NO_x sensor development

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Overview

- **Timeline**
  - Start: FY 2002
  - Finish: FY 2012
  - 80% Complete
- **Budget**
  - Total project funding
    - DOE: $2792K
    - Ford (in kind): $1000K
  - Funding received in FY09: $360K
  - Funding for FY10: $500K
- **Barriers**
  - Technical gap in materials performance that limit expanded capabilities in advanced combustion engines: **need for emission control technology in light-duty diesel**
  - **Cost disadvantages of diesel emission control technology** hinder widespread adoption of better efficiency vehicles that work towards goal of petroleum reduction of 2.5 billion gallons per year by 2020
- **Partners**
  - Ford Motor Company: technical support and advanced testing facilities; leading effort to find commercialization entities

Relevance - If 33% of U.S. drivers switched to diesel, EPA estimated that oil consumption could be reduced by about 1.5 million barrels per day

- Overall objective: To develop low-cost, durable sensor technology for NO_x measurement and control to accelerate the introduction of clean, high-efficiency, light-duty diesel vehicles
  - Demonstrate sensor performance able to meet stringent California Air Resources Board (ARB) and U.S. EPA requirements
  - Build on robust solid-state electrochemical sensor platform, which is a proven technology for controlling emissions (i.e., oxygen sensor)
  - Characterize and understand sensing mechanisms in order to optimize materials composition/microstructure and sensor configuration/operation
  - Demonstrate suitable sensor platform for commercialization
  - Commercialization decision point for mass production in FY 2012

- Objectives for May 2009 to May 2010:
  - Develop sensor designs/materials to improve performance during thermal cycling and dynamometer testing – mechanical robustness for sensor packaging and engine vibrations
  - Determine and then mitigate major noise factors by developing strategies to reduce cross-sensitivity and estimate sensor accuracy

Relevance: Commercially available NO_x sensor technology does not meet the needs of the automotive industry

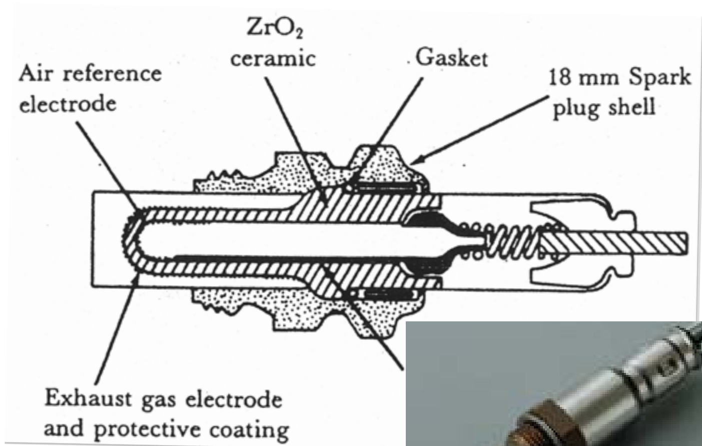
- Only one type of electrochemical NO_x sensor available on the market with little or no competition (based on 1992 Ford patent)
  - **<u>Expensive</u>** due to complicated multiple-chamber design and amperometric operation which requires complex electronics to measure nanoamp current
  - Stability and reliability may be problematic
  - Does not meet present or future diesel emission requirements

- Sensor technical performance to meet California (ARB) and EPA requirements presents **<u>significant development barriers</u>** for a low-cost durable NO_x sensor:

Sensitivity: < 5ppm	Stability to achieve ± 1 ppm accuracy
Durability: 10 years/150k miles	Low cross-sensitivity to O_2, H_2O, and CO
Response time: $\tau_{10\text{-}90\%} \leq 2$ seconds for 10 to 50 ppm	Operating temperatures from 150-650°C with potential excursions to 900°C

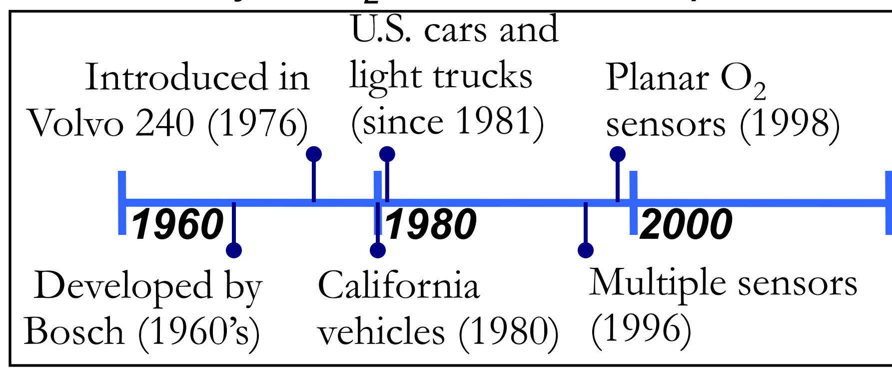
Relevance: Solid-state electrochemical sensors are a proven robust technology for measuring O_2 in exhaust to control emissions—NO_x sensors build upon this technology

- O_2 sensor development based on well-understood sensing mechanism (equilibrium concentration cell) with modest technical requirements: still required nearly 15 years development effort to commercialize with improvements still being made today



E.M. Logothetis in Chemical Sensor Technology, 3, Kodansha Ltd.: 1991, p. 89

History of O_2 sensor development



- In contrast, NO_x sensor development requires newer understanding of sensing mechanisms (non-equilibrium phenomena), with challenging requirements for sensitivity and accuracy
  - Developing new sensors is time-intensive and costly
  - Ultimate success relies on a sustained research and development effort for achieving commercialization decision point in FY 2012

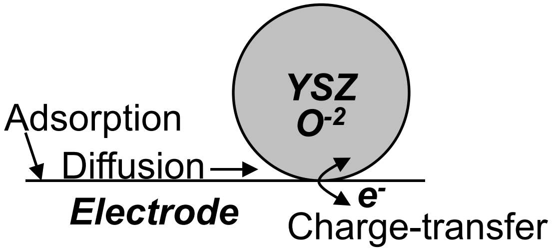
Major milestones for FY 2009 and 2010

- **<u>FY 2009</u>**
  - Receive initial feedback from potential commercialization entities, with Ford leading the discussions
  - Improve design and materials to address stability degradation due to thermal cycling
  - Complete longer-term tests for stability of FY08 prototypes and initiate testing with integrated (imbedded) heater substrates
  - Evaluate methods for compensating for cross-sensitivity
- **<u>FY 2010</u>**
  - Evaluate temperature, oxygen, and water cross-sensitivity on current materials
  - Perform engine dynamometer test of improved prototypes
  - Compile sensor performance data suitable for discussions with potential commercialization entities
  - Down-select for improved materials and design/platform for longer-term laboratory and vehicle/engine dynamometer testing
  - Refine sensing strategy and update electronics measurement system for on-vehicle operation (most recent system designed in FY07)
  - Continue discussions with potential commercialization entities

Approach: LLNL developed unique design and measurement strategy leverages proven robust solid-state electrochemical technology

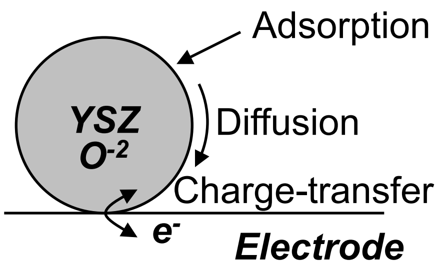
- Novel impedance-based sensing uses complex ac impedance (electrical response to low-amplitude alternating current signal) as opposed to dc (direct current) signals
- Advantages over conventional dc-based sensors: higher sensitivity (< 5 ppm NO_x), better stability (small ac signal possibly stabilizes interface), and less expensive and simpler device (suitable for commercialization and does not rely on exotic materials)
- Understanding sensing mechanisms is key to sensor development: parallel contributions of O_2 and NO_x reactions at porous YSZ/electrode interface

Low sensitivity



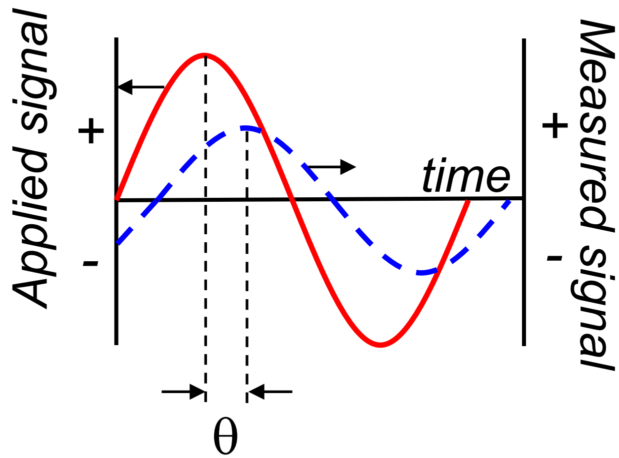
Minimal NO_x response when electrode surface dominates

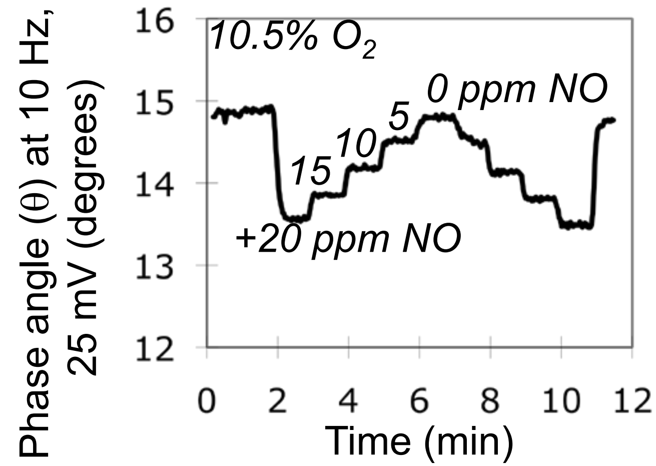
High sensitivity



Larger NO_x response: controlling microstructure and composition is essential

Approach: In our alternating current (ac) measurement strategy, the phase angle (θ) is correlated with the level of NO_x in the exhaust

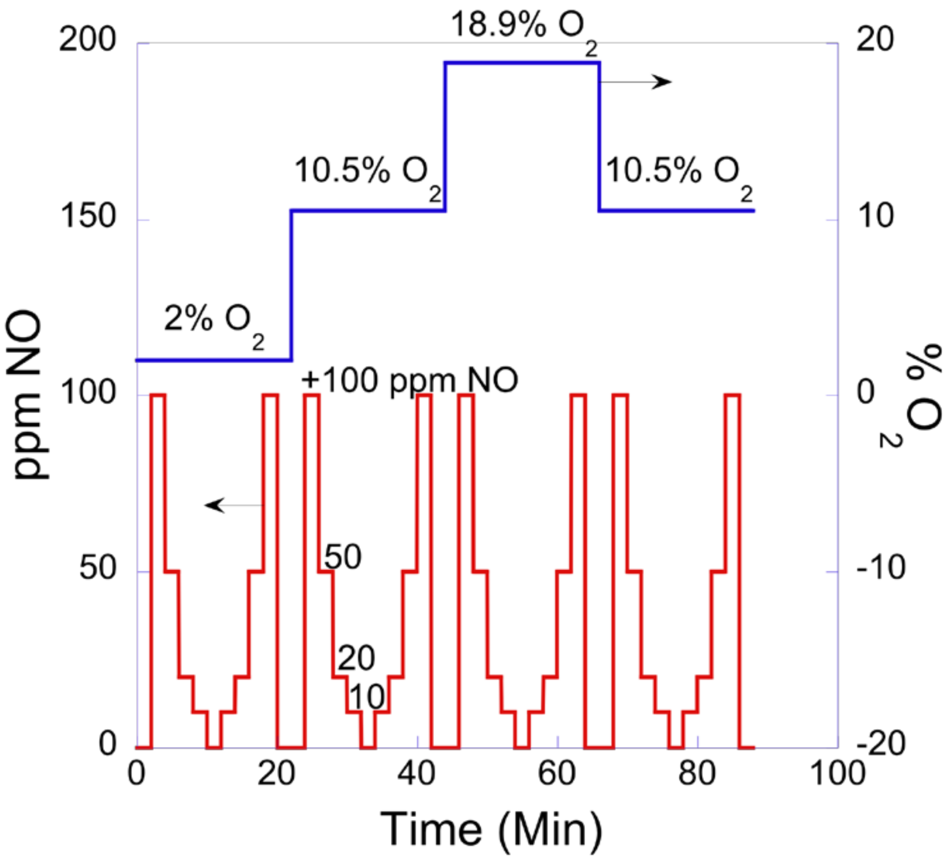




- Similar to electrical resistance, which measures the opposition to an electrical current, impedance measures the opposition to a time-varying current (i.e., alternating current, ac)
  - Impedance is a complex quantity with both magnitude and phase angle (θ) information
- For the electrochemical LLNL sensors, both magnitude and phase angle are affected by ppm changes in NO_x
  - Phase angle (θ) has better stability and sensitivity, and serves as a sensing signal at a predetermined frequency and excitation amplitude

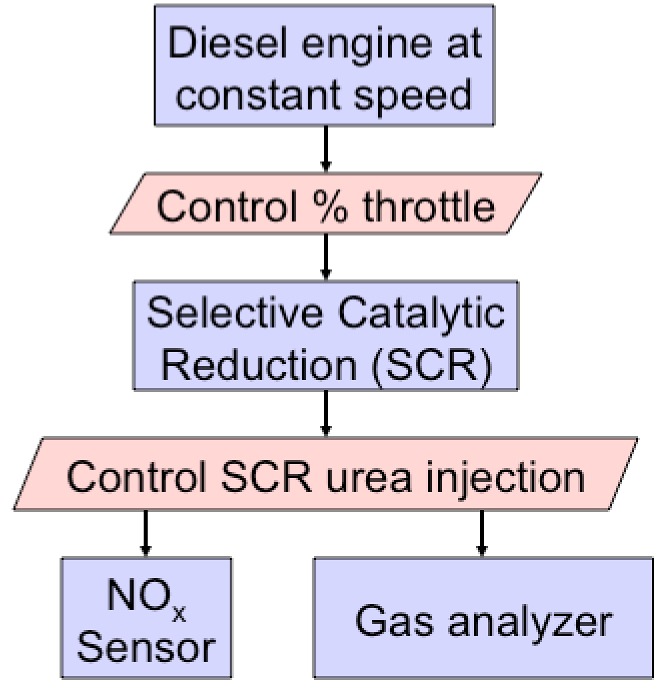
Approach: Systems approach combining controlled laboratory testing with vehicle/engine dynamometer analysis to develop commercializable technology

Laboratory



- Sensor response evaluated over a defined range of controlled gas concentrations

Dynamometer



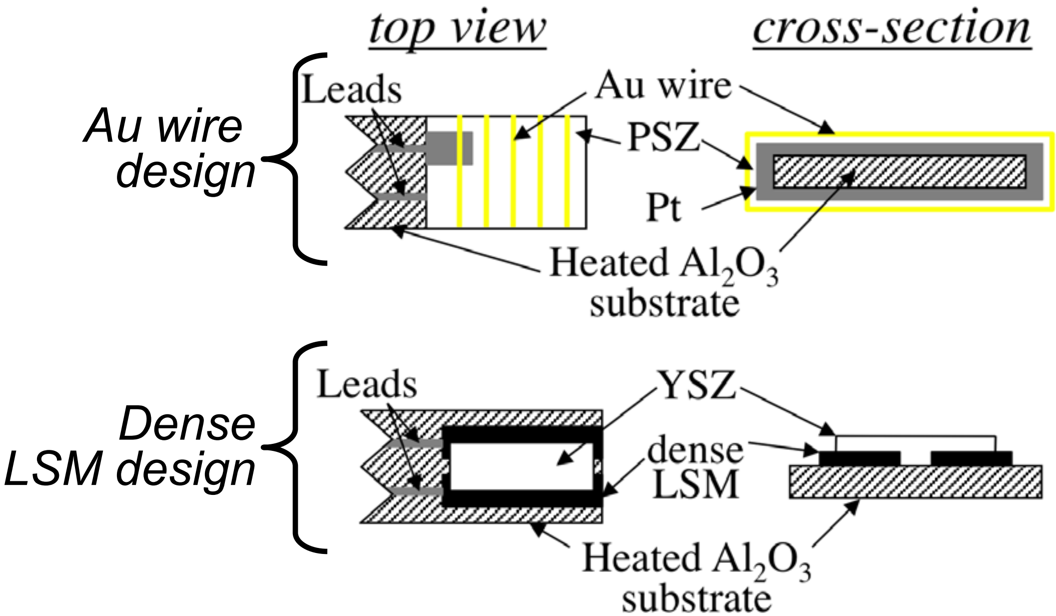
- Sensor response evaluated in real diesel exhaust: controlled engine parameters (e.g., throttle and urea injection) then influence resulting gas concentration, which is measured with a gas analyzer

Technical accomplishment: In May 09 review, demonstrated more advanced prototypes using suitable packaging for engine/vehicle testing as well as promising oxide material

More advanced packaging

- Built on an alumina (Al_2O_3) substrate, provided by Ford, with an integrated (imbedded) heating element
- Packaged into commercial sensor housing, provided by U.S. automotive supplier

Choice of materials influences design

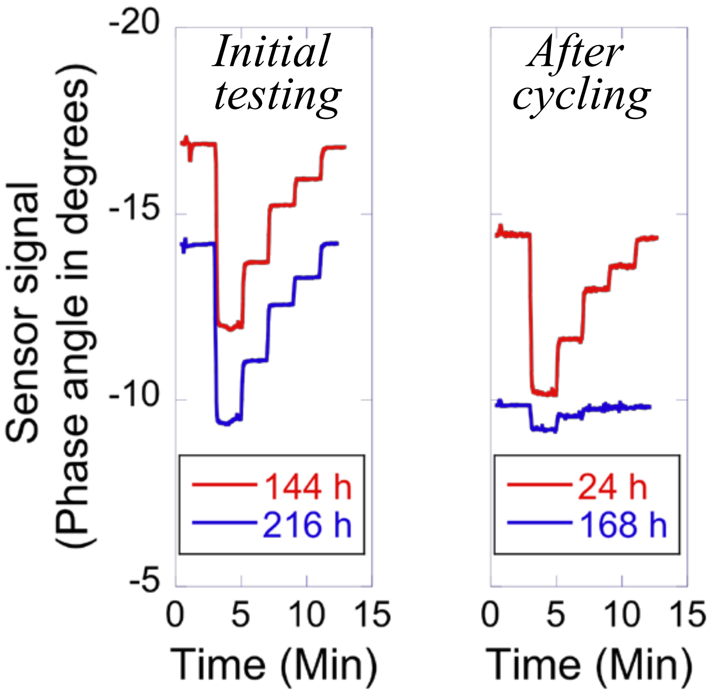


- (top) Au wire with yttria partially-stabilized zirconia (PSZ) for better mechanical properties
- (bottom) Dense LSM (Strontium-doped lanthanum manganite oxide) with yttria fully-stabilized zirconia (YSZ) for better electrical properties

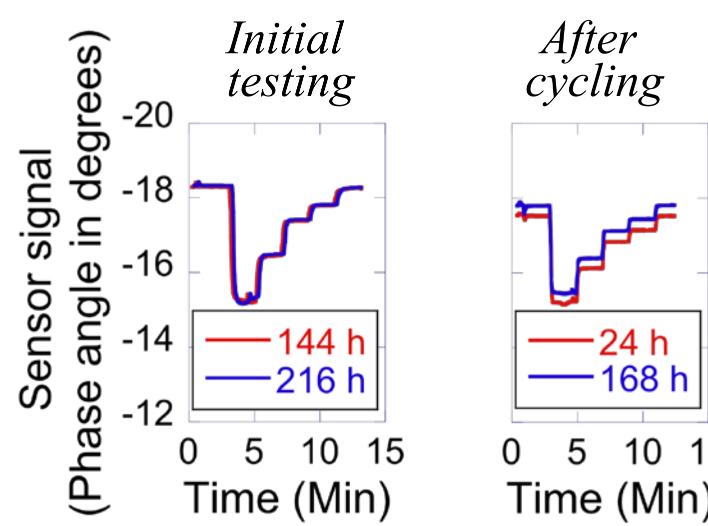
Technical accomplishment: Achieved milestone of developing materials that have improved performance with thermal cycling

Testing in 1000 sccm 2% O_2: stepping from 0-100-50-20-10-0 ppm NO

Au wire sensor prototype

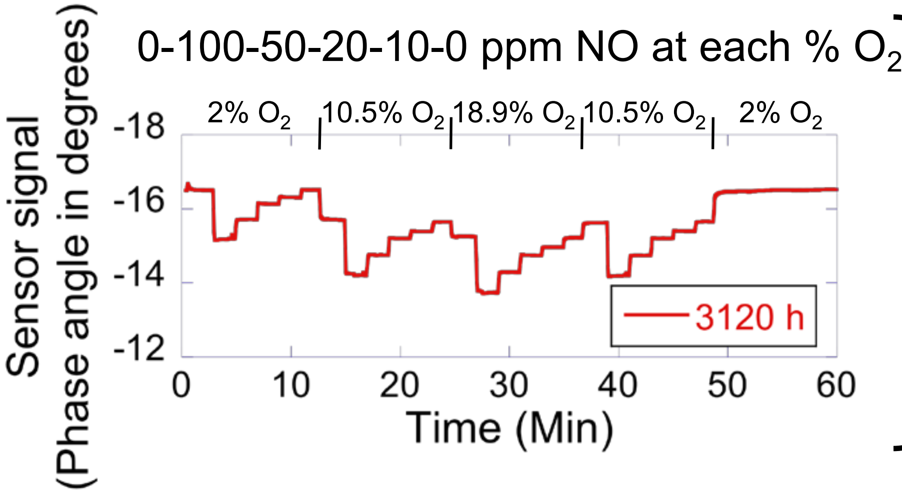


Dense LSM sensor prototype



- **Au wire:** Baseline change during initial testing with loss in NO_x sensitivity after cycling from operating (10.5 V on heater) to room temperature
- **Dense LSM:** Good baseline stability and NO_x sensitivity during initial testing and after cycling from operating (8.5 V on heater) to room temperature

Technical accomplishment: Achieved milestone of longer-term testing (over 3000 hrs) for more advanced prototypes incorporating integrated (imbedded) heater

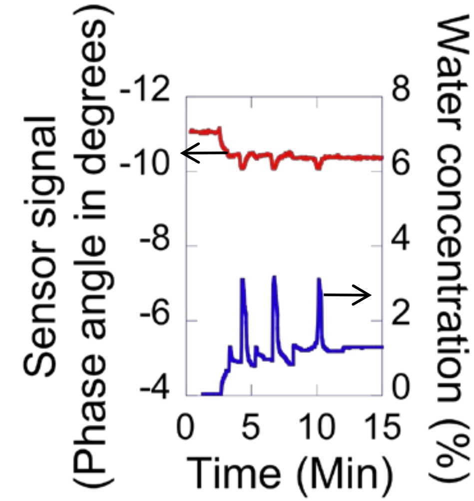


Dense LSM sensor prototype

- Good performance after testing for 3120 hours in various water, oxygen, and ppm NO levels (8.5 V on heater)

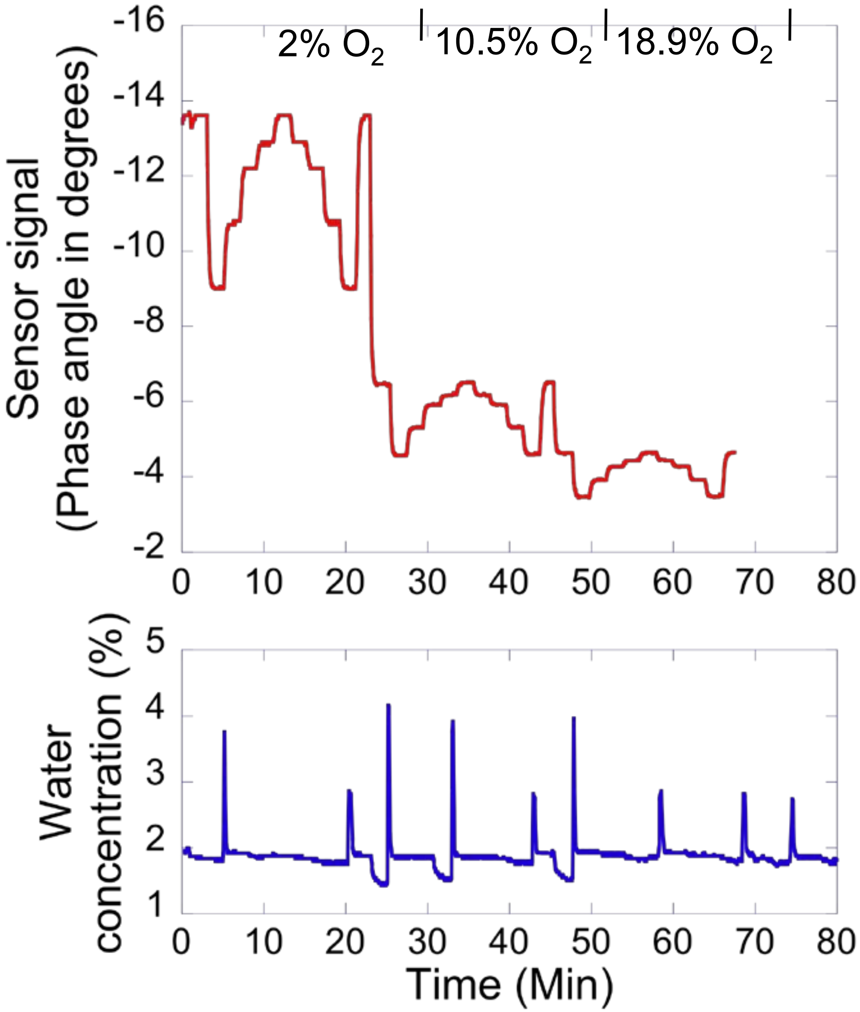
Controlled furnace test at 525°C in 2% O_2

- Instead of imbedded heater, used Al_2O_3 substrate with similar design as dense LSM sensor prototype
- Sensor signal (top red curve) and corresponding water concentration (bottom blue curve) indicated cross-sensitivity to water degrading accuracy
- Previous Ford studies on Au wire sensors indicated that optimizing temperature decreased water cross-sensitivity



Technical accomplishment: Achieved milestone to evaluate oxygen, water, and temperature cross-sensitivity in order to develop strategy to improve accuracy (Au wire)

0-100-50-20-10-0 ppm NO at each % O_2

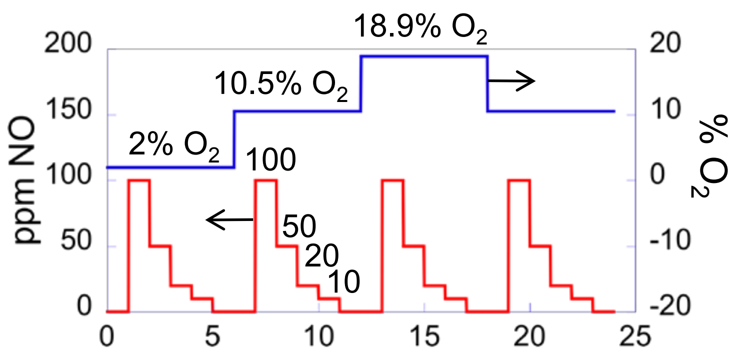


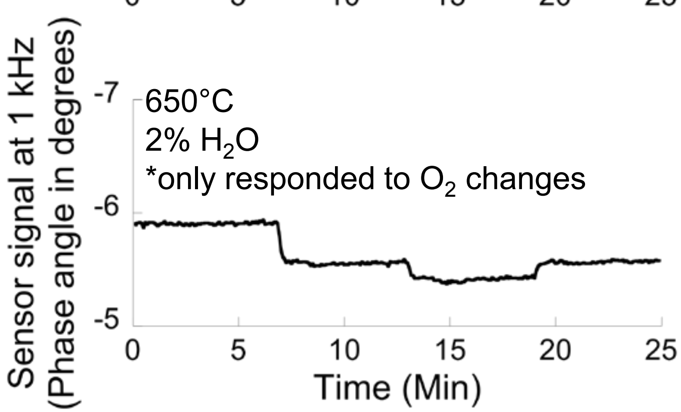
Au wire sensor prototype

- Initial dry testing for 720 hrs (stable and reproducible) then in ~2% H_2O for 96 hrs
- Followed by sensor evaluation:
  - Various % O_2 and ppm NO
  - H_2O: 2, 4, and 6%
  - Temperature: 625, 650, and 675°C
- Sensor signal (top red curve) and corresponding water concentration (bottom blue curve) indicated minimal H_2O cross-sensitivity
  - Water cross-sensitivity minimized for operation at 650°C

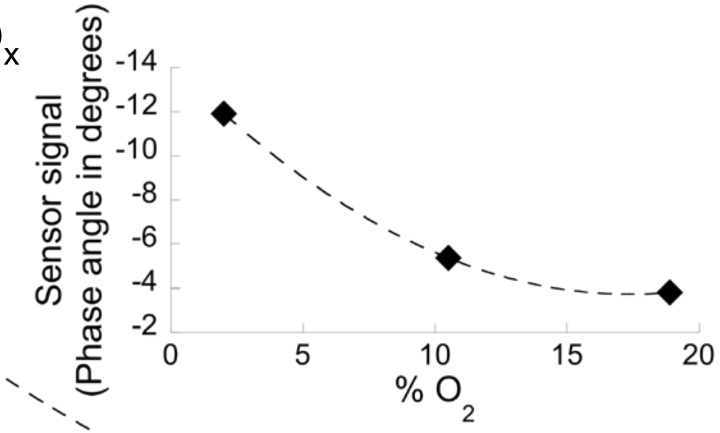
Technical accomplishment: Achieved milestone to develop strategy for reducing cross-sensitivity to oxygen, water, and temperature (Au wire)

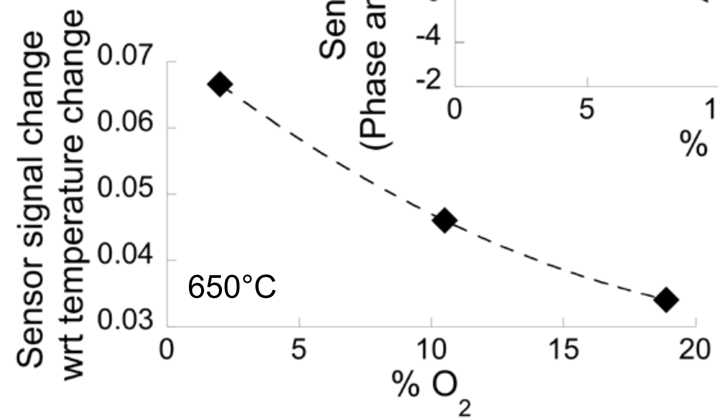
1. Measure temperature (±1°C) and O_2 (±4%): Method for measuring O_2 with higher frequency (1 kHz) signal



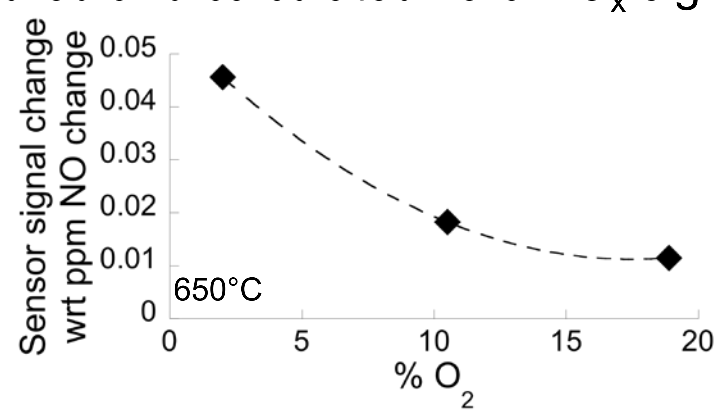


2. Calculate zero NO_x signal using measured O_2 and temperature



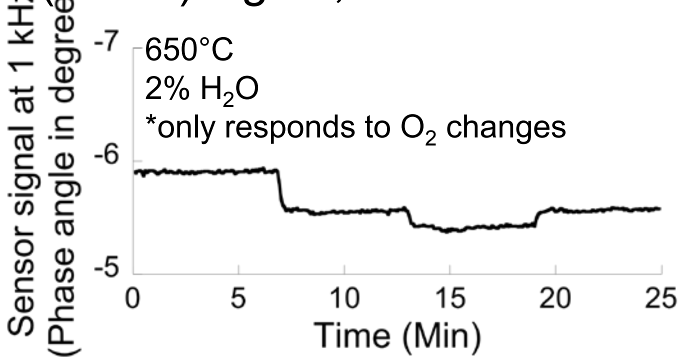


3. Calculate ppm NO using difference between measured and calculated zero NO_x signal

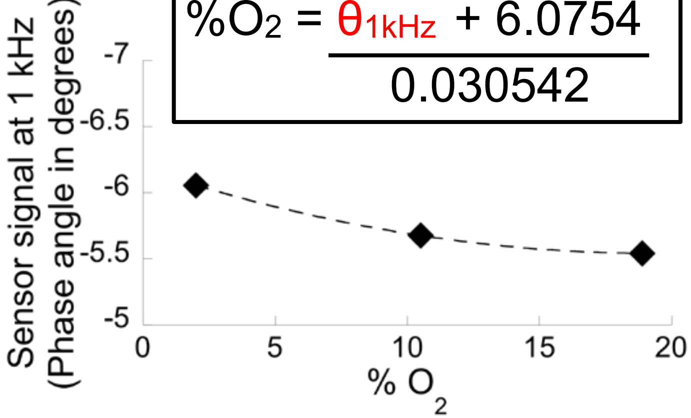


Technical accomplishment: Achieved milestone to evaluate strategy for reducing cross-sensitivity with numerical algorithm (Au wire)

1. Measure temperature, T_{meas}, (±1°C) and O_2 (±4%): Method for measuring O_2 with higher frequency (1 kHz) signal, θ_{1kHz}



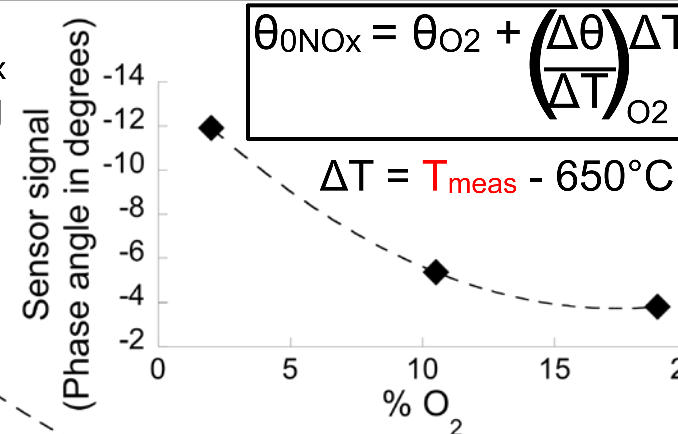
$$\%O_2 = \frac{\theta_{1kHz} + 6.0754}{0.030542}$$



2. Calculate zero NO_x signal (θ_{0NOx}) using measured O_2 and temperature

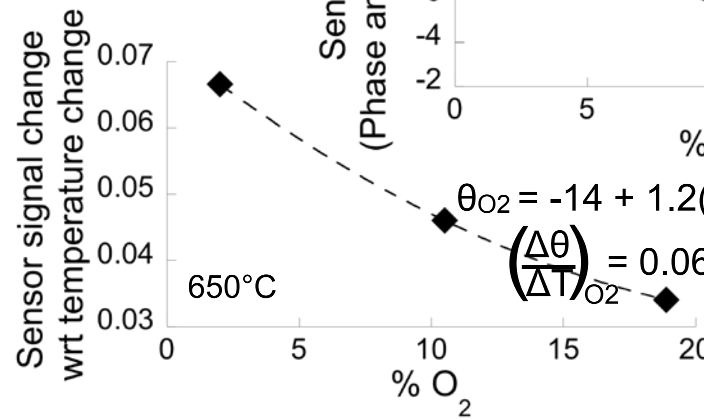
$$\theta_{0NOx} = \theta_{O2} + \left(\frac{\Delta\theta}{\Delta T}\right)_{O2}\Delta T$$

$$\Delta T = T_{meas} - 650°C$$



$$\theta_{O2} = -14 + 1.2(\%O_2) - 0.035(\%O_2)^2$$

$$\left(\frac{\Delta\theta}{\Delta T}\right)_{O2} = 0.069 - 0.0019(\%O_2)$$

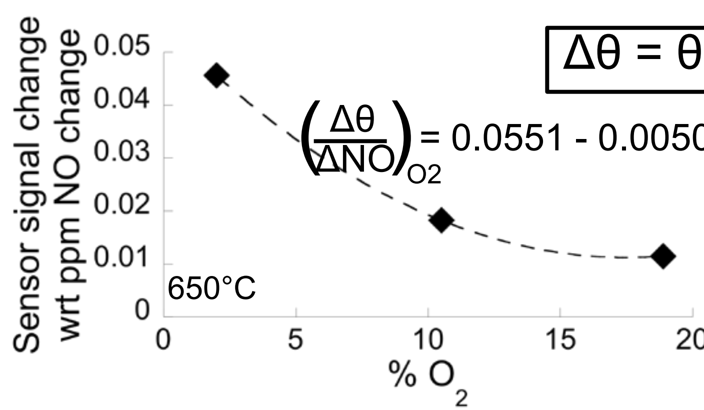


3. Calculate ppm NO using difference between measured and calculated zero NO_x signal

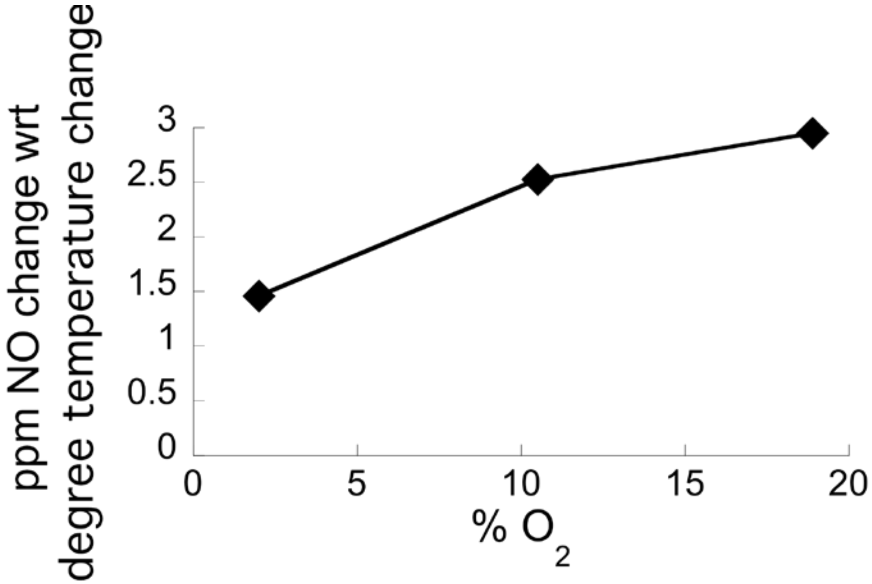
$$\Delta\theta = \theta_{0NOx} - \theta_{meas}$$

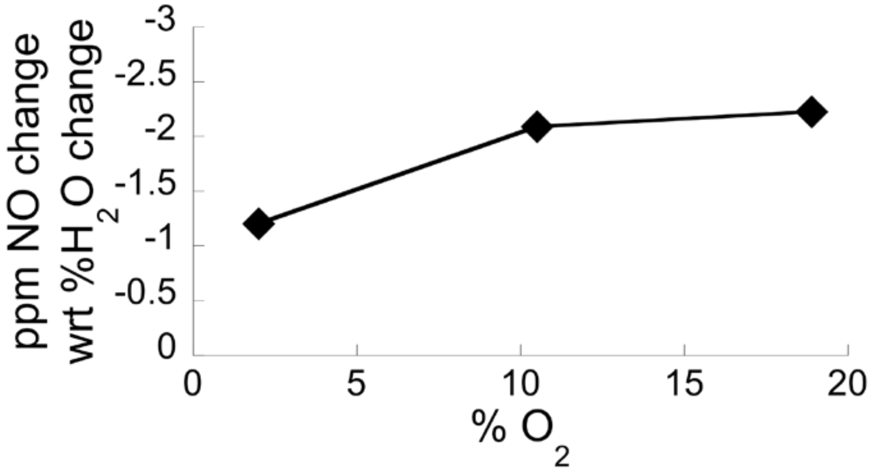
$$\left(\frac{\Delta\theta}{\Delta NO}\right)_{O2} = 0.0551 - 0.00501(\%O_2) + 0.000143(\%O_2)^2$$

$$\Delta NO = \frac{\Delta\theta}{\left(\frac{\Delta\theta}{\Delta NO}\right)_{O2}}$$



Technical accomplishment: Achieved milestone to assess sensor accuracy by determining noise introduced by fluctuations in temperature and water (Au wire)



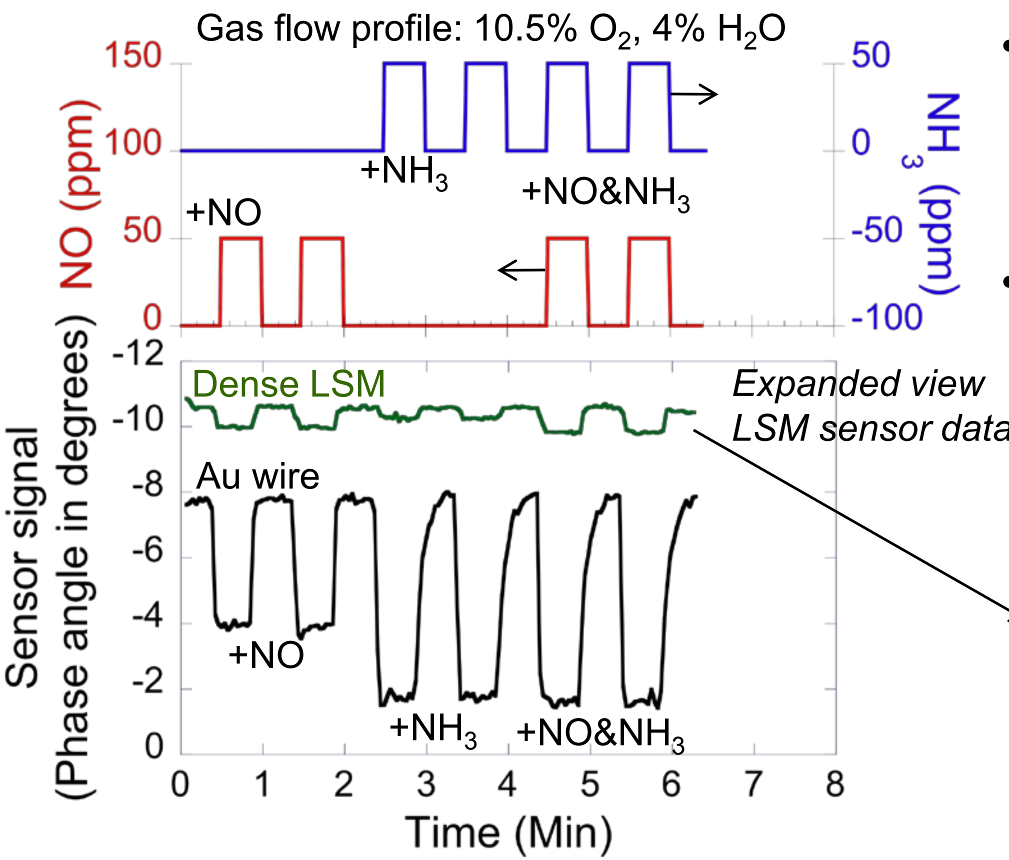


- To assess sensor accuracy, related how the signal changes with respect to (wrt) interferences (i.e., water and temperature) and the corresponding values of how the signal changes wrt ppm NO concentration
- For ± 1% H_2O, the corresponding change in ppm NO varies with oxygen
  - Minimum interference occurs at 2% O_2: ~ 1.2 ppm NO
- For ± 1°C temperature, the corresponding change in NO varies with oxygen
  - Minimum interference occurs at 2% O_2: ~ 1.5 ppm NO

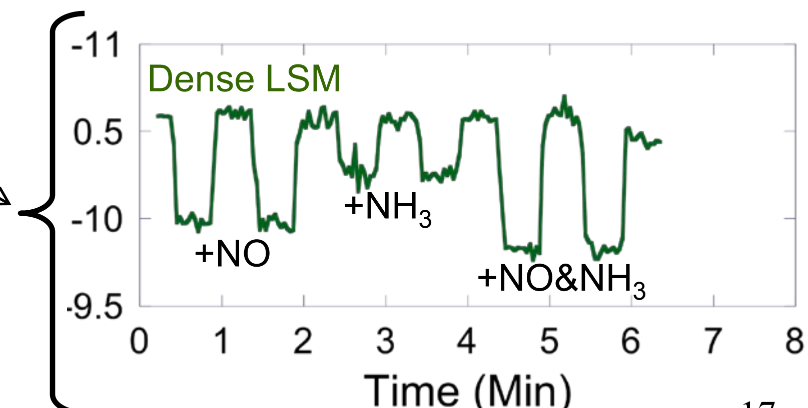
Technical accomplishment: Achieved milestone to further improve sensor design to withstand engine vibrations and prevent mechanical failure during dynamometer testing

- Sept '09: Failure during integration into sensor housing and direct testing in engine manifold; also needed to address ammonia (NH_3) slip from exhaust treatment system
- Feb '10: Improved sensor integrity using design improvements with a ceramic adhesive to secure electrodes; evaluation of NH_3 sensitivity in advanced high-flow test stand

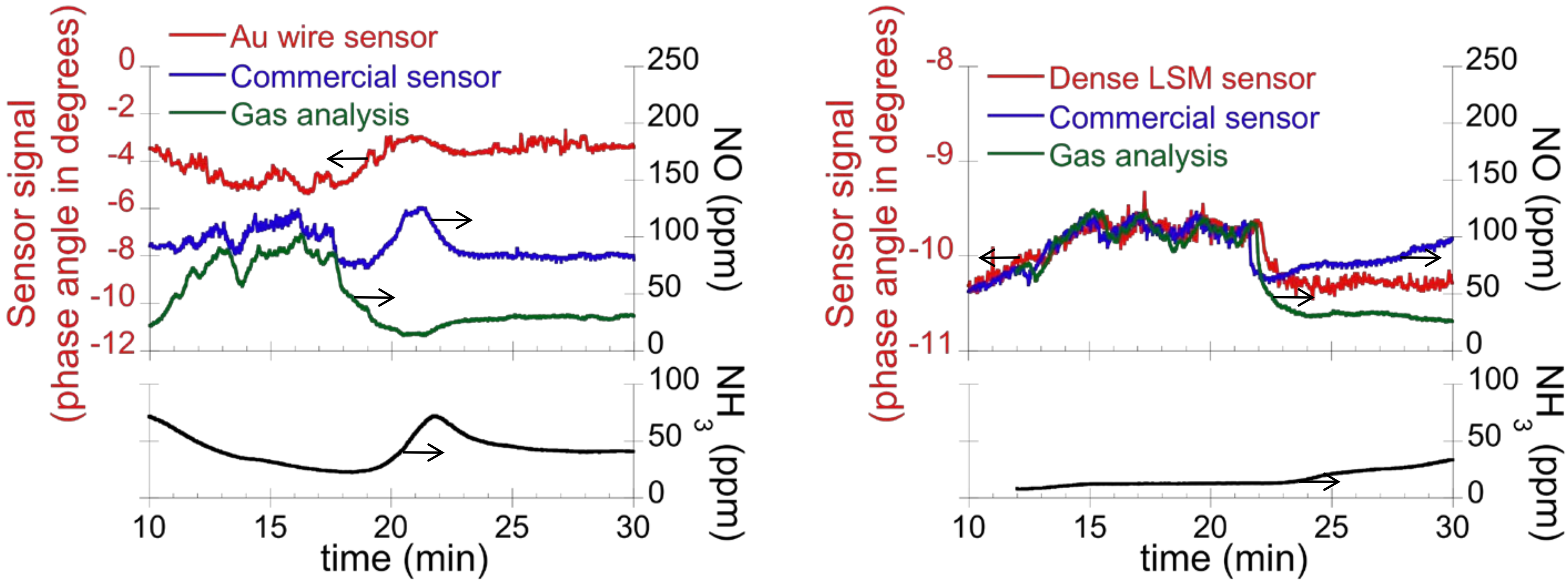
Good response AFTER direct engine manifold dynamometer



- Au wire sensor (9 V on heater): More selective to NH_3 when both NO and NH_3 added; similar response times for both with slower recovery times for NH_3
- LSM sensor (9.5 V on heater): More selective to NO when both added; similar response and recovery times for both



Technical accomplishment: Achieved milestone to complete direct engine manifold dynamometer testing, and evaluated ammonia cross-sensitivity



- Difficult to control NO and NH_3 concentrations: reliant upon condition and history of exhaust treatment system and engine
- Poor correlation of Au wire sensor (9 V on heater) and commercial sensor with gas analysis: large cross-sensitivity to ammonia (20-75 ppm NH_3)
- Good correlation of Dense LSM sensor (9.5 V on heater) and commercial sensor with gas analysis: Dense LSM showed less cross-sensitivity to ammonia (20-30 ppm NH_3)
- Need to refine engine testing protocol: Developing test bed for vehicle on-road testing for better control of gas concentrations and real-world sensor performance data

Collaboration

- Partners:
  - Ford Motor Company
    - Biweekly conference calls to coordinate research and development activities
    - 2-3 site visits each year at either Ford or LLNL
      - Face-to-face meetings
      - Vehicle/engine dynamometer testing and advanced high-flow test stand
  - In discussion with Cummins for a possible partnership
- Technology transfer:
  - Ford collaborators leading effort to interface with commercialization entities
  - Preliminary (first stage) interactions with four potential suppliers
    - Emisense
    - Delphi
    - Beru
    - Watlow

Proposed Future Work: Remainder of FY 2010

- Continue updating compilation of sensor performance data suitable for discussions with potential commercialization entities – including newer stability and cross-sensitivity data
- Refine sensing strategy and update electronics measurement system for on-vehicle testing (most recent system designed in FY07)
- Define materials and design/platform with temperature control appropriate for stable operation suitable for longer-term laboratory testing and vehicle and engine dynamometer testing
- Complete evaluation of sensor accuracy and general sensitivity: completed for Au wire, but more data needed for dense LSM sensor prototye
- Down-select electrode materials choice: metals or oxide materials, based on sensitivity, aging properties, interferences, temperature stability, etc.

Proposed Future Work: Fiscal year 2011

- Preliminary solution for drift issues by appropriate materials choice, pre-use aging, experimental protocol, and design
- Down-select on alternative sensor designs/geometries
- Second stage discussions with supplier(s) about commercialization prospects
- Improve packaging strategy for long-term durability testing including on-board testing of sensors in road vehicles
    - Long-term and accelerated testing protocol developed based on results from on-road vehicle testing
- Address systems protocols for comprehensive vehicle emissions measurement and control needs – down-select for current strategy or parallel development (stand-alone operation or integrated systems approach)

Summary

- High sensitivity, low-cost NO_x sensors are needed to meet emission targets and enable widespread use of diesel vehicles with better fuel economies: We are developing a novel sensor with the potential to meet OEM cost and operational requirements.
- Our technical accomplishments in the last year include:
  - Improved materials/designs for stability against degradation from (a) thermal cycling, (b) integration with protective commercial housing, and (c) engine vibrations.
  - Demonstrated good performance of more advanced prototype (i.e., with imbedded heater) in various water, oxygen, and NO_x conditions for over ~3000 hrs.
  - Assessed cross-sensitivity (including ammonia) in laboratory and dynamometer tests and began developing strategies to improve accuracy using a numerical algorithm.
- Our strong collaboration with Ford has enabled real-world performance data and a commercialization pathway with preliminary interactions with four suppliers; we are in discussions with Cummins to potentially expand partnerships.
- Next year plans include completing sensor evaluation and refining sensing strategies to prepare for a down-select of materials/designs as well as second-stage discussions with suppliers; we are on target for a commercialization decision point for mass production in FY2012.