NO_x sensor development

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Overview

- **Timeline**
  - Start: FY02
  - Finish: FY13
  - 85% Complete
- **Budget**
  - Total project funding
    - DOE: $3292K
    - Ford (in kind): $1200K
  - Funding received in FY10: $500K
  - Funding for FY11: $500K
- **Barriers**
  - Long lead times for materials commercialization.
  - Cost…any new materials technology will have to meet stringent cost targets to achieve commercial success.
  - Goal: By 2013, develop NOx sensor materials and prototypic NOx sensors that meet the sensitivity requirements identified by industry for emissions control in light duty diesel engines.
- **Partners**
  - Ford Motor Company: technical support and advanced testing facilities; leading commercialization efforts.
  - Technology transfer and commercialization being discussed with Delphi, Emisense, and Watlow.

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 2010 to May 2011:
  - Continue performance evaluation, evaluate processing techniques suitable for mass manufacturing, and develop electronics for on-board vehicle testing
  - Build on initial discussions (began in FY10) with commercialization entities including face-to-face meetings and, based on these interactions, implement advanced performance evaluation methods for laboratory and vehicle testing

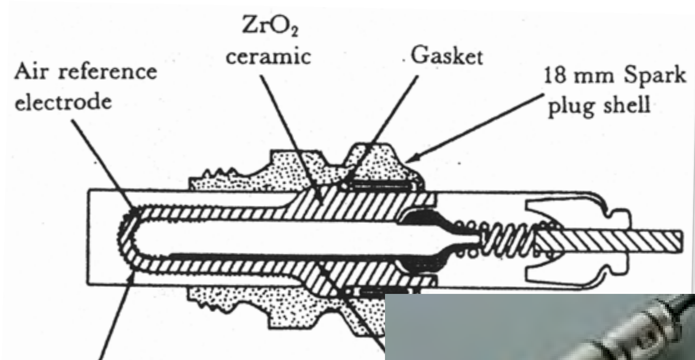
Relevance: Commercially available NO_x sensor technology does not meet the needs of the automotive industry

- Only one type of exhaust NO_x sensor available on the market (two commercial vendors) with little competition – based on 1992 Ford patent
  - **Expensive** due to complicated multiple-chamber design and amperometric operation which requires complex electronics to measure nanoamp current
  - Significant upgrades necessary to meet Low Emission Vehicle III (LEV III)
- Sensor technical performance to meet California (ARB) and EPA requirements presents **significant development barriers** 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

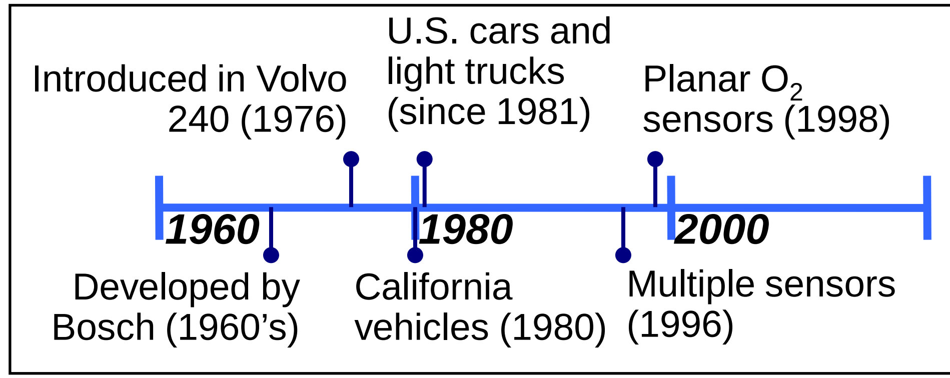
Relevance: Solid-state electrochemical sensors are a proven robust technology for measuring O_2 in exhaust to control emissions—NO_x sensors build upon this technology

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



E.M. Logothetis in Chemical Sensor Technology, 1991.

History of O_2 sensor development



- In contrast, NO_x sensor R&D requires newer understanding of sensing mechanisms (non-equilibrium phenomena), with challenging requirements for sensitivity and accuracy – *developing new sensors is time-intensive and costly*
  - Much academic research (and our past efforts prior to FY06) focused on potentiometric sensing – progress to date indicates minimal chance for commercialization
  - *Our impedancemetric approach (started ~FY06) is making significant progress for achieving commercialization decision point in FY12*

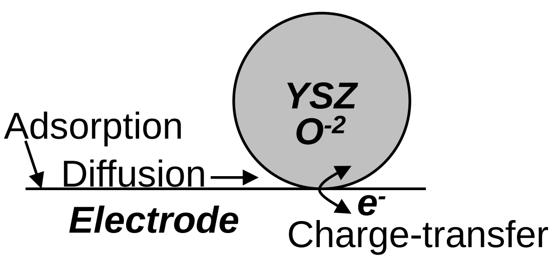
Major milestones for FY10 and FY11

- **<u>FY10 (completed)</u>**
  - Evaluated temperature, oxygen, and water cross-sensitivity on current materials
  - Performed engine dynamometer test of improved prototypes
  - Compiled sensor performance data suitable for discussions with potential commercialization entities
  - Continued discussions with potential commercialization entities and new partnerships being developed
- **<u>FY11 (partially completed)</u>**
  - Designed advanced sensor evaluation methods based on discussions with commercialization entities
  - Evaluated materials processing techniques suitable for mass manufacturing
  - 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

Approach: LLNL developed unique design and measurement strategy leverages proven robust solid-state electrochemical technology (patents filed FY06 & FY09)

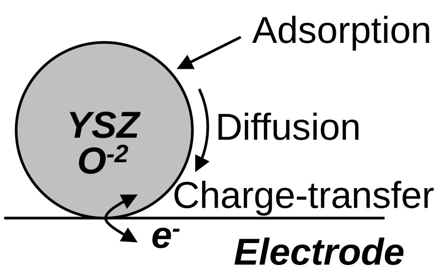
- Novel impedance-based sensing uses complex ac impedance (electrical response to low-amplitude alternating current signal) as opposed to dc (direct current) signals – patent application filed in FY06, continuation-in-part filed in FY09
- Advantages over conventional dc-based sensors: higher sensitivity (< 5 ppm NO_x) detecting both NO and NO_2 simultaneously, 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



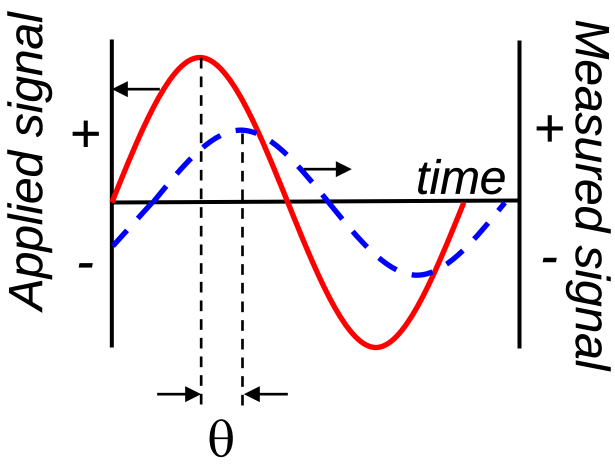
Minimal NO_x response when electrode surface dominates

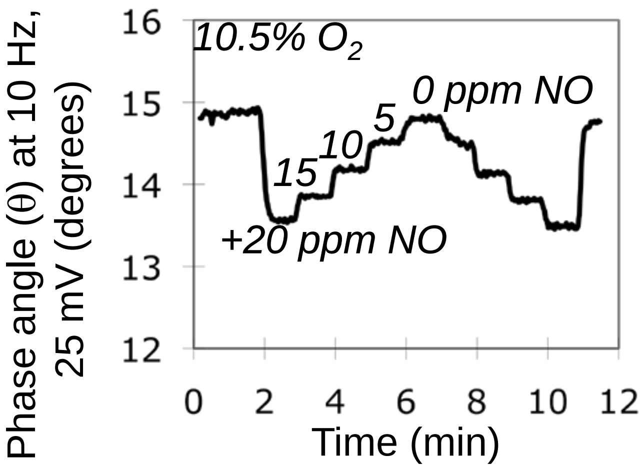
High sensitivity



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



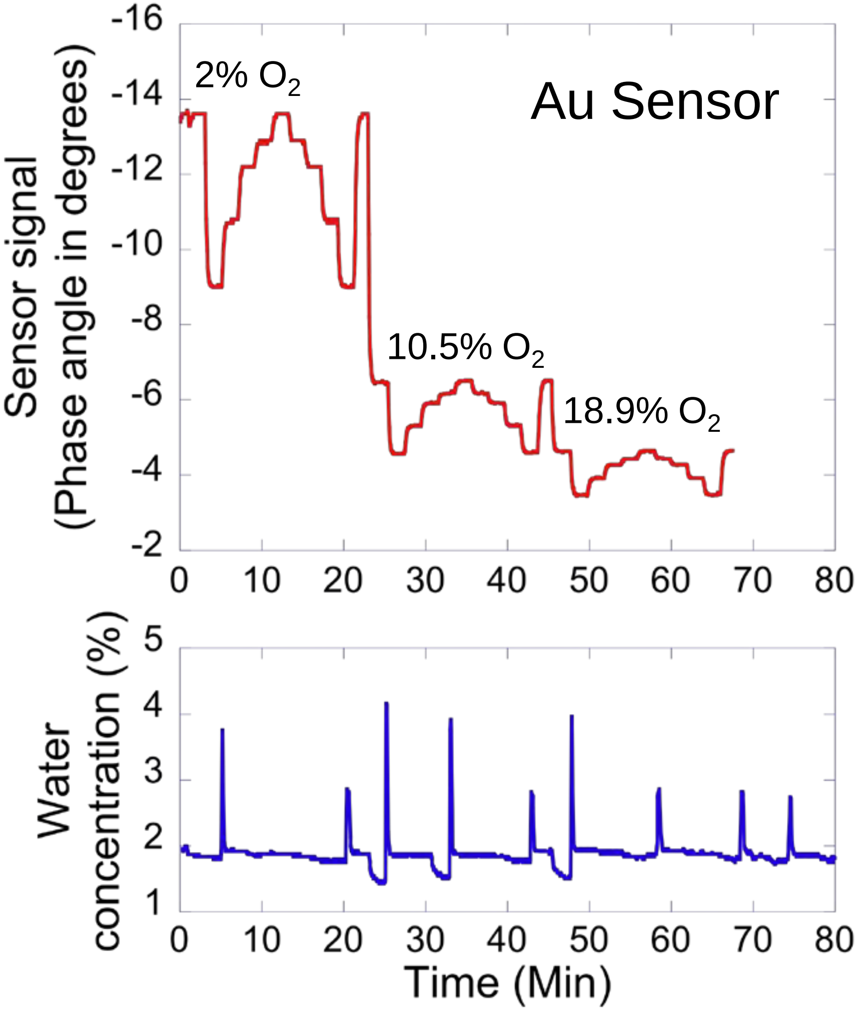


- Similar to electrical resistance, which measures opposition to an electrical current, impedance measures opposition to a time-varying (alternating) current
- Impedance is a complex quantity with both magnitude and phase angle (θ) information
- For the electrochemical LLNL sensors, both magnitude and 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

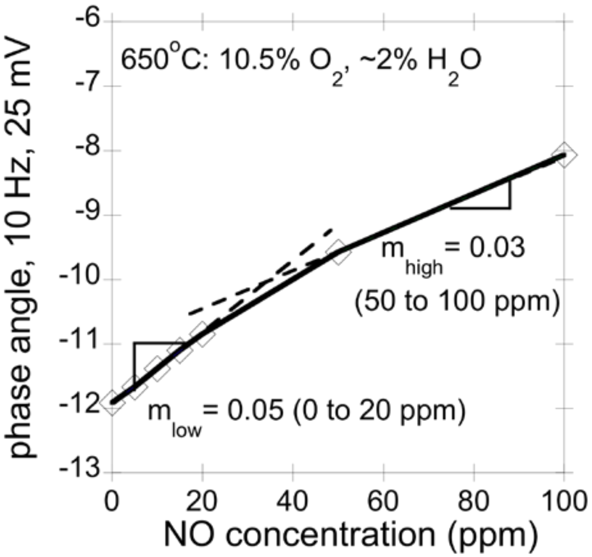
Technical accomplishment: Previously in FY10, demonstrated more advanced prototypes in laboratory cross-sensitivity and engine dynamometer testing

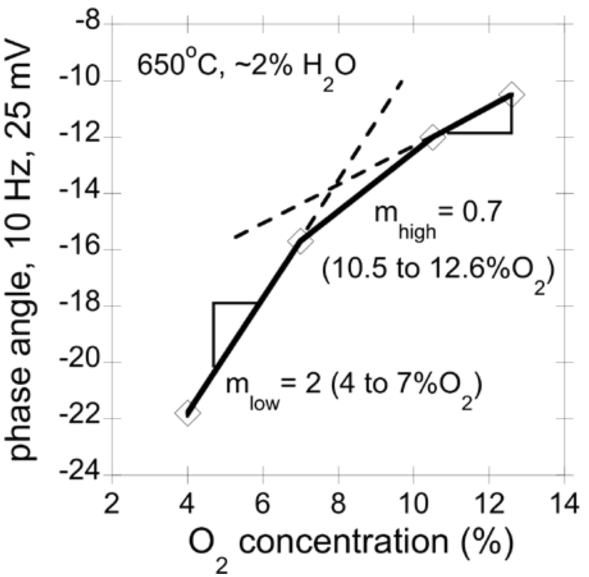
- Built on alumina substrate, provided by Ford, with an imbedded heating element – packaged into commercial housing, provided by U.S. automotive supplier
- Two sensing materials, Au and strontium-doped lanthanum manganite (LSM)
  - Lower melting point of Au, compared to LSM, limits processing flexibility
  - Au: better accuracy due to lower water cross-sensitivity
  - LSM: better tolerance to ammonia
- Initial development of strategies to improve accuracy using numerical algorithm and laboratory cross-sensitivity data

NO stepped in the following sequence at each % O_2: 0-100-50-20-10-0 ppm



Technical accomplishment: Applied cross-sensitivity mitigation strategy to engine dynamometer data – using behavior measured in laboratory testing



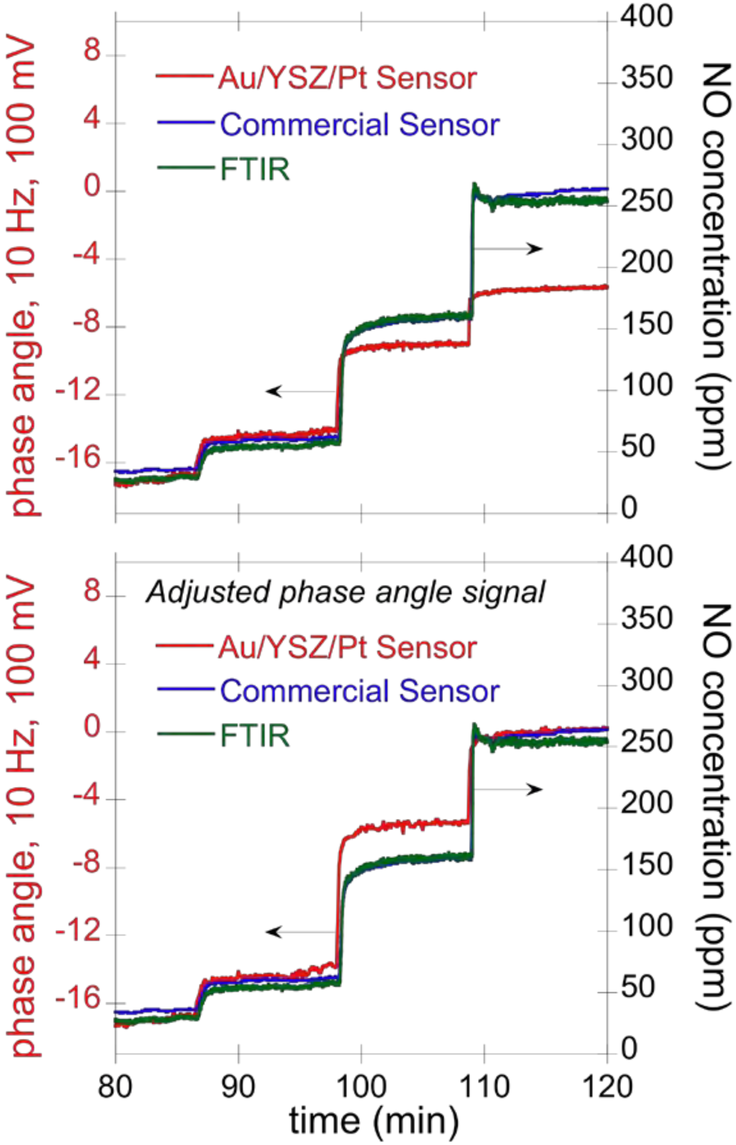


- Laboratory testing showed nonlinear sensitivity to NO and O_2
  - Behavior of phase angle (sensor) signal approximated with slopes (m) from two linear regimes
    - Low concentration
      - 0 to 20 ppm NO: $m_{low} = 0.05$
      - 4 to 7% O_2: $m_{low} = 2$
    - High concentration
      - 50 to 100 ppm NO: $m_{high} = 0.03$
      - 10.5 to 12.6% O_2: $m_{high} = 0.7$
- Use behavior from laboratory testing to adjust measured phase angle in dynamometer testing:

$$\theta_{adjusted} = \theta_{baseline} + \Delta\theta_{adjusted}$$

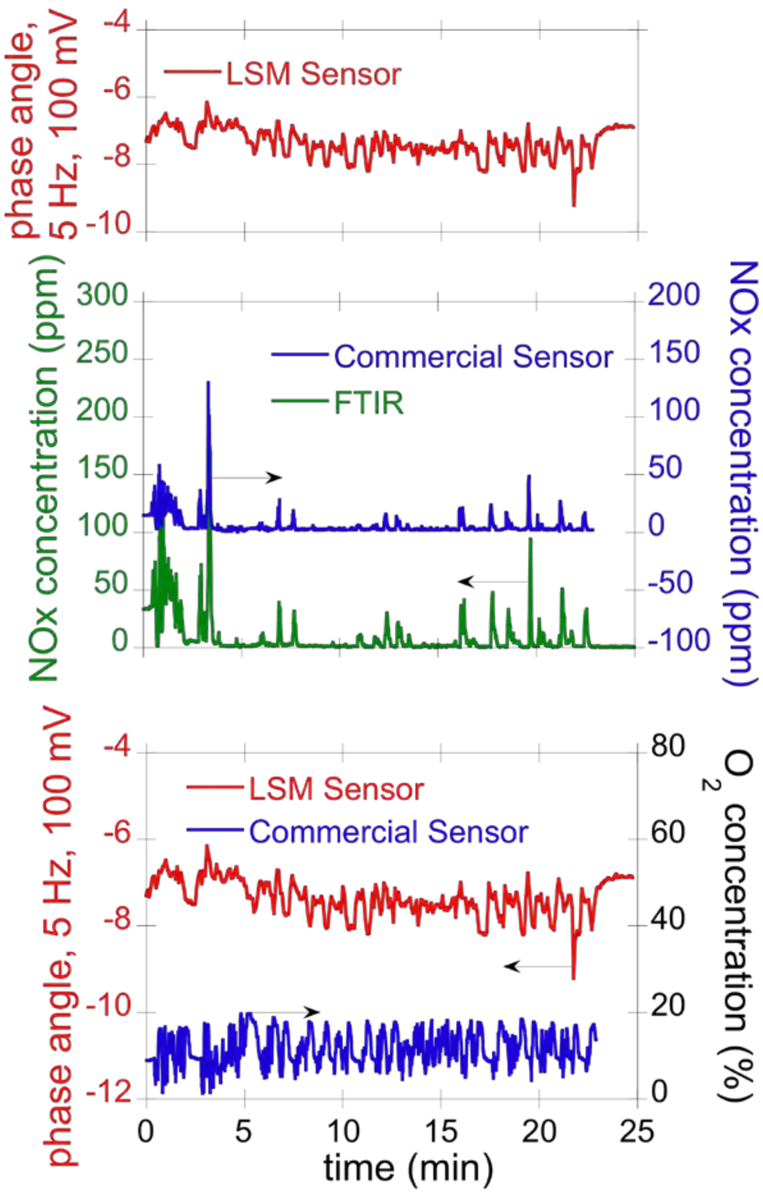
$$\Delta\theta_{adjusted} = \frac{\theta_{measured} - \theta_{baseline}}{m_{high}} m_{low}$$

Technical accomplishment: Applied cross-sensitivity mitigation strategy to engine dynamometer data – comparison with expensive commercial sensor



- Engine dynamometer testing under constant O_2 conditions – isolated the effect of NO_x
  - (top) Qualitative agreement of LLNL prototype (Au/YSZ/Pt Sensor) with commercial sensor and Fourier transform infrared (FTIR) gas analysis, but larger deviations at high NO_x concentrations > 100 ppm
  - (bottom) Using behavior from laboratory testing to adjust measured phase angle with two slope approximation resulted in better agreement
  - Strategy can be refined to include more precise fitting than two slope approximation

Technical accomplishment: Vehicle dynamometer test confirmed robust performance of LSM sensor – additional advanced tests requested by commercialization entities

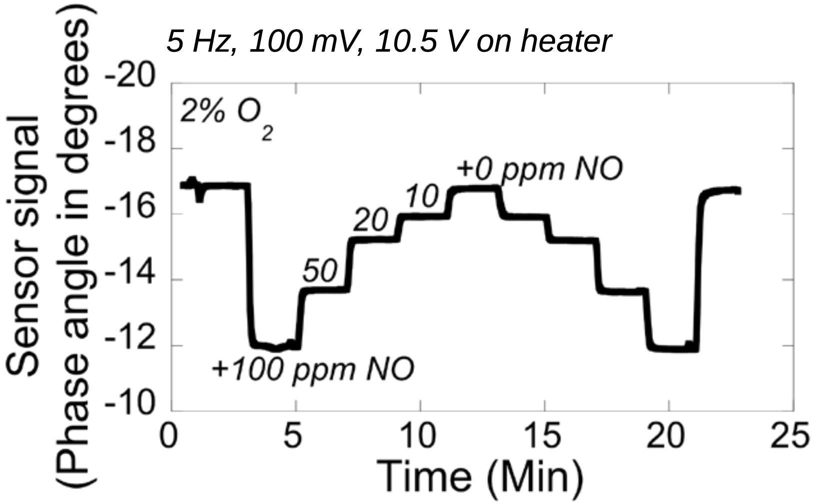


- Federal test protocol (FTP)-75: advanced emission testing for light-duty diesel certification consisting of cold start, transient, and hot start phases:
  - Distance traveled: 11.04 miles
  - Duration: 1874 s (~30 min)
  - Average speed: 21.2 mph
- Data for LLNL prototype (LSM Sensor) compared with commercial sensor and Fourier transform infrared (FTIR) gas analysis
- FTP-75 results indicated robustness of LSM Sensor, which was previously tested multiple times in engine and vehicle dynamometer
- LSM Sensor primarily responded to transients in oxygen concentration – need for cross-sensitivity mitigation strategy

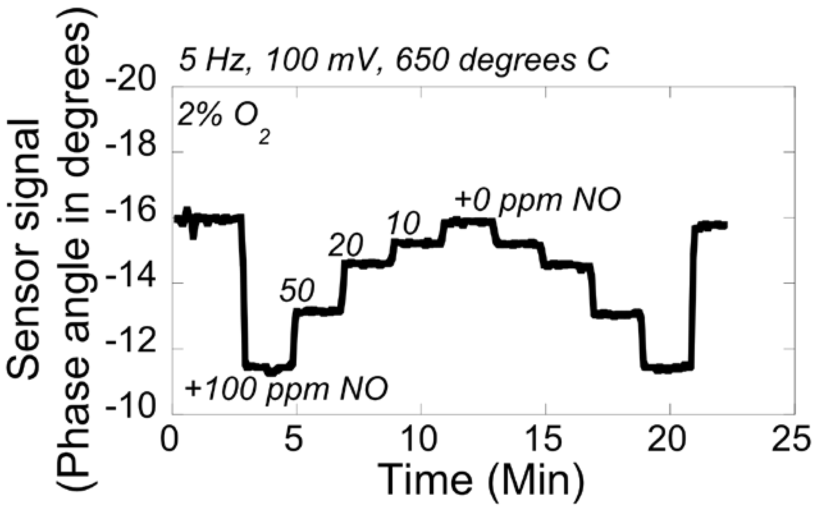
Technical accomplishment: Evaluated advanced materials processing methods suitable for mass manufacturing – sputtered dense sensing electrodes

- Laboratory Au wire prototypes to date: primarily low-volume techniques for materials processing and sensor assembly – sputtering evaluated as method for mass manufacturing and for thin film deposition to miniaturize dimensions
- Sputtered both Au and strontium-doped lanthanum manganite (LSM): performed at Ford Motor Company with thin film thickness ranging from ~250 to 500 nm

Au wire prototype

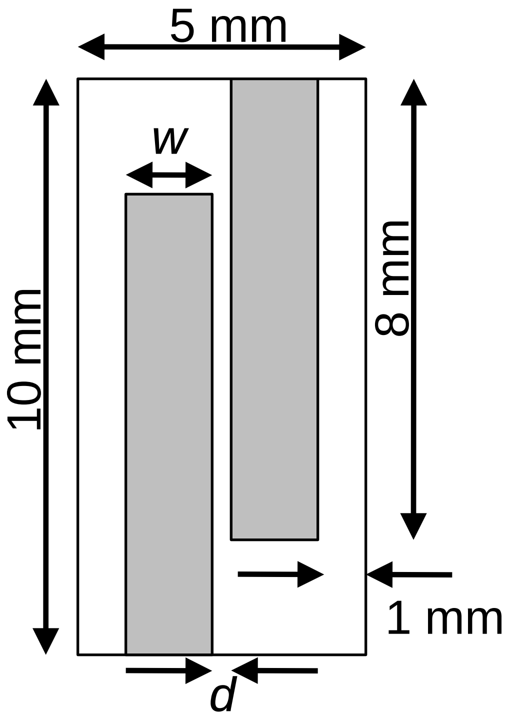


Sputtered Au prototype

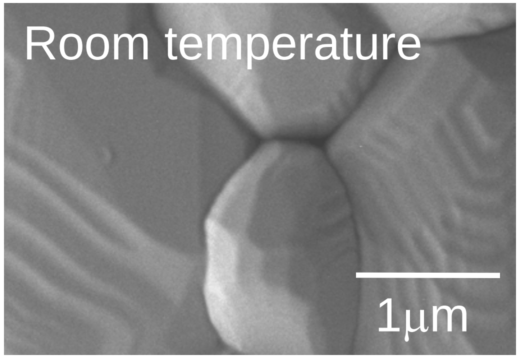


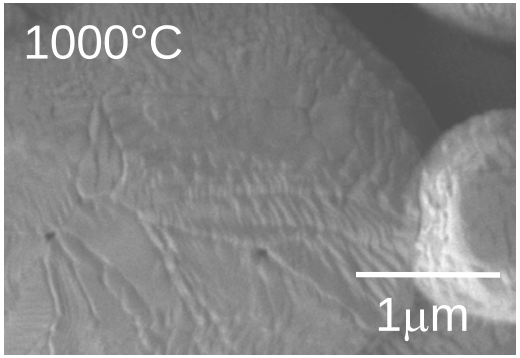
- Similar response magnitudes and baseline values measured for laboratory Au wire and sputtered Au prototype

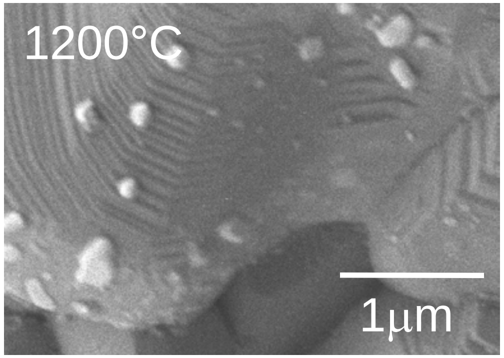
Technical accomplishment: Evaluated advanced materials processing methods suitable for mass manufacturing – microfabrication and co-firing of sputtered materials



- Photolithography and etching process developed for side-by-side electrode configurations on 100 mm dia. round alumina substrates
  - Vary electrode spacing (d): 50, 100, and 250 μm
  - Vary electrode thickness: 250 and 500 nm
  - Final 5 mm x 10 mm size suitable for mounting onto heater substrates and packaging into housing
- Began investigation of potential co-firing routines (desired single-step processing) with different annealing temperatures of sputtered LSM – loss of uniform dense film with formation of particles at 1200°C

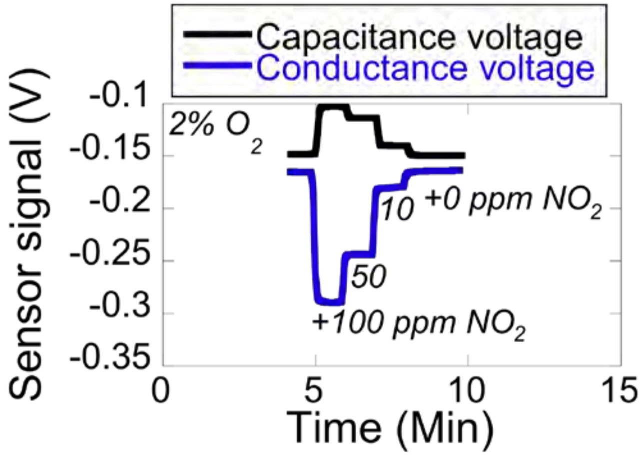




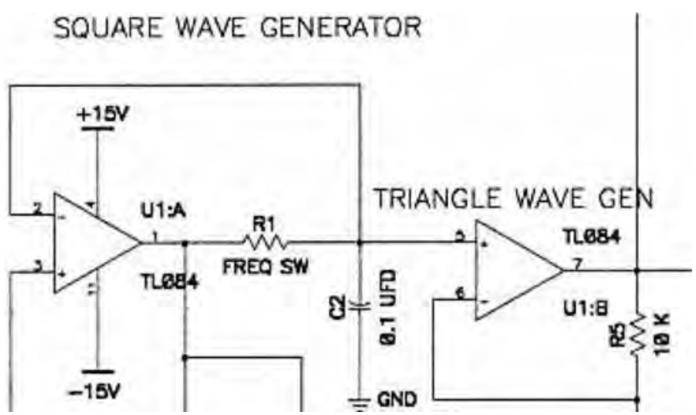


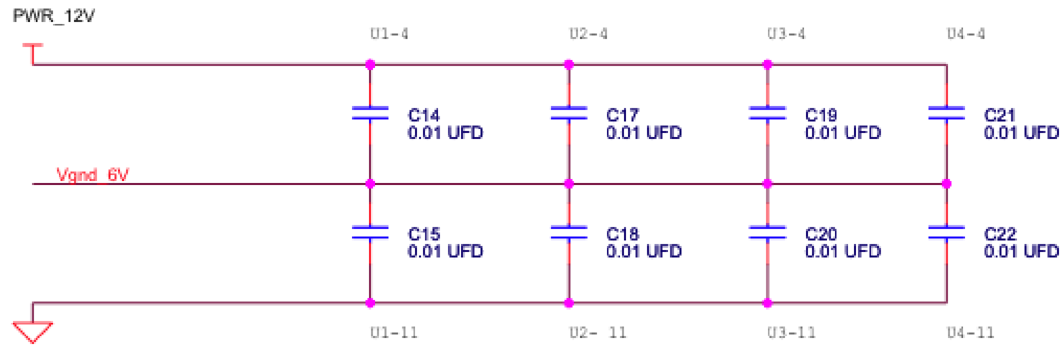
Technical accomplishment: Updated simple prototype electronics for on-board vehicle testing

- Prototype circuit board developed by Ford Motor company to demonstrate simple electronics for impedancemetric sensing: generated triangle wave ac signal input (partially shown below on left) then outputs two response voltages, associated with conductance and capacitance – reasonable performance measured with first generation portable prototype electronics box



- Additional modifications to the circuit: addition of new test frequencies and amplitudes as well as appropriate electronics for compatibility with on-board vehicle power supply (12 V battery), shown below on right.





Collaboration

- Partners with Ford Motor Company (Industry)
  - Biweekly conference calls to coordinate R&D activities and several in-person interactions, including sensor evaluation
  - Unique Ford capabilities include advanced processing techniques such as sputtering and advanced evaluation techniques such as vehicle/engine dynamometer testing
- Commercialization pathway:
  - Ford is OEM and needs supplier/manufacturer for NO_x sensor technology: leading effort with commercialization entities
  - Building on preliminary interactions in FY10, began face-to-face meetings and discussions about advanced testing protocols, technology licensing, and commercialization pathways
    - Delphi (Industry)
    - Emisense (Industry)
    - Watlow (Industry)
    - Ongoing conversations with other potential commercialization entities/suppliers

Proposed Future Work: Remainder of FY 2011

- Additional discussions with potential commercialization entities including face-to-face meetings, technology licensing agreements, and development of advanced sensor evaluation methods
- Evaluate and refine materials processing techniques suitable for mass manufacturing – 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
- Update compilation of sensor performance data suitable for discussions with potential commercialization entities – including sensitivity, stability, and cross-sensitivity data
- Define materials and design/platform with temperature control appropriate for stable operation suitable for longer-term laboratory testing and vehicle and engine dynamometer testing
- Down-select electrode materials choice: metals or oxide materials, based on sensitivity, aging properties, interferences, temperature stability, etc.

Proposed Future Work: Fiscal year 2012

- Preliminary solution for drift issues by appropriate materials choice, pre-use aging, experimental protocol, and design
- Down-select on alternative sensor designs/geometries
- Down-select for commercialization partners
- 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:

– Demonstrated application of cross-sensitivity mitigation strategies to data from engine dynamometer testing using controlled laboratory cross-sensitivity data

– Confirmed robust performance of LSM sensor in vehicle dynamometer testing including additional advanced emission test protocols requested by commercialization entities

– Began evaluating advanced materials processing methods suitable for mass manufacturing – sputtering dense sensing electrodes, microfabrication techniques, and co-firing routines

– Updated simple prototype electronics for on-board vehicle testing

- Our strong collaboration with Ford has enabled real-world performance data and a commercialization pathway including interactions with potential suppliers
- Next year's plans include completing sensor evaluation and refining sensing strategies to prepare for a down-select of materials/designs as well as continuing discussions with suppliers about licensing technology; we are on target for a commercialization decision point in FY2012.