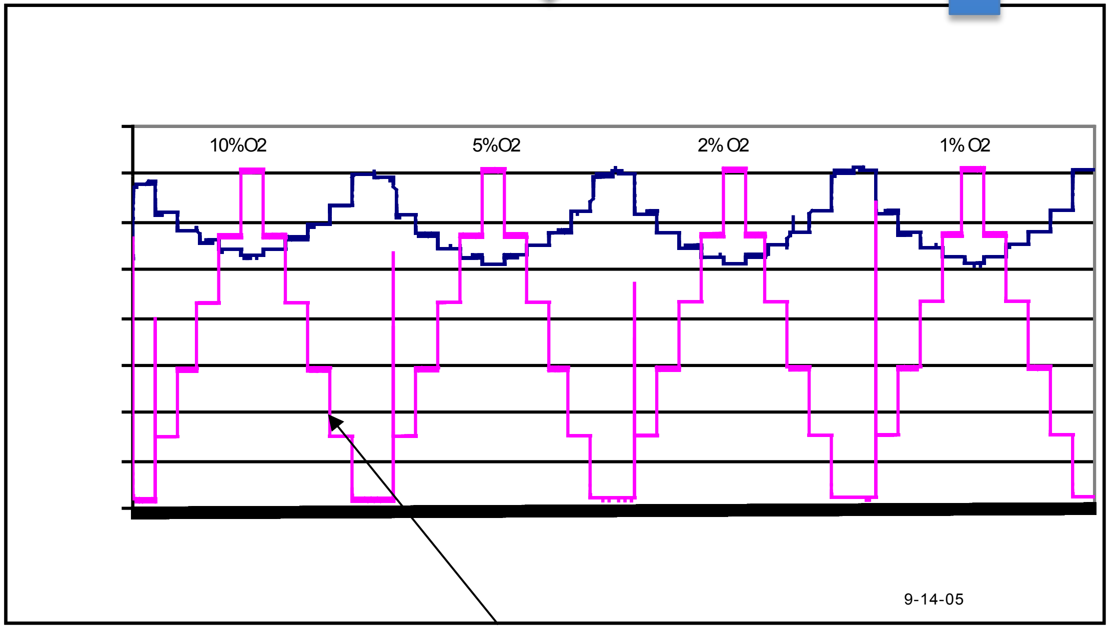
Dense Electrodes, Porous/thin film electrolyte, Controlled interface

Conventional Configuration : Porous electrode and dense electrolyte

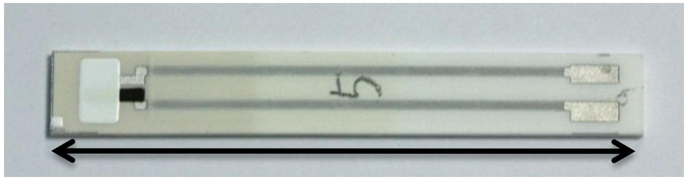
- Minimize heterogeneous catalysis (maximize sensor sensitivity)
  - Avoid gas diffusion through a catalytic material
  - Minimize diffusion path to 3-phase interface
- Avoid changes in morphology: Control interface (Robustness)
  - Fixed and reproducible interface
  - Need not have ability to sustain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

Approach (Previous Project)

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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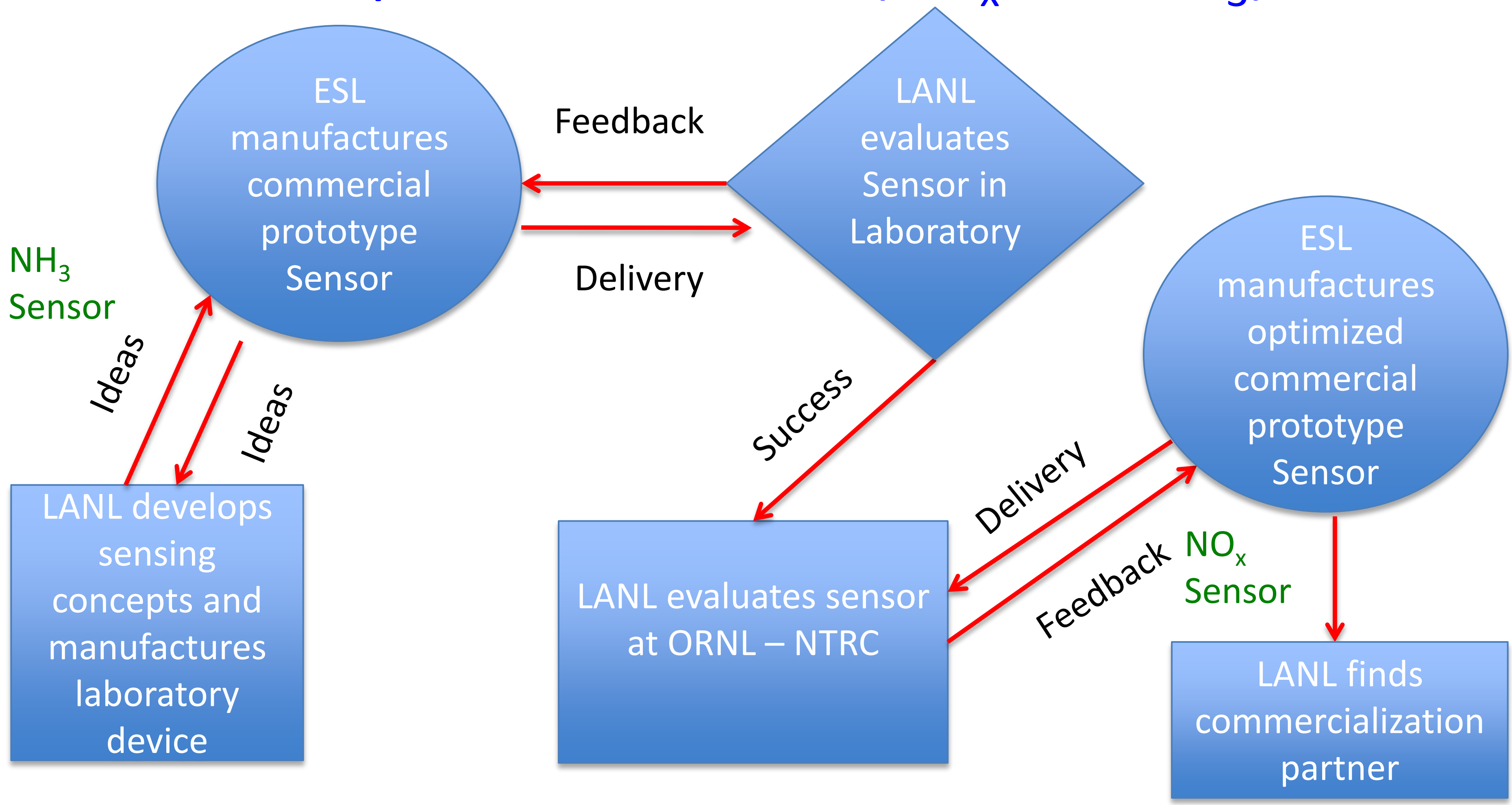
Approach

- Solve key issues impeding commercialization of mixed potential sensors (NO_x and NH_3)

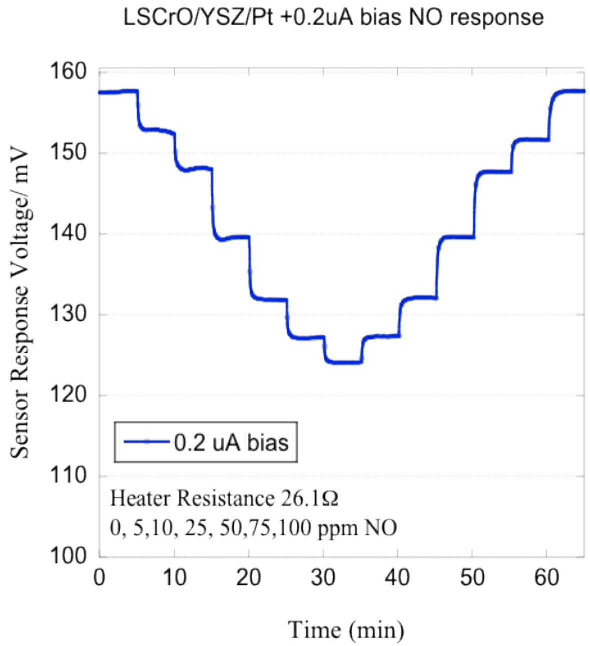


Milestones

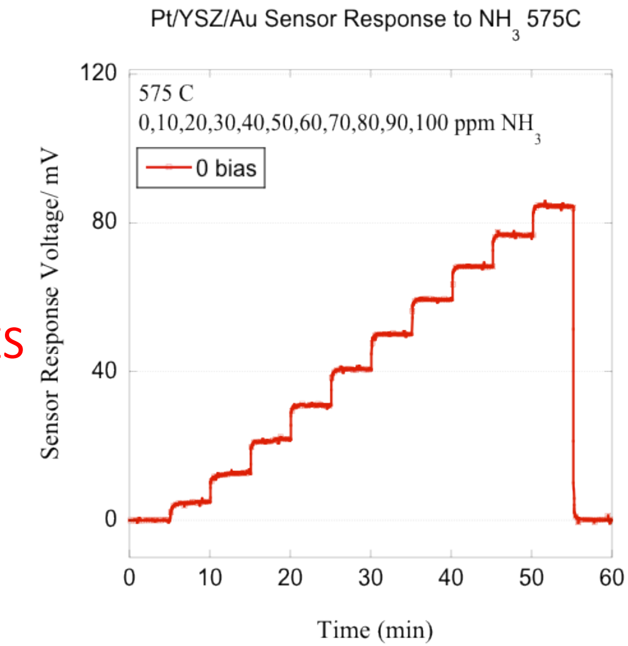
- Milestone 1 (Dec 2012): Prepare and test stick NO_x sensors with integrated heater. (Complete)
- Milestone 2 (May 2013): Report on engine testing at ORNL (Complete)
- Milestone 3 (Oct 2013): Report on 2nd round of Engine Testing at ORNL – NTRC (On track)

Technical Accomplishments

Sensor Sensitivity



MILESTONES

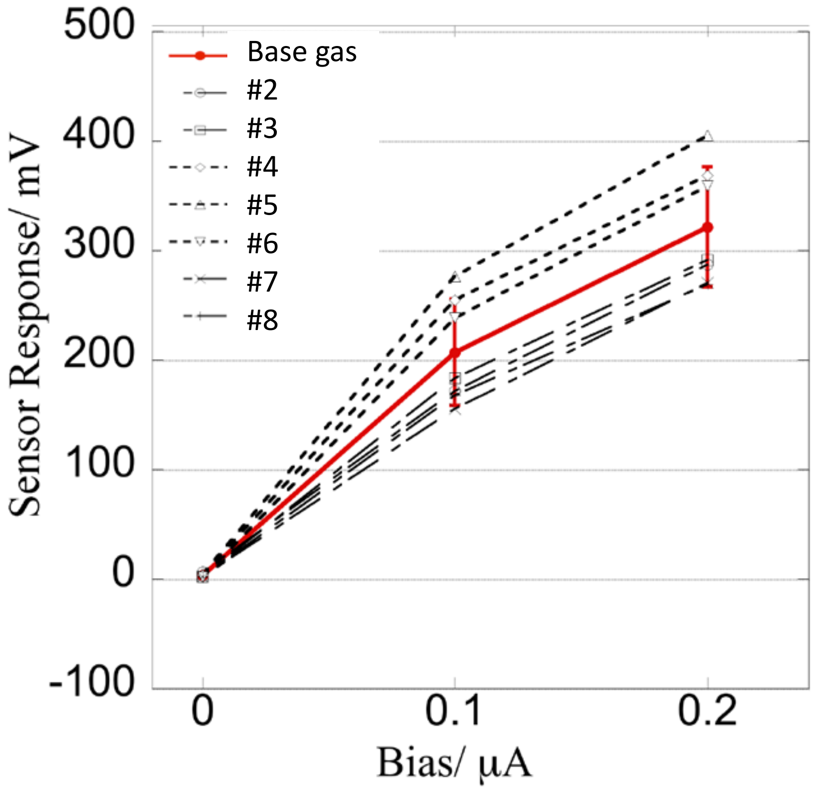


- LSCO/YSZ/Pt has ± 5ppm NO/NO_2 sensitivity
- Au/YSZ/Pt device has ± 5ppm NH_3 sensitivity
  - Temperature of operation is similar to that of NO_x sensor
  - Can be incorporated into a single sensor package
    - Will require multiple firing temperatures for the various layers

NO_x sensor reproducibility

Technical Accomplishments

Sensor response vs. Bias
Base gas 10%O_2/N_2



10 Sensors Delivered by ESL

4,5,6:

- Larger baseline voltage response for given applied current bias
- Larger unbiased response to test gas (NO and NO_2)

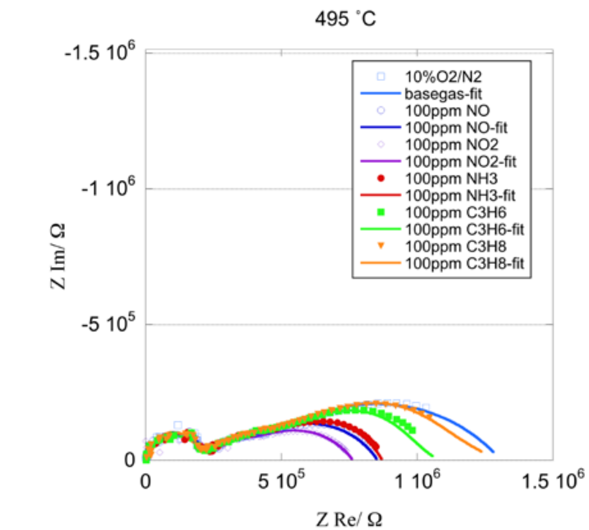
→ Consistent with lower operating temperature due to higher heater resistance

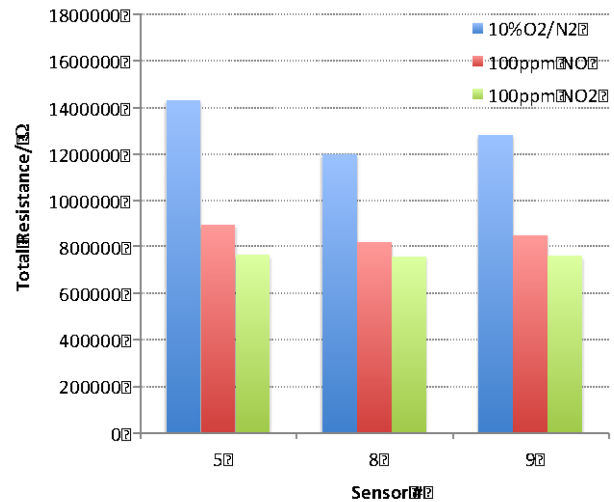
→ Operating at constant temperature critical for sensor to sensor reproducibility

Sensor	Resistance at RT	Resistance at 12V	R/ro	T based on RTD ratio
4	11.1	27.9	2.51	480
5	11.1	27.9	2.51	480
6	11.1	27.9	2.51	480
2	10.2	26.09	2.56	500
3	10.2	26.09	2.56	500
7	10.2	26.09	2.56	500
8	10.2	27.9	2.74	510

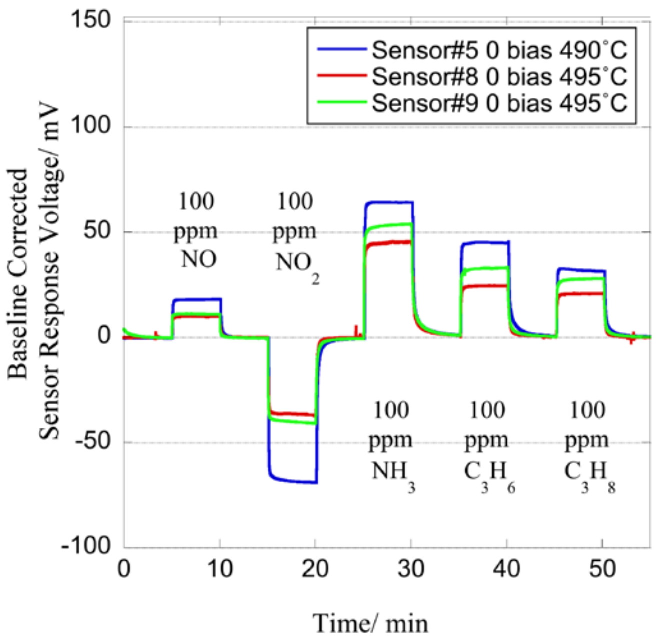
NO_x sensor reproducibility

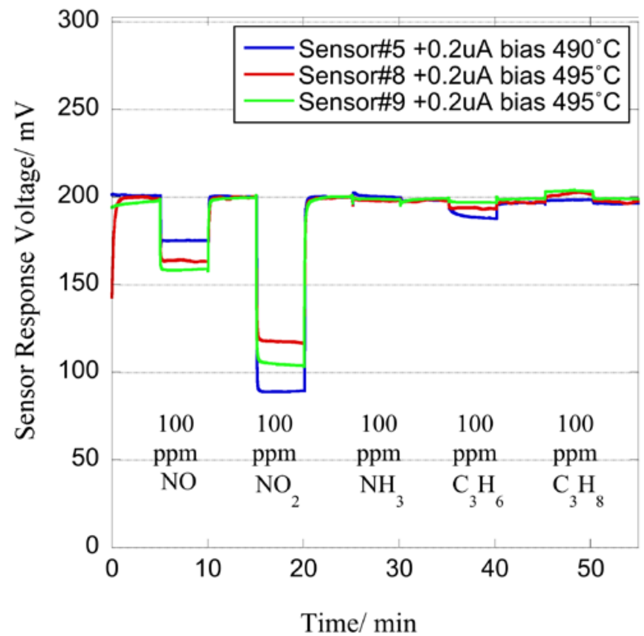
Technical Accomplishments





→Operating at constant temperature critical for sensor to sensor reproducibility

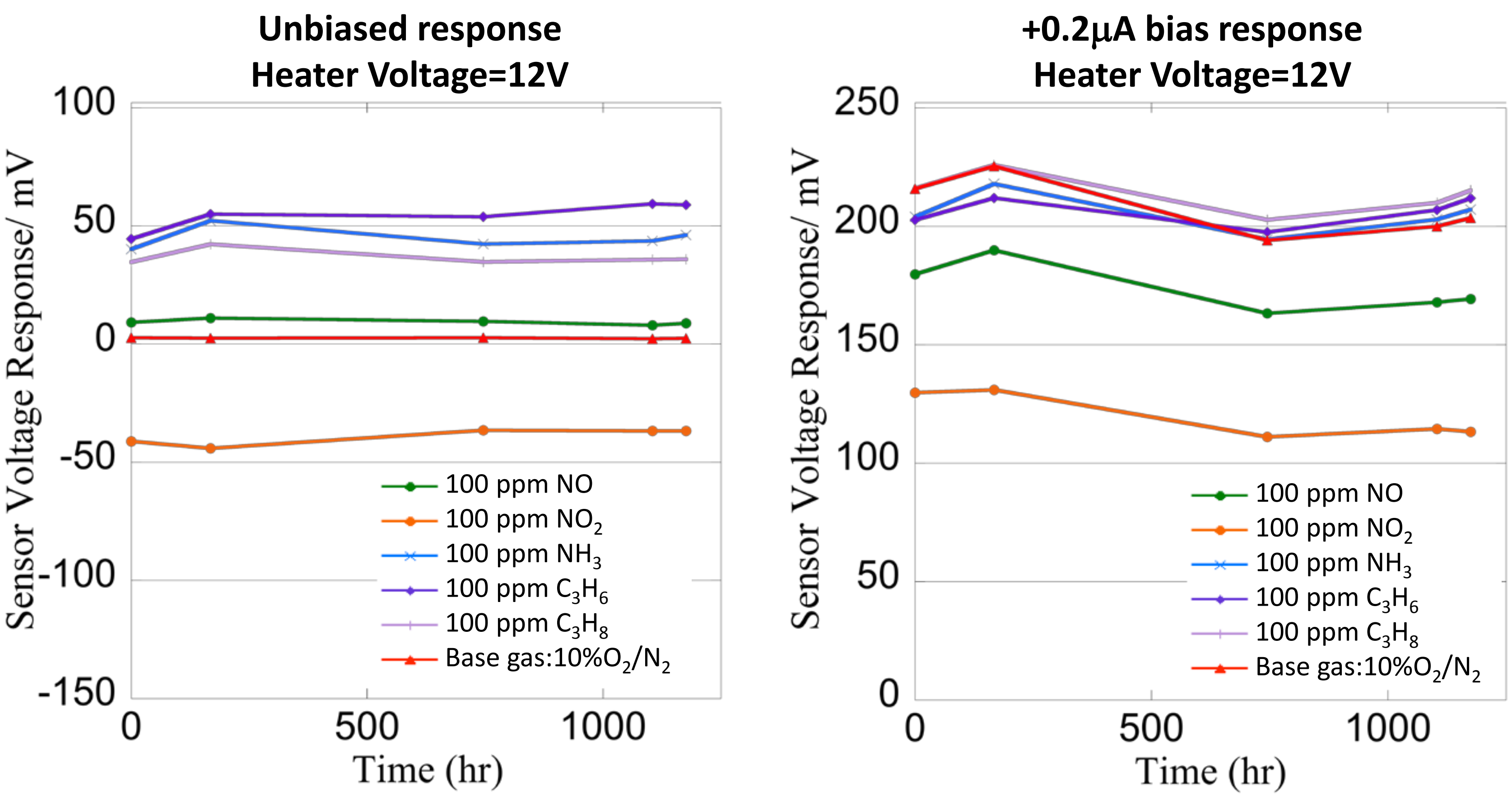




→Build sensors with identical heater resistance and operate them at constant heater resistance

NO_x sensor stability

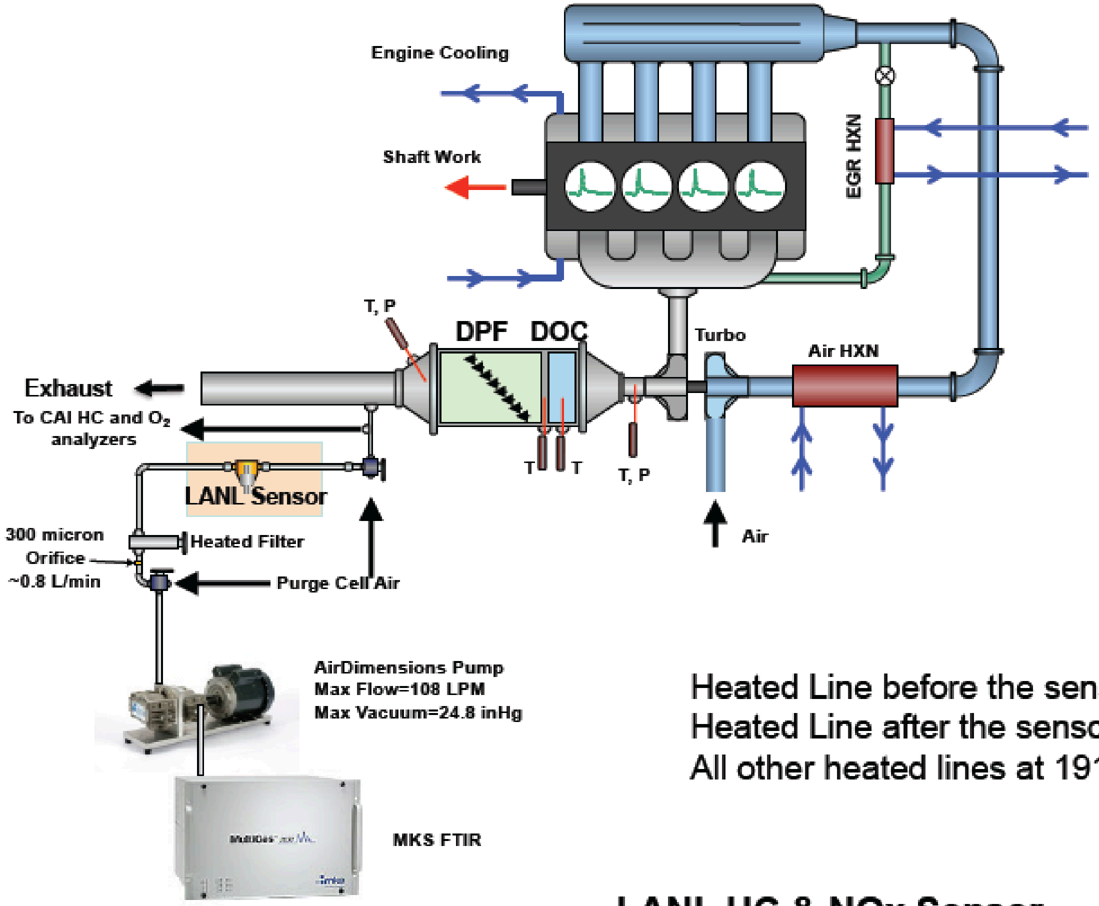
Technical Accomplishments



- Good durability over 1000 hours
- No systematic degradation. Greatest variability probably due to sensor temperature.
- Sensor operated at fixed heater power

→ Incorporate heater feedback control for better durability

Engine testing



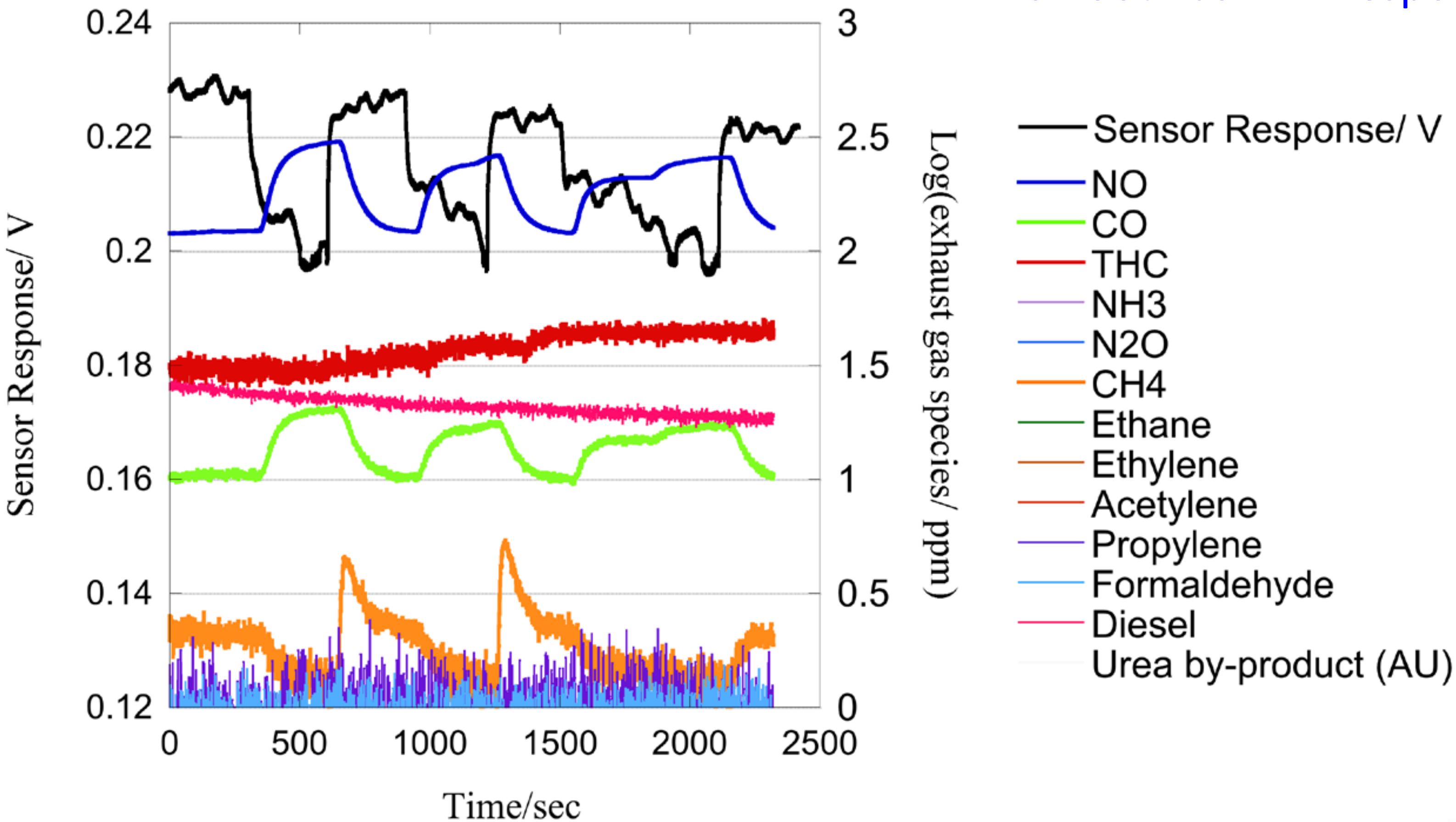
Heated Line before the sensor at 150C
Heated Line after the sensor at 125C
All other heated lines at 191C

LANL HC & NOx Sensor
Engine Setup at ORNL, March 2013

- Test LANL sensors under realistic conditions
- Validate response with analysis equipment
- Identify potential issues with sensor
- Provide feedback to develop better sensors

Qualitative agreement with FTIR response

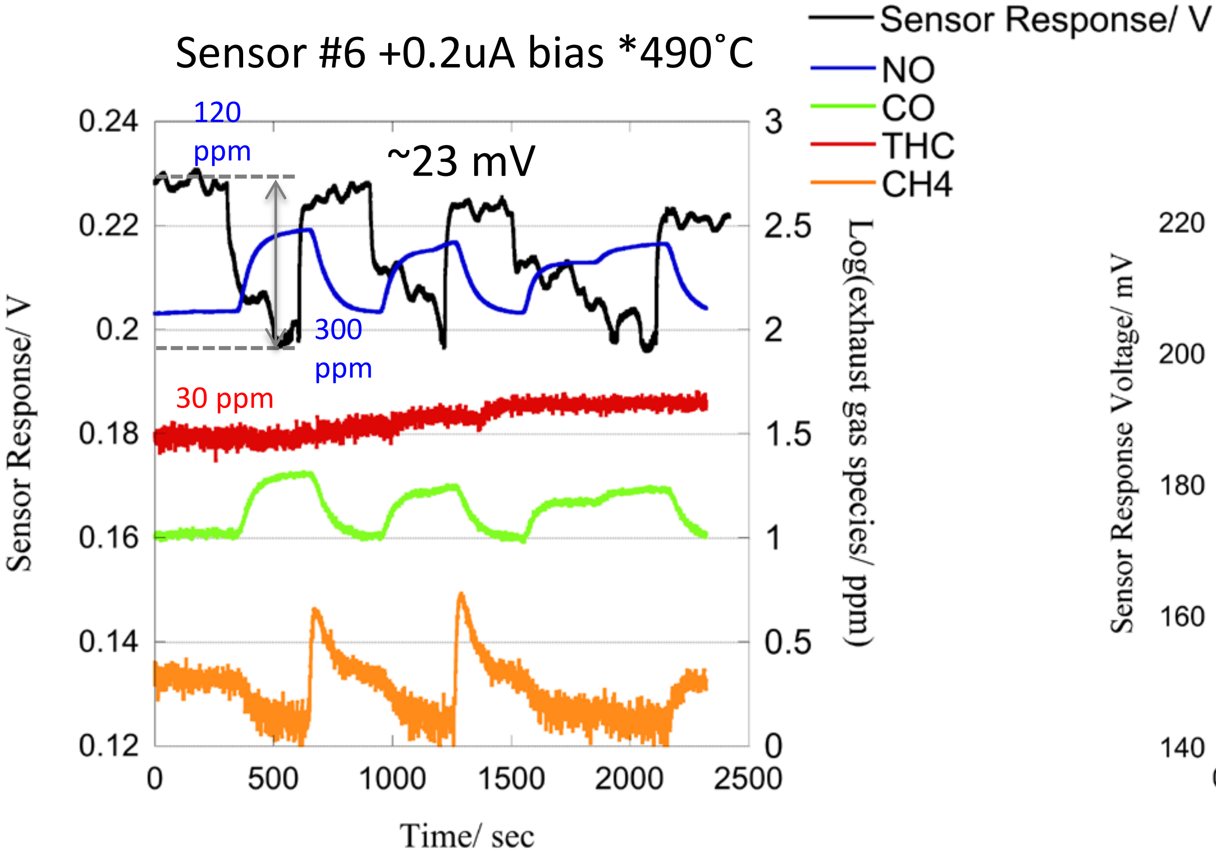
Test #1: Sensor in NO_x sensing mode
Hold engine load constant at 1600rpm- cycle EGR on/off

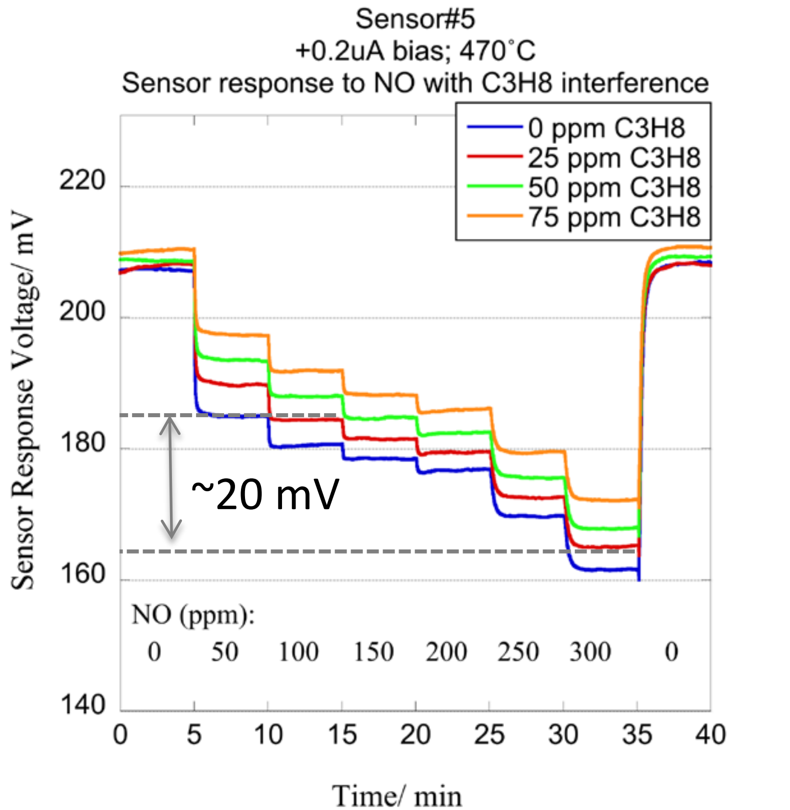


- Sensor tracks NO concentration from FTIR
- Sensor response not as smooth as FTIR response

Technical Accomplishments

Quantitative agreement with FTIR response



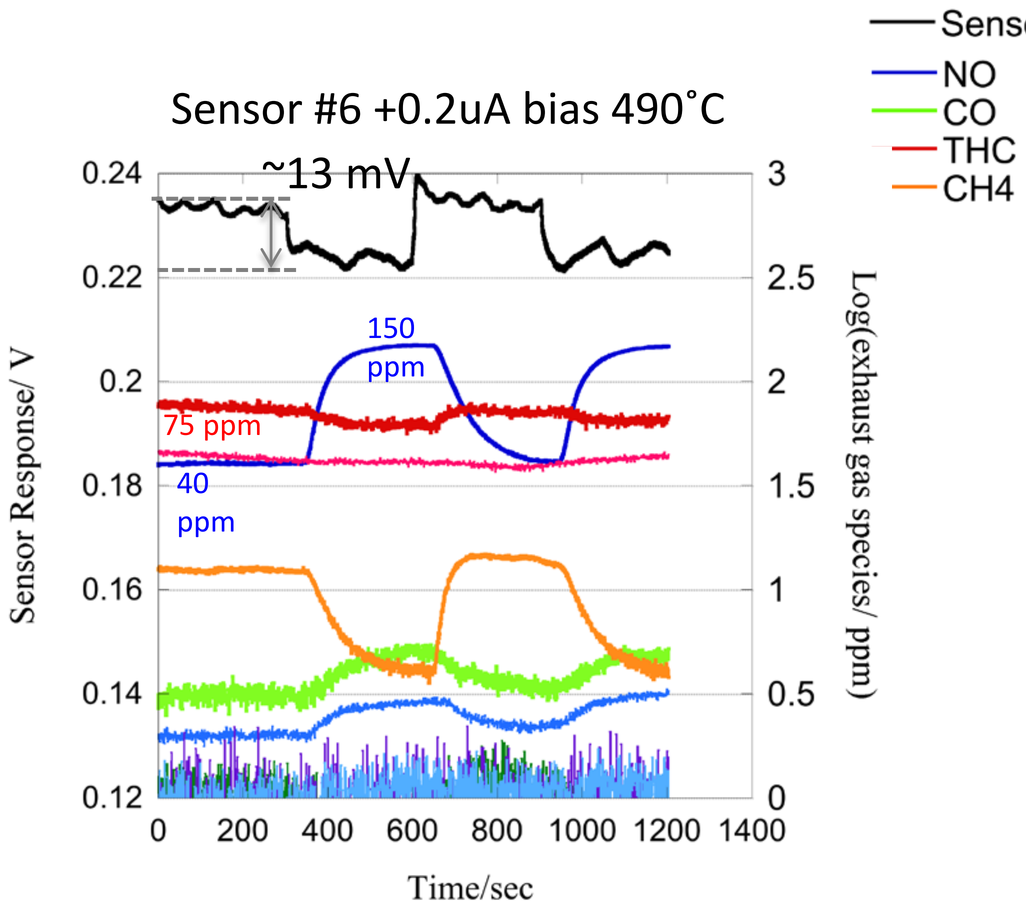


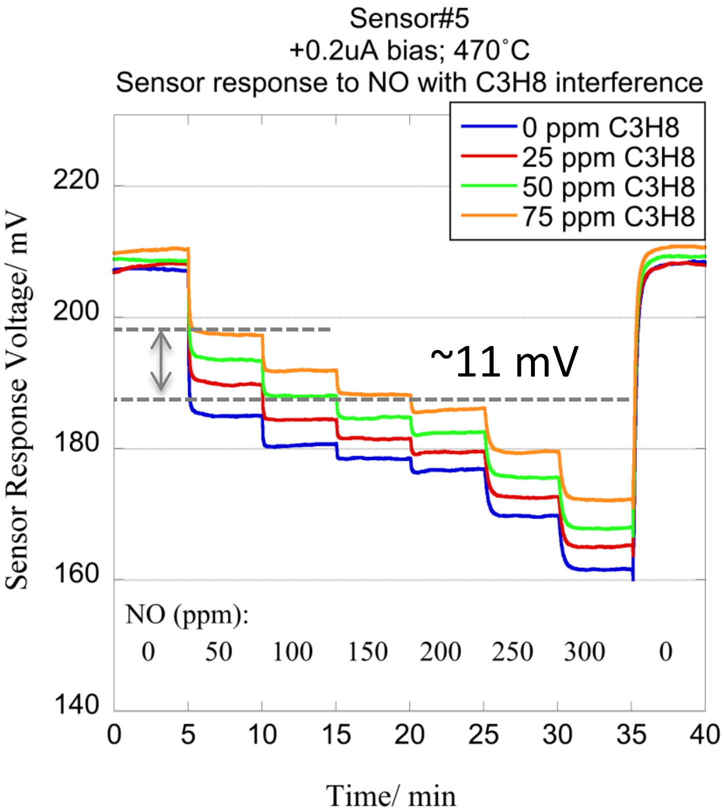
- Sensor calibration in the lab with test gases agrees with data obtained in realistic engine exhaust
- Need to obtain calibration from same sensor to quantify (in progress)

Technical Accomplishments

Quantitative agreement with FTIR response

Test#2: 2000rpm- cycle EGR on/off



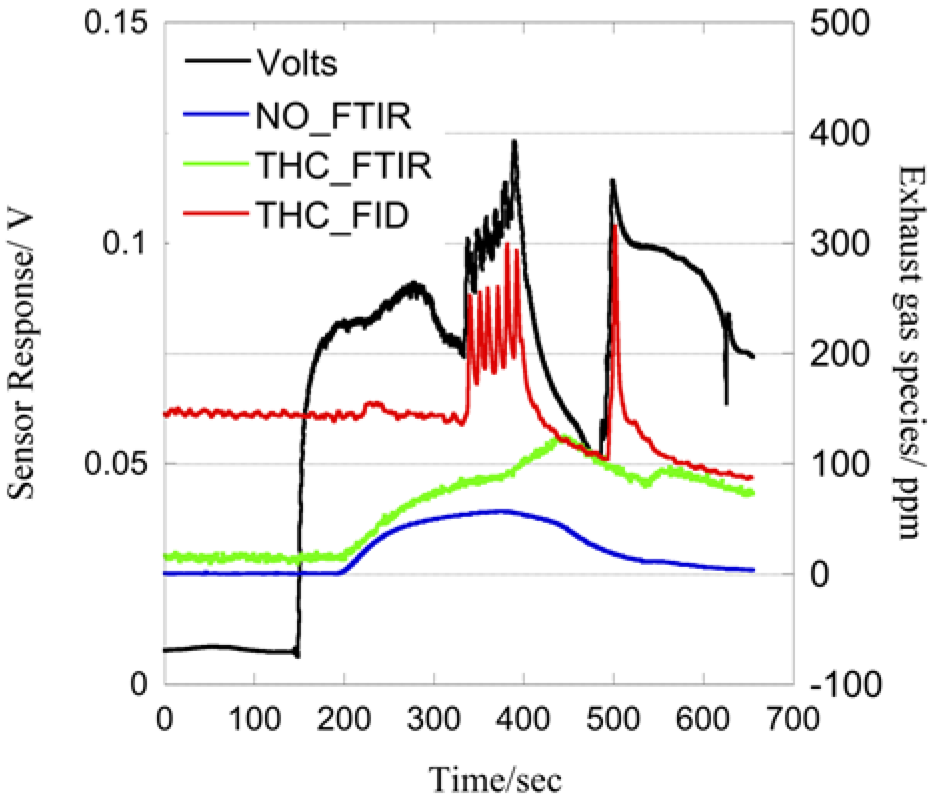


- Sensor tracks NO under realistic conditions with varying temperature, oxygen, humidity, carbon dioxide, carbon monoxide and hydrocarbon concentration

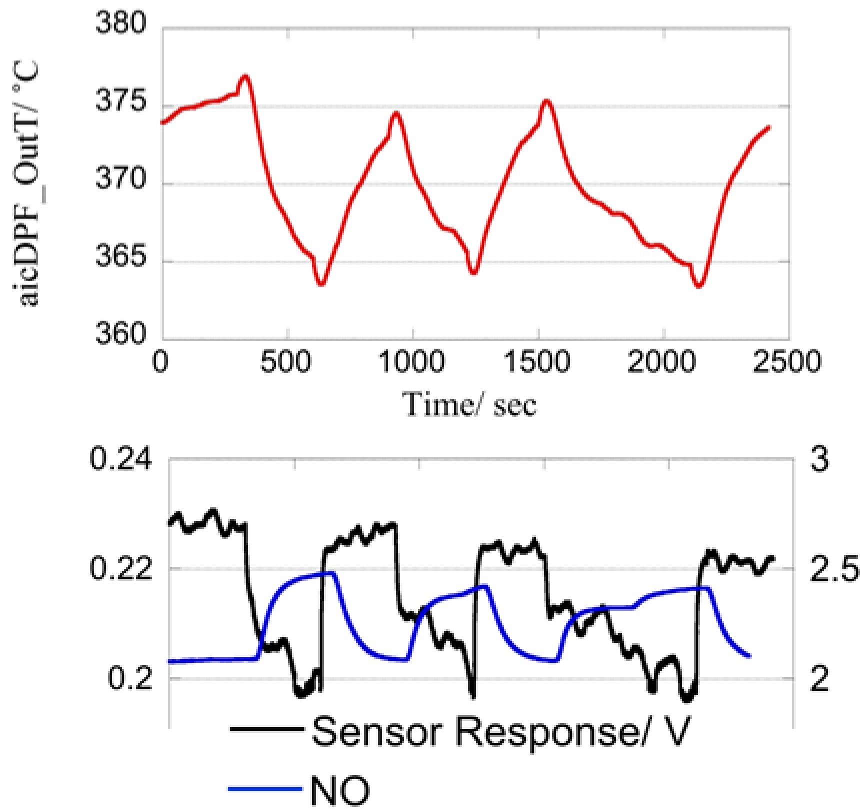
Sensor response time

Technical Accomplishments

Test #4: Sensor in HC sensing mode
PCCI test with rapid fluctuations in HC (due to low fuel)



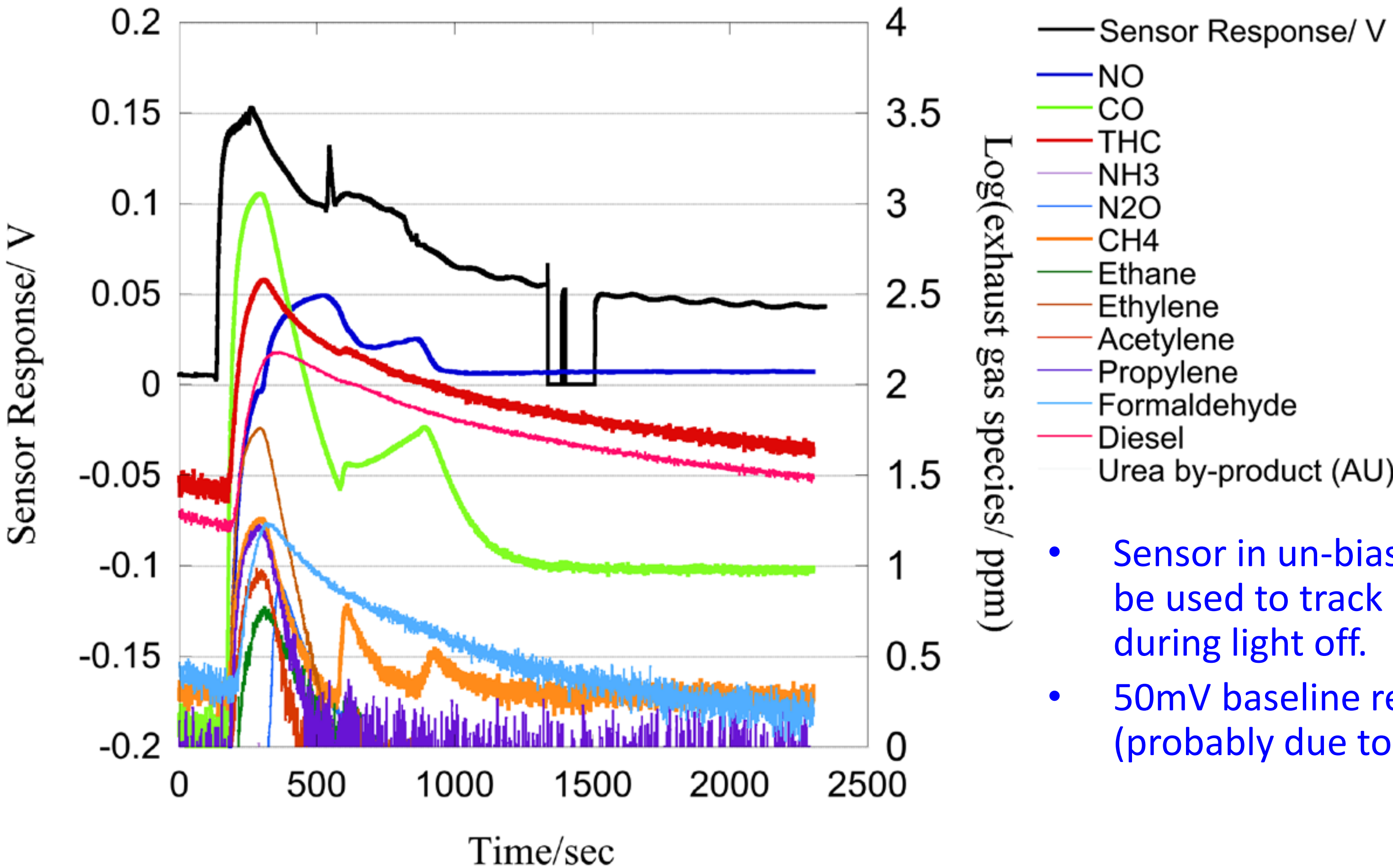
Test #1: Sensor in NO_x sensing mode
Hold engine load constant at 1600rpm- cycle EGR on/off



- Sensor tracks FID in HC mode. FTIR response is dampened probably due to position of FTIR after flow restrictor
- Noise in sensor data (compared to FTIR) is probably real variations. There is fluctuation in engine out exhaust temperature corresponding to sensor fluctuations

Hydrocarbon Response

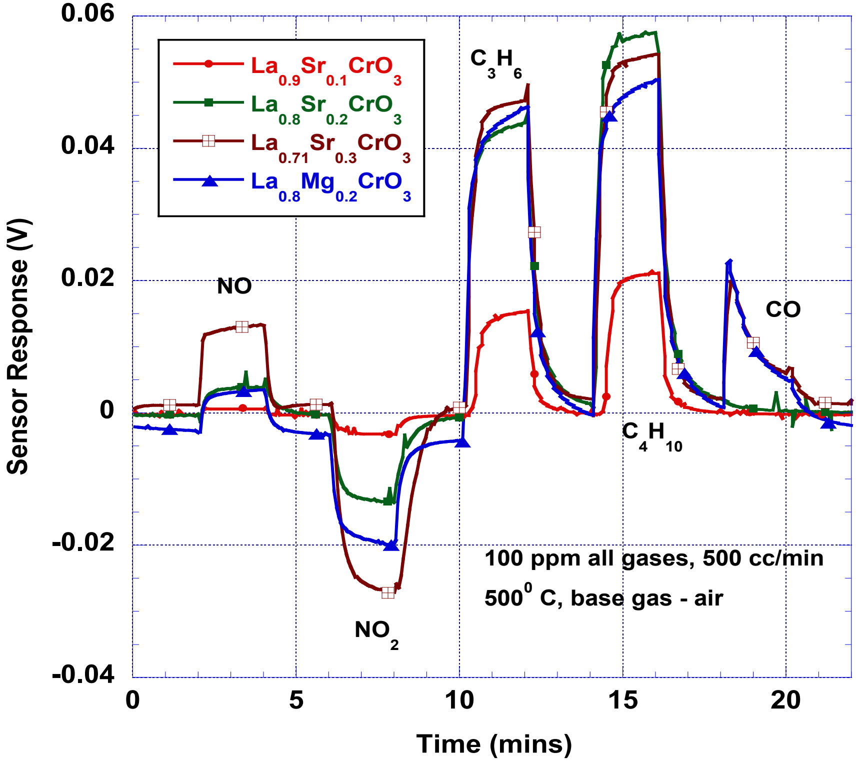
Test #3: Sensor in HC sensing mode (un biased)
Engine Start-up: Measure HC output while DOC and DPF warm to operating temp

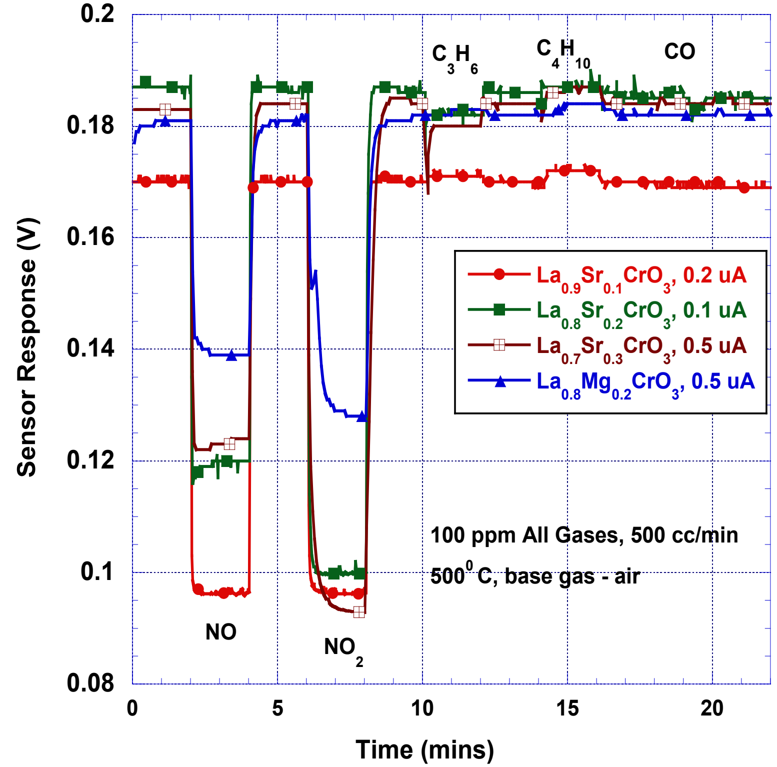


- Sensor in un-biased mode can be used to track hydrocarbons during light off.
- 50mV baseline response (probably due to interferents)

→ Need to eliminate NO interference when in HC sensing mode and need to optimize NO response when in biased mode

Optimizing sensor response





- Optimize electrode composition for next round of testing
- Several hardware improvements from lessons learnt during 1st visit to NTRC

P.K. Sekhar, M. Rangachary, E. Brosha, F. Garzon, Effect of Perovskite Electrode Composition on Mixed Potential Sensor Response, Sensors and Actuators B: Chemical (2013), In print
http://dx.doi.org/10.1016/j.snb.2013.03.110

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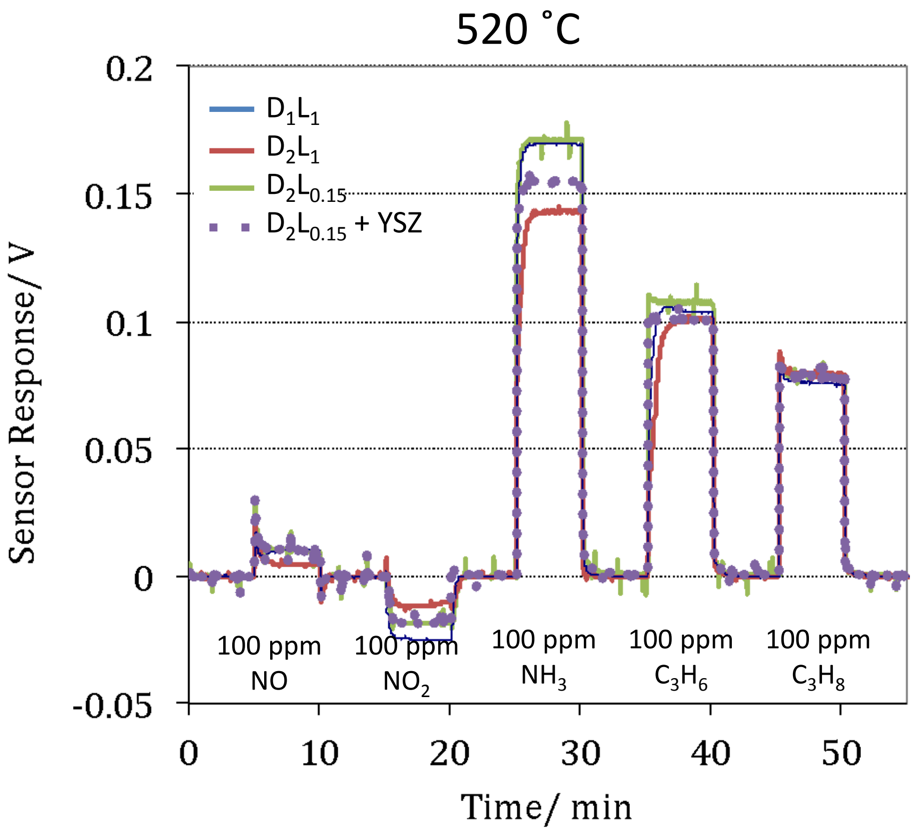
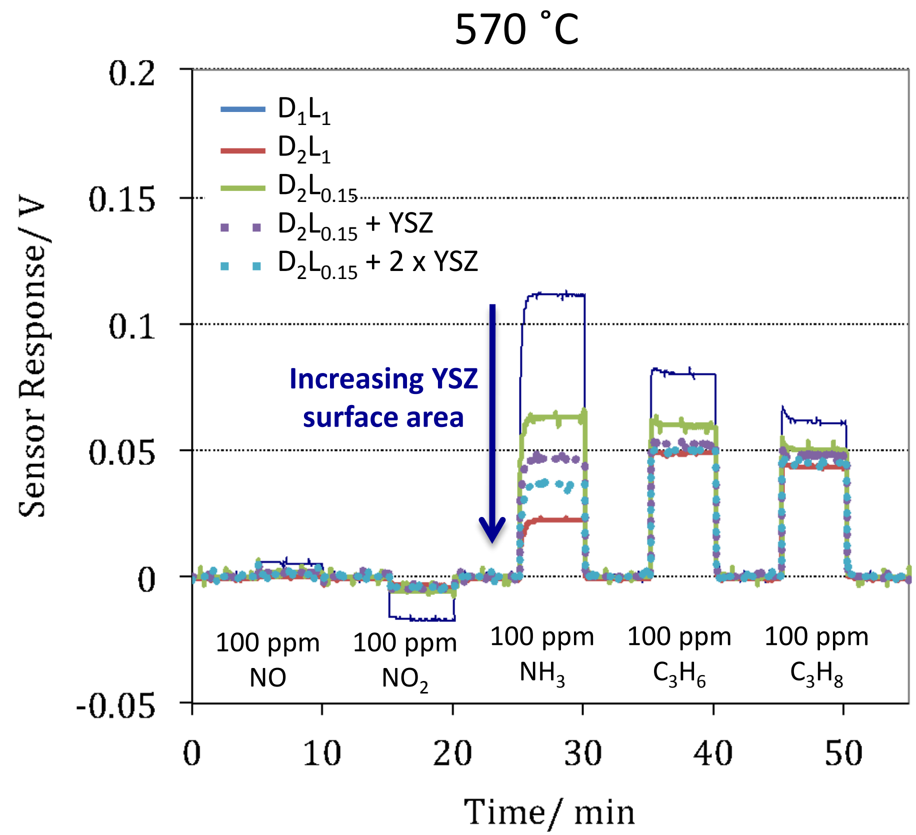
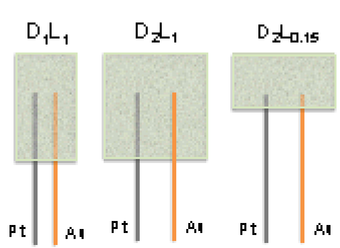
NH_3 sensor

Technical Accomplishments







- 2 pathways identified for NH_3 sensor manufacture

Collaboration / Future work

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

ESL ElectroScience

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

Custom Sensor Solutions, Inc. ...since 1997

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

Oak Ridge National Laboratory

National Transportation Research Center
Sensor test site.
Vitaly Y. Prikhodko, Josh A. Pihl, and James E. Parks II
No Cost Partner
Directly funded by VT

EmiSense smart sensors – clean emissions

Exploring potential commercialization partner.
IP needs to be negotiated.
Talks with Caterpillar were not successful.

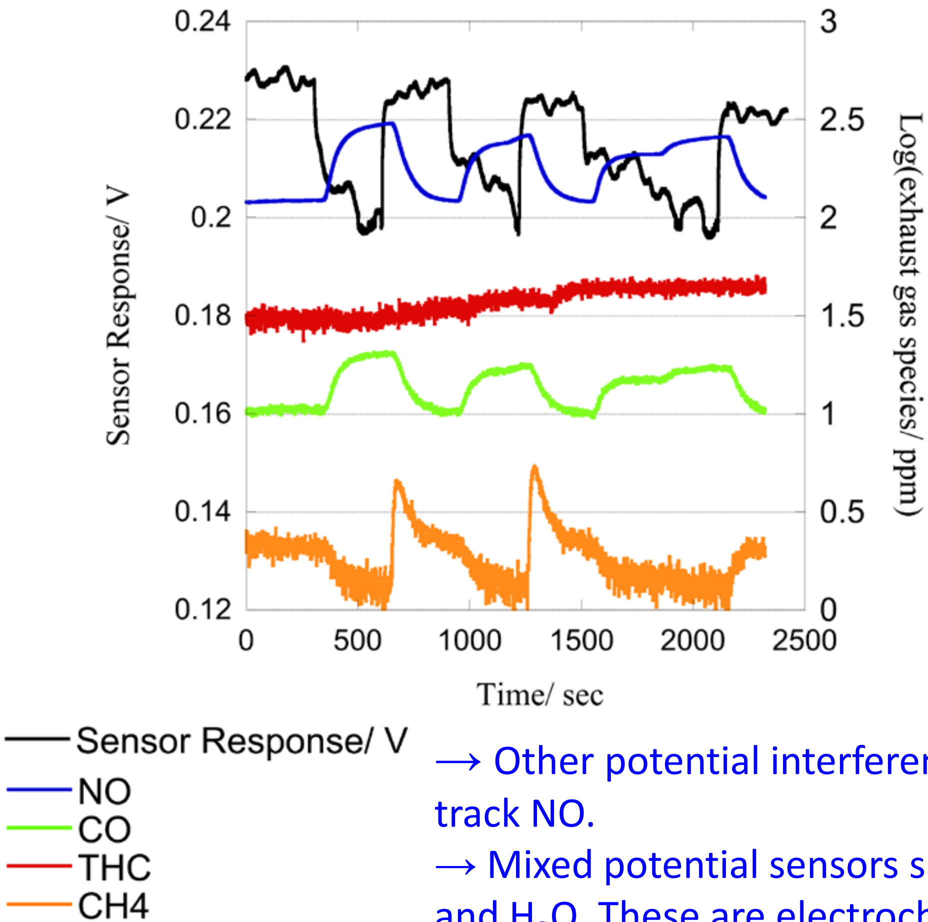
Summary

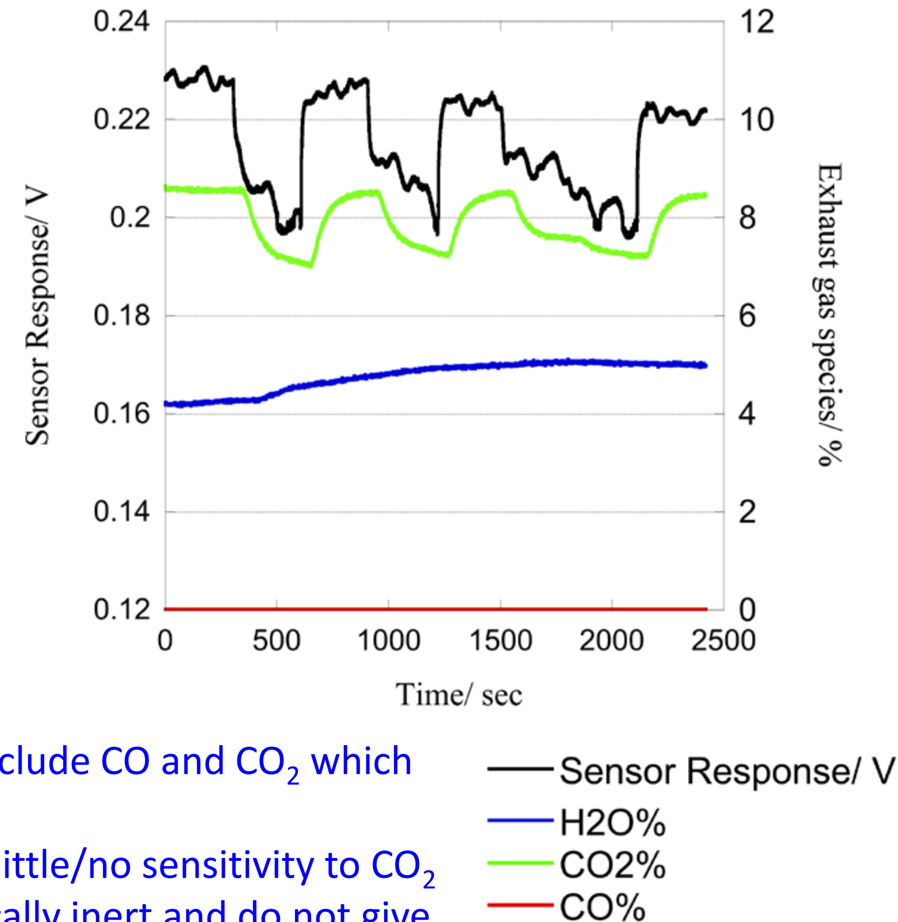
- Unique LANL mixed potential NO_x sensor has been adapted to a low cost commercially manufacturable high temperature cofired ceramics (HTCC) technology.
- Sensors exhibit good stability and sensor to sensor reproducibility
  - Temperature control critical
- Incorporated temperature feedback control in NO_x sensors
- First round of testing under realistic conditions completed at ORNL-NTRC (directly funded by VT)
  - Promising initial results
- NH_3 sensor development underway. ESL will provide the first batch of sensors to LANL before July of 2013
- Improvements in hardware/sensor design identified. Next round of testing with improvements to be performed at ORNL-NTRC in August of 2013. NH_3 testing will also be performed at that time.

Technical Back-Up Slides

Interferents

Test #1: Sensor in NO_x sensing mode
Hold engine load constant at 1600rpm- cycle EGR on/off





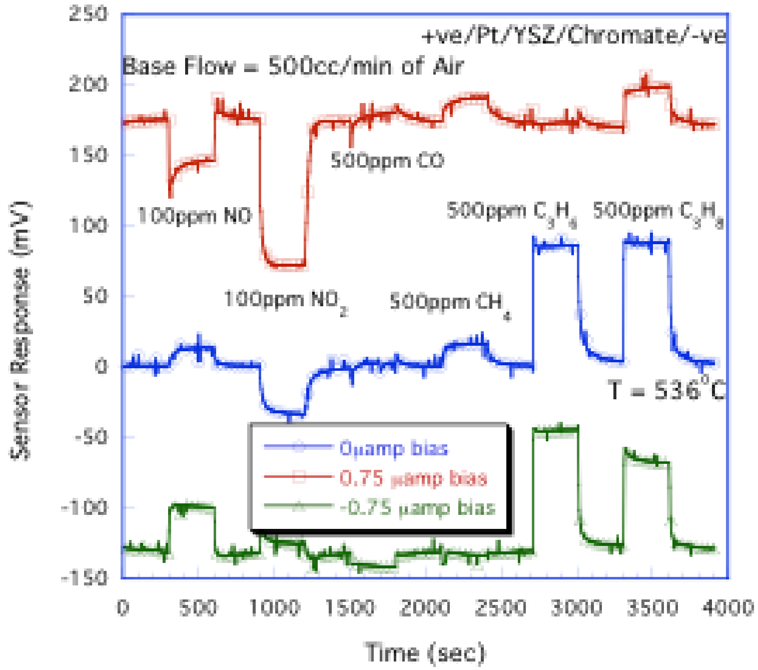
→ Other potential interferents include CO and CO_2 which track NO.

→ Mixed potential sensors show little/no sensitivity to CO_2 and H_2O. These are electrochemically inert and do not give rise to mixed potentials.

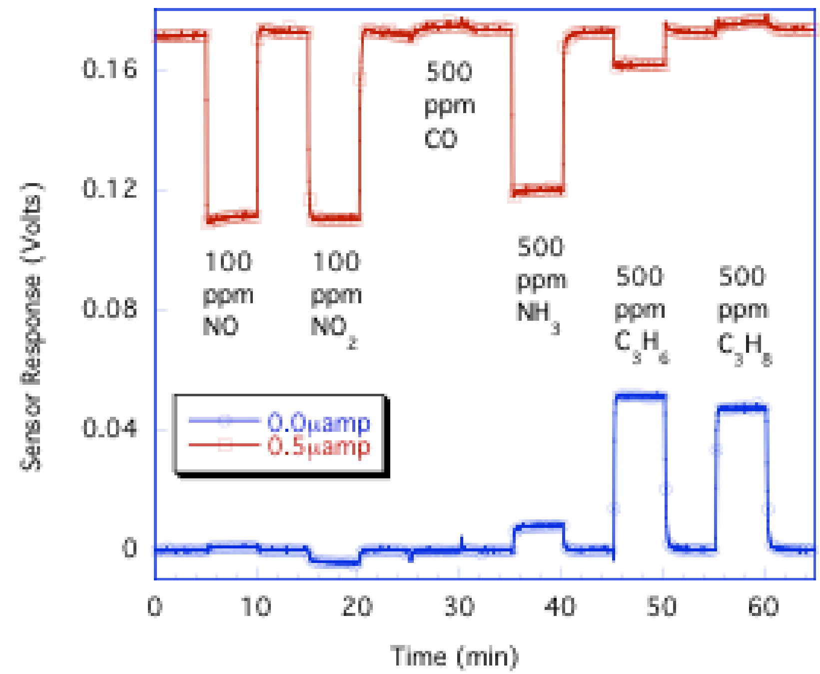
→ These sensors also insensitive to CO (see next slide)

Negligible CO response

LANL NO_x sensor operated at different bias currents (bulk sensor)



Optimized LANL NO_x and HC sensor (bulk sensors)



- LANL mixed potential NO_x and HC sensors are insensitive to CO.
- CO is easily electrochemically oxidized and the two electrodes used in these sensors (Pt and Lanthanum chromite) exhibit little response to CO.

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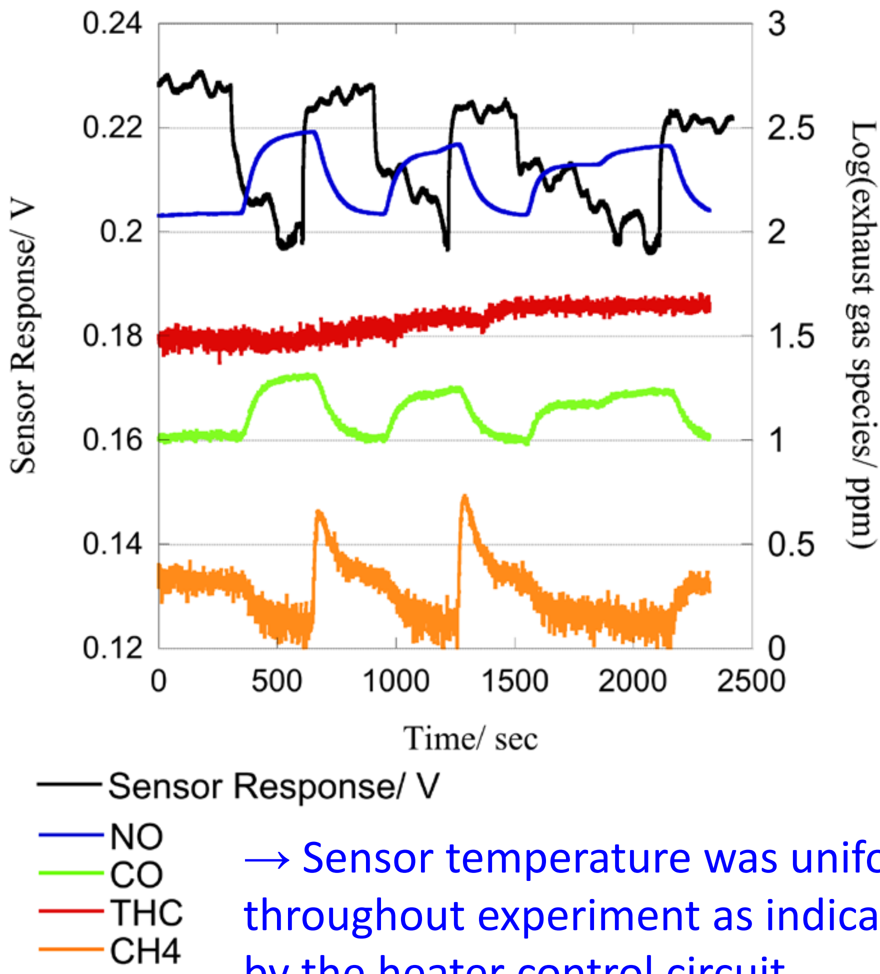
Variables during Engine testing : Temperature

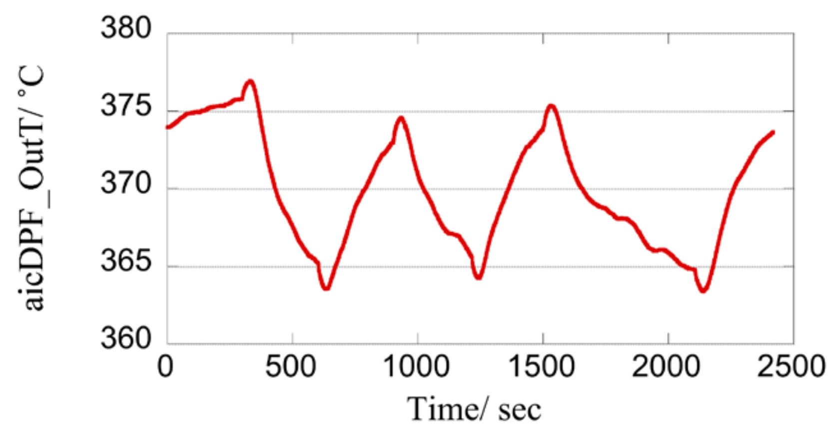
Test #1: Sensor in NOx sensing mode
Hold engine load constant at 1600rpm- cycle EGR on/off



→ Sensor temperature was uniform throughout experiment as indicated by the heater control circuit

Effect of engine variables on sensor response:

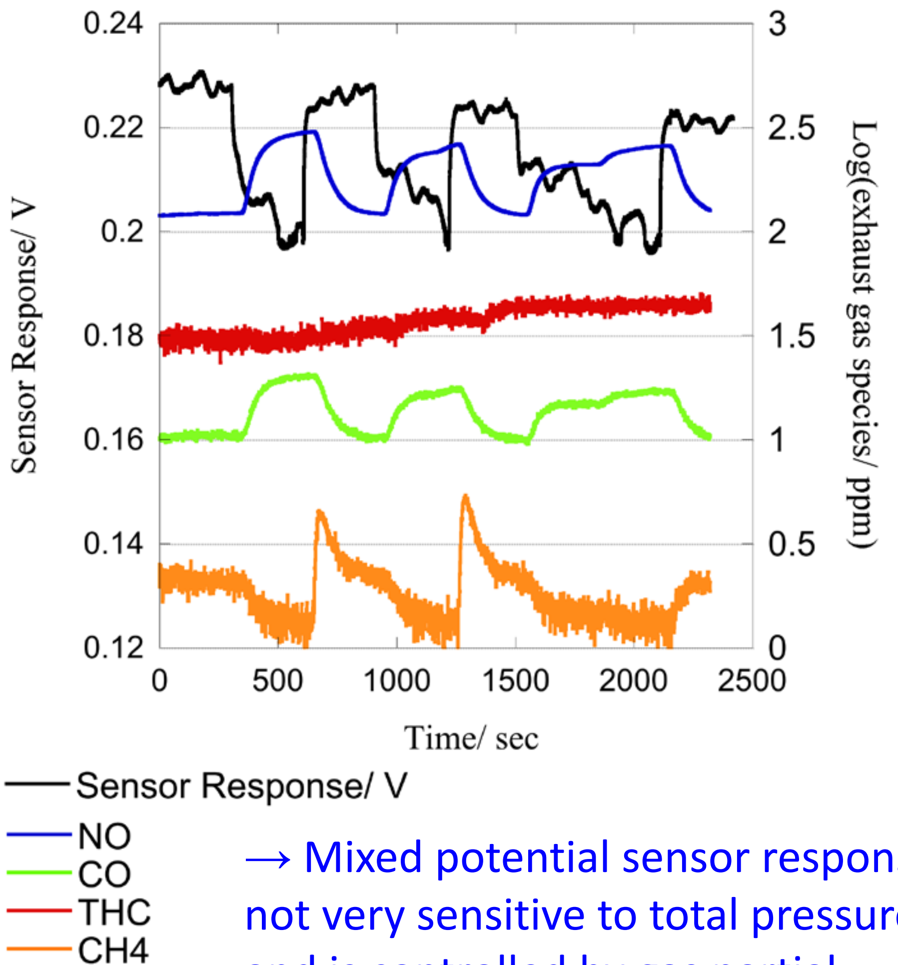
1. Temperature



If gas flow temperature influenced sensor response, then decrease in temperature would correspond to positive shift in sensor response voltage.

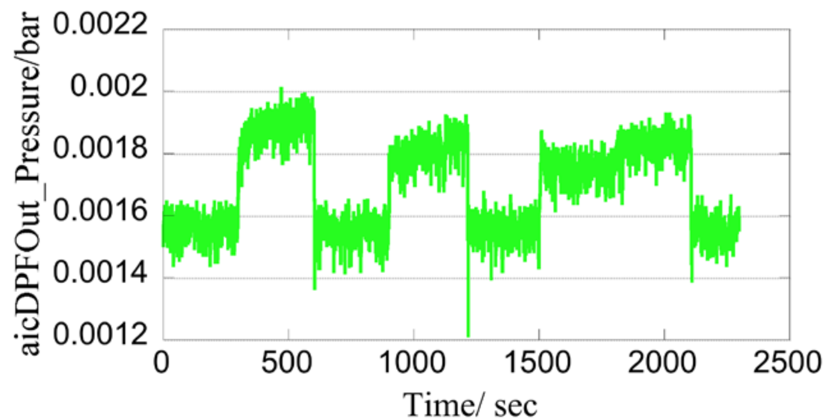
Variables during Engine testing : Pressure

Test #1: Sensor in NOx sensing mode
Hold engine load constant at 1600rpm- cycle EGR on/off



Effect of engine variables on sensor response:

2. Pressure

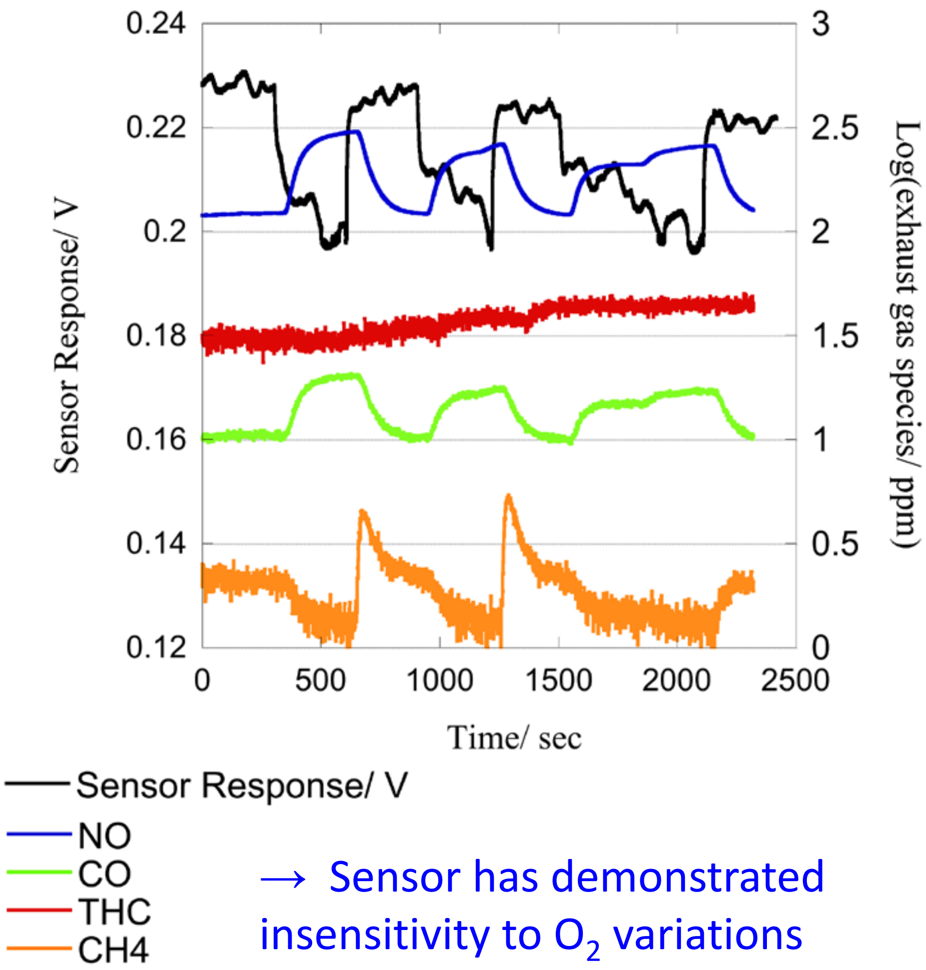


→ Mixed potential sensor response is not very sensitive to total pressure and is controlled by gas partial pressures.

Effects of pressure not fully characterized. However, observed ΔP very small relative to atmospheric.

Variables during Engine testing : P_{O2}

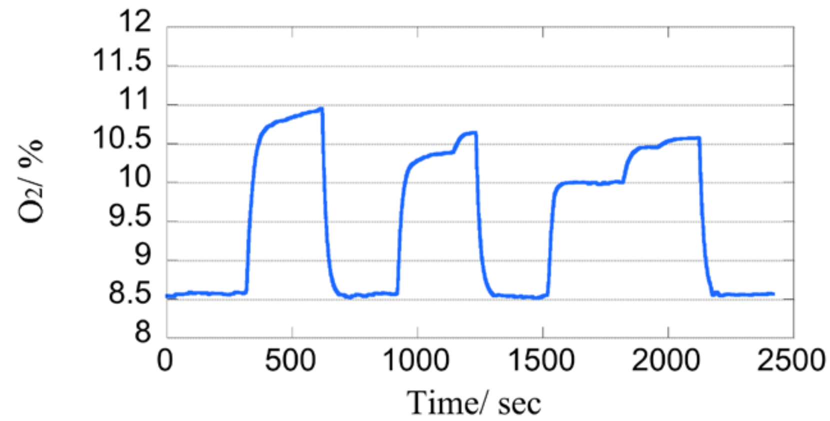
Test #1: Sensor in NOx sensing mode
Hold engine load constant at 1600rpm- cycle EGR on/off



→ Sensor has demonstrated insensitivity to O_2 variations between 8-12%.

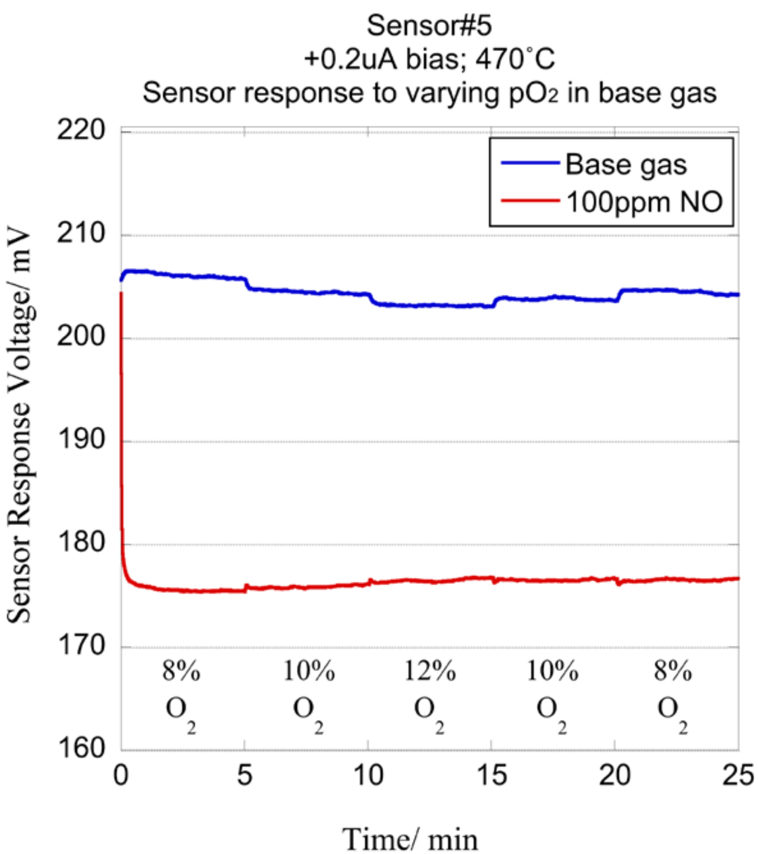
Effect of engine variables on sensor response:

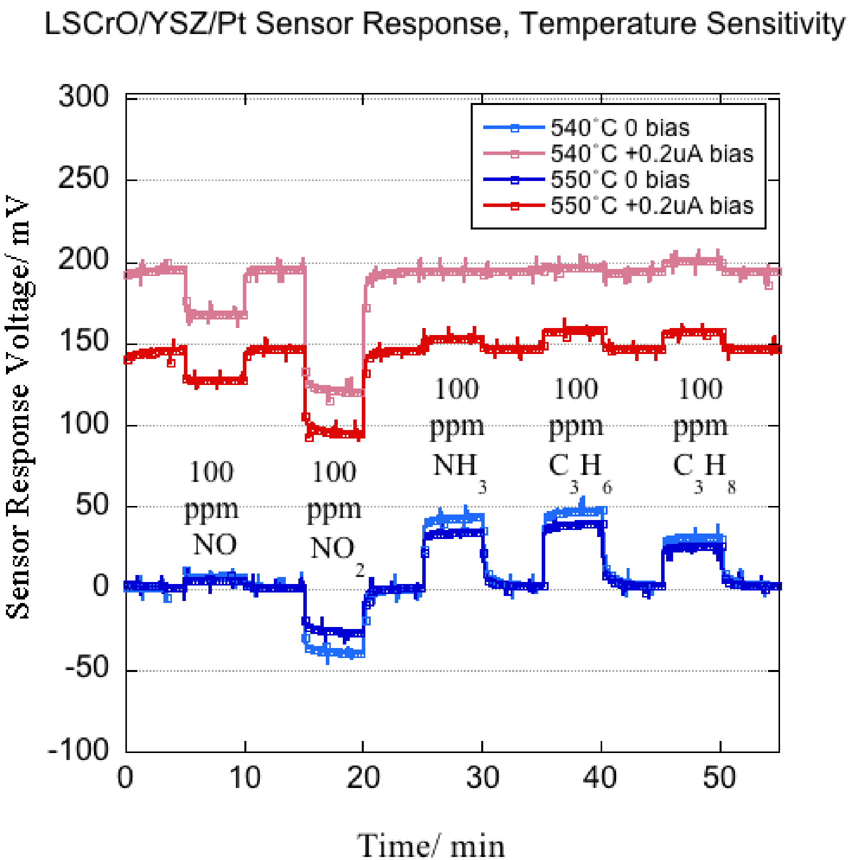
3. Change in O_2 content



Additionally, for a wider range of O_2 variation, increasing pO_2 decreases sensor impedance, thus also reducing voltage response to a given current bias (+0.2 μA).

Sensor Response to P_{O2} and T





→ Sensor insensitive to PO2 in the range 8 – 12%

→ Temperature should be controlled accurately for good reproducibility and sensitivity since temperature not only affects response but also baseline voltages