NO_x sensor development

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Overview

- **Timeline**
  - Start: FY02
  - Finish: FY13
  - 90% Complete
- **Budget**
  - Total project funding
    - DOE: $3692K
    - Ford (in kind): $1400K
  - Funding received in FY12: $400K
- **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.
  - EmiSense LLC: licensed LLNL NOx technology and CRADA partners for continued development.

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
  - Mass production decision point in FY 2013
- Objectives for March 2011 to March 2012:
  - Building on previous work, continue modifying prototypes to improve performance, including drift and sample-to-sample reproducibility
  - Continue evaluating prototypes in laboratory and engine testing for sensor performance validation

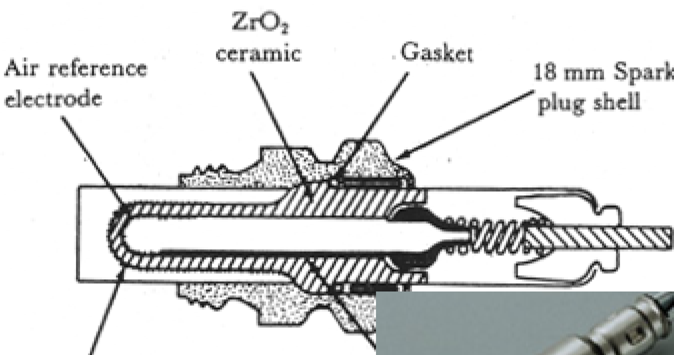
Relevance: Commercially available NO_x sensor technology does not meet the needs of the automotive industry

- 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 nanoampere 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

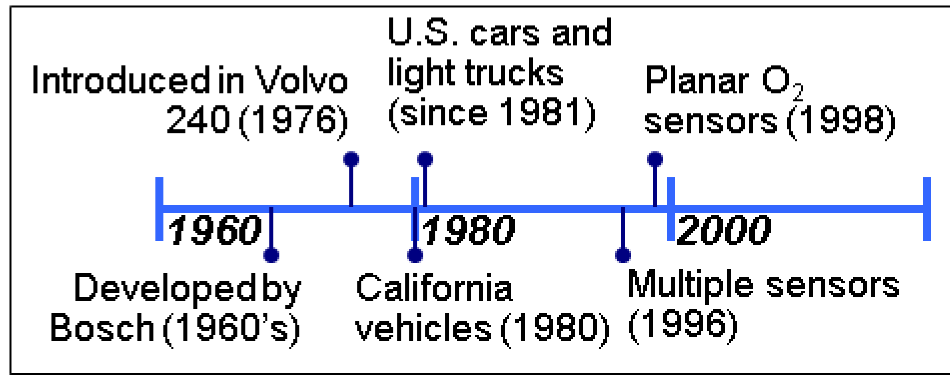
Relevance: Solid-state electrochemical sensors are a proven robust technology for measuring O_2 in exhaust to control emissions—NO_x sensors build upon this technology

- 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 – <u>*developing new sensors is time-intensive and costly*</u>
  - 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) has been experimentally verified for potential commercialization*

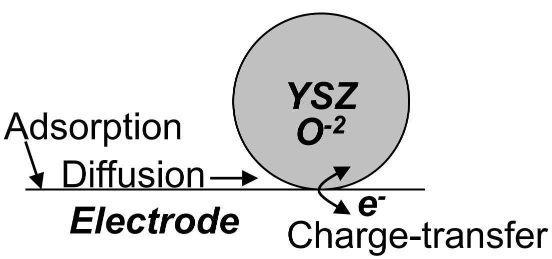
Major milestones for FY11 and FY12

- **FY11 (completed)**
  - EmiSense Technologies, LLC obtained Exclusive Patent License Agreement for LLNL NO_x technology (June 2011)
  - Completed longer-term laboratory evaluation of FY10 prototypes
  - Refined design/platform for better sample-to-sample reproducibility and reduced drift
  - Evaluated performance by testing side-by-side with commercial sensors
- **FY12 (partially completed)**
  - Developed CRADA with EmiSense Technologies, LLC; executed March 6, 2012
  - Completed advanced engine/vehicle testing at Ford Motor Company of FY12 prototypes
  - Refine fabrication processing methods for incorporating active components in collaboration with EmiSense
  - Refine sensing strategy and electronics (also in collaboration with EmiSense)
  - Down-select for improved materials and design/platform

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

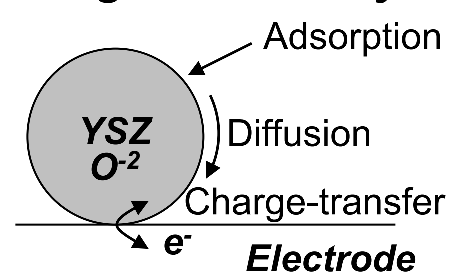
- Novel impedance-based sensing uses complex ac impedance (electrical response to low-amplitude alternating current signal) as opposed to dc (direct current) signals – patent application filed in FY06, continuation-in-part filed in FY09
- Advantages over conventional dc-based sensors: higher sensitivity (< 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 interface between the porous yttria-stabilized zirconia (YSZ) electrolyte and the electrode

Low sensitivity



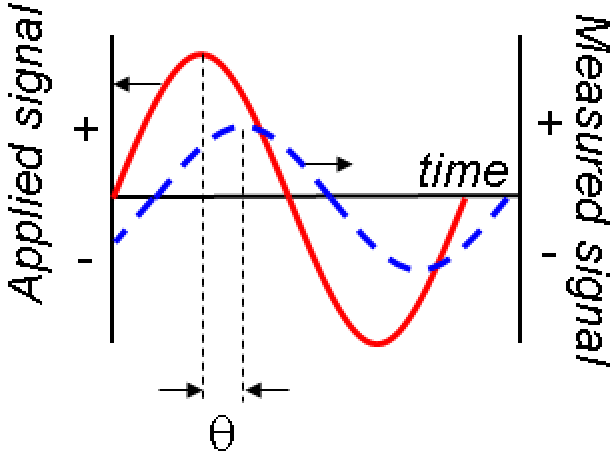
Minimal NO_x response when electrode surface dominates

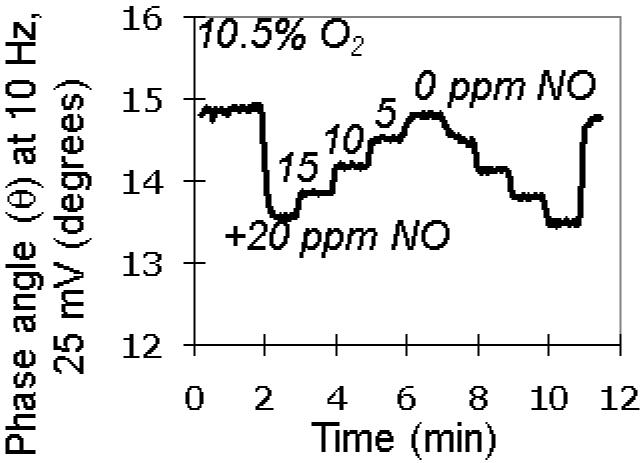
High sensitivity



Larger NO_x response: controlling microstructure and composition is key

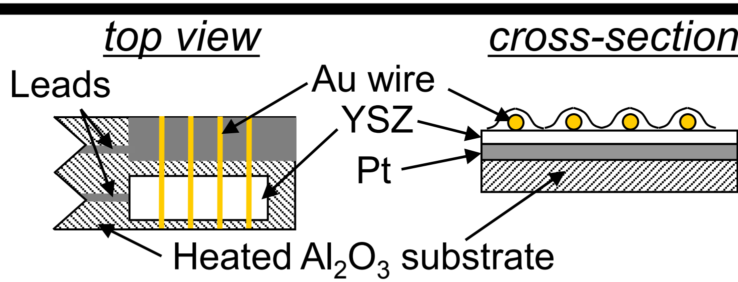
Approach: In our alternating current (ac) measurement strategy, the phase angle (θ) is correlated with the level of NO_x in the exhaust

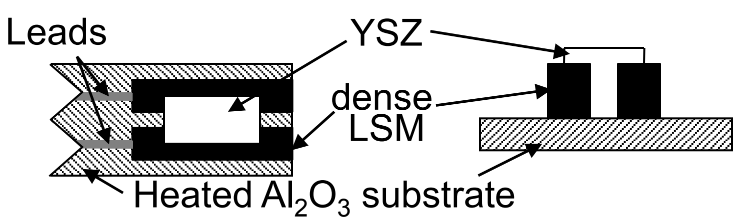




- Similar to electrical resistance, which measures opposition to an electrical current, impedance measures opposition to a time-varying (alternating) current
- Impedance is a complex quantity with both magnitude and phase angle (θ) information
- For the electrochemical LLNL sensors, both magnitude and 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 demonstrated more advanced prototypes in laboratory cross-sensitivity and engine dynamometer testing

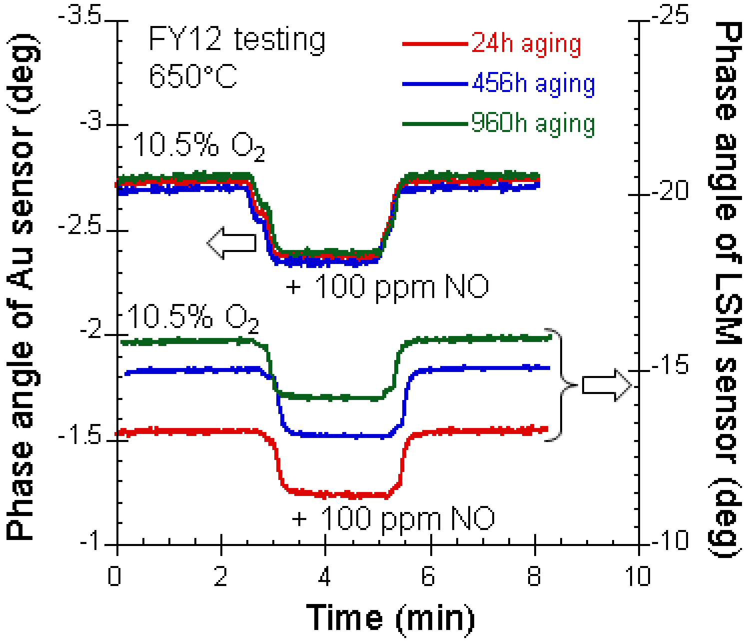


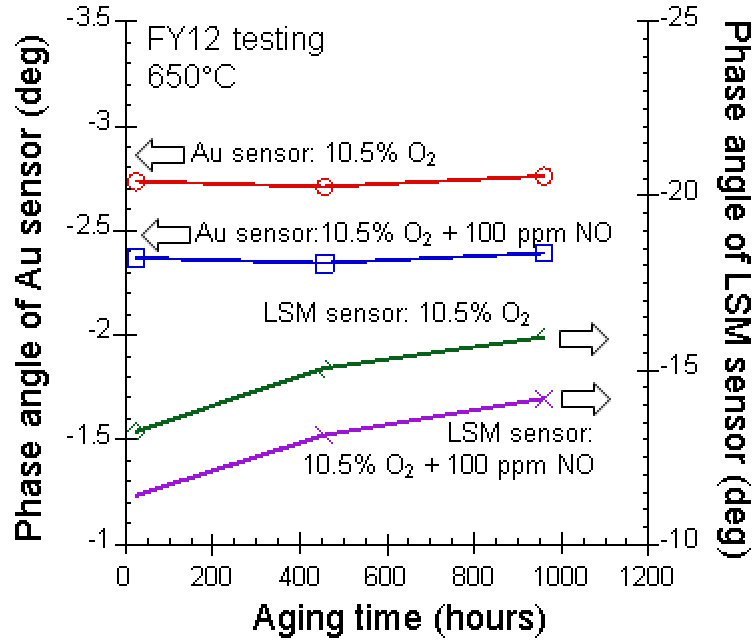


Built on alumina substrate, provided by Ford, with an imbedded heating element – packaged into commercial housing, provided by U.S. automotive supplier

- Two different 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
- Development of strategies to improve accuracy and selectivity using numerical algorithm and cross-sensitivity data including multiple frequency technique to remove oxygen interference
- Demonstrated sensitivity and robustness in laboratory and engine dynamometer testing
- Investigated mass fabrication methods such as spin coating, sputtering, and photolithography
- Demonstrated prototype electronics package using triangle waveform to simulate desired sinusoidal input waveform for impedance measurements

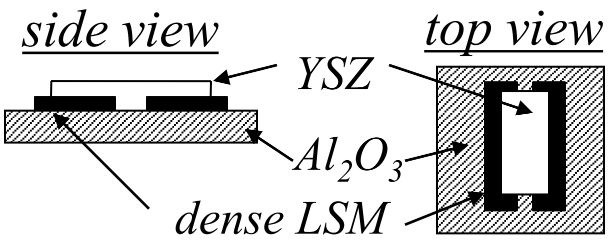
Technical accomplishment: FY12 laboratory long-term aging confirmed previously measured minimal drift in Au prototype, but indicated variance in LSM prototype





- Prior to FY12, previously demonstrated stable sensor response with minimal drift for both Au and LSM with aging to ~500 hours in older generation prototypes
  - Continued laboratory testing in FY12, shown above, of more recent generation prototypes (with newer YSZ formulation) confirmed previously measured stable Au performance with minimal drift but showed variation among samples in LSM performance, including some samples with significant drift in the baseline
- Variation in LSM (sample-to-sample reproducibility and baseline drift) attributed to formation and growth of random micro-cracks within the YSZ electrolyte due to thermal expansion coefficients mismatch and will be resolved using mass manufacturing processes

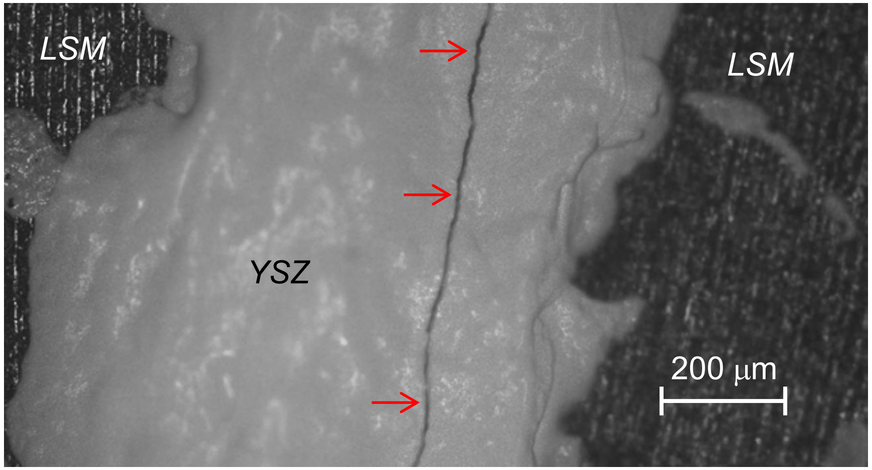
Technical accomplishment: Improved performance by minimizing micro-crack formation and growth investigated using modifications to the substrate composition



Sensor test design used to investigate the effect of micro-cracks

Material	Coefficient of thermal expansion (10^{-6}/°C)
Al_2O_3	8
YSZ	10.5
LSM	10

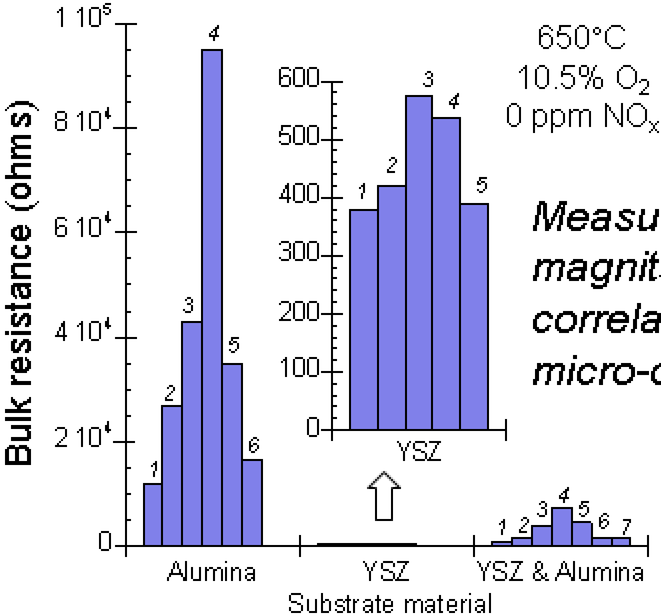
Thermal mismatch between Al_2O_3 substrate and other active sensor components (YSZ and LSM) produce strain at the interface



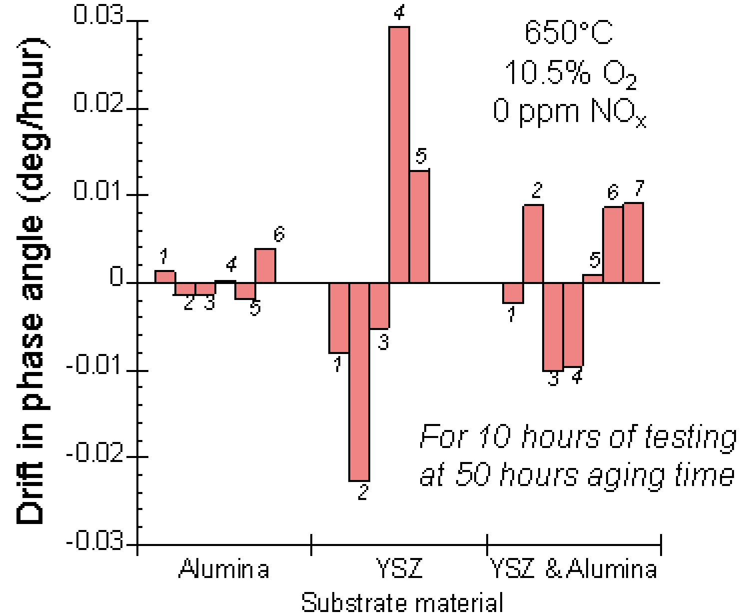
- Thermal strain produced during processing at 1000°C relieved by the formation of micro-cracks visible within the lower strength porous YSZ electrolyte
- Micro-cracks lead to poor sample-to-sample reproducibility

Technical accomplishment: Demonstrated acceptable solution that optimized the trade off between micro-crack formation and signal drift by modifying substrate composition

Each bar represents a separate sample (labeled by number)

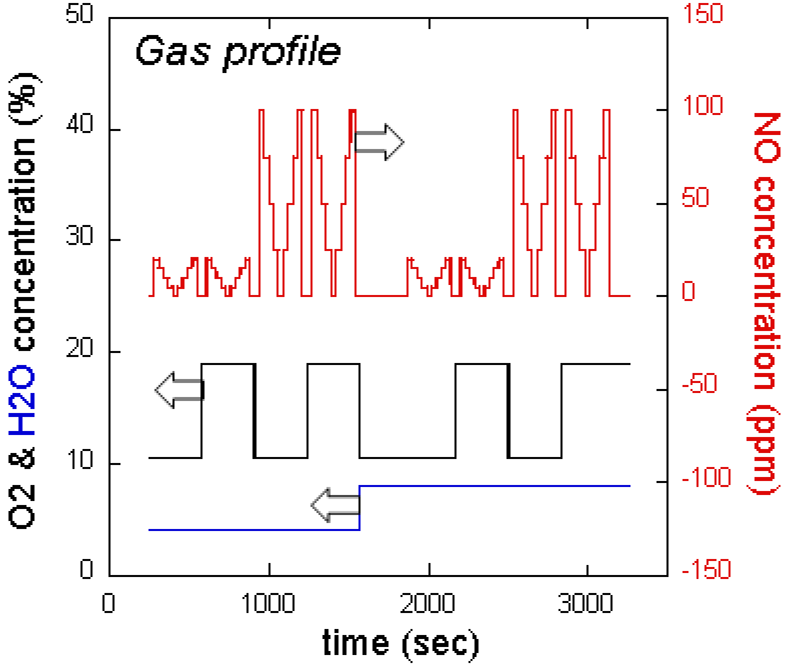


Measured bulk resistance magnitude and variance correlated with extent of micro-cracks

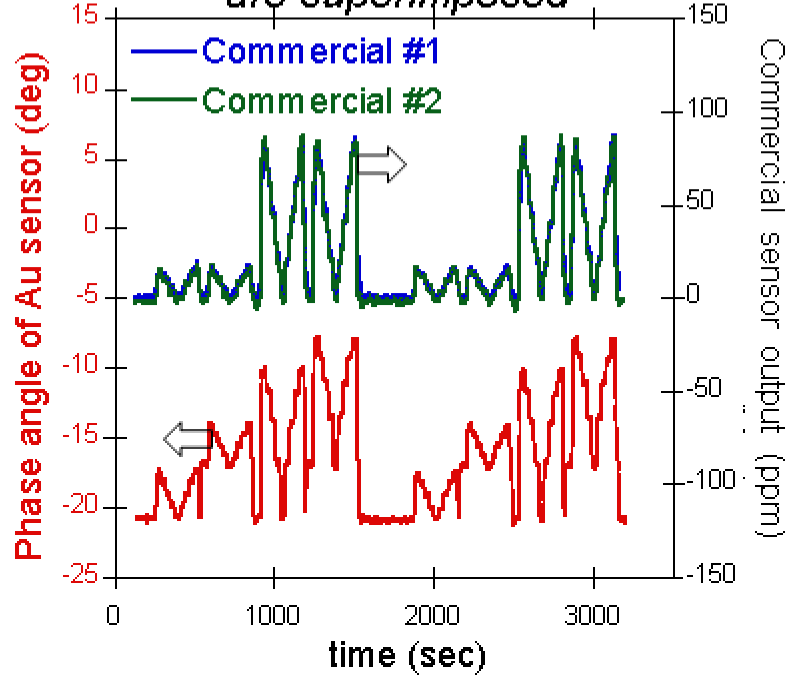


- Alumina substrate (six samples): large resistances and variance indicating presence of micro-cracks
- YSZ substrate (five samples): small resistances with less variance indicating few micro-cracks; however large drift indicated undesired contribution of YSZ substrate to the signal
- YSZ substrate with alumina layer to isolate active components (seven samples): intermediate resistances and variance indicating minimal micro-cracks; intermediate drift indicated thin alumina layer only partially effective

Technical accomplishment: Completed advanced laboratory testing of Au sensor comparing performance with commercial amperometric NO_x sensors (two different suppliers)

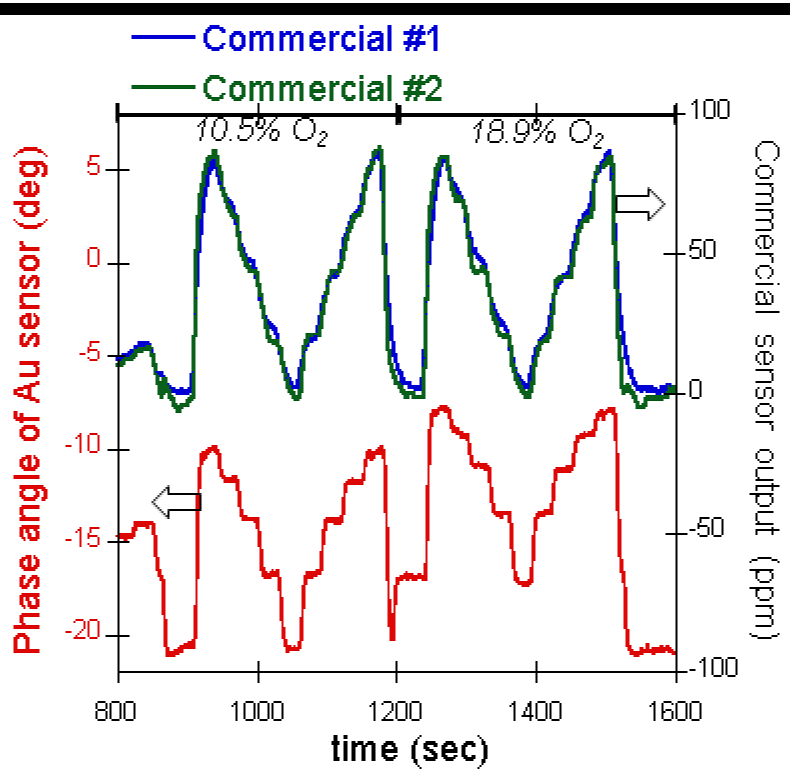


Commercial #1 and #2 data are superimposed

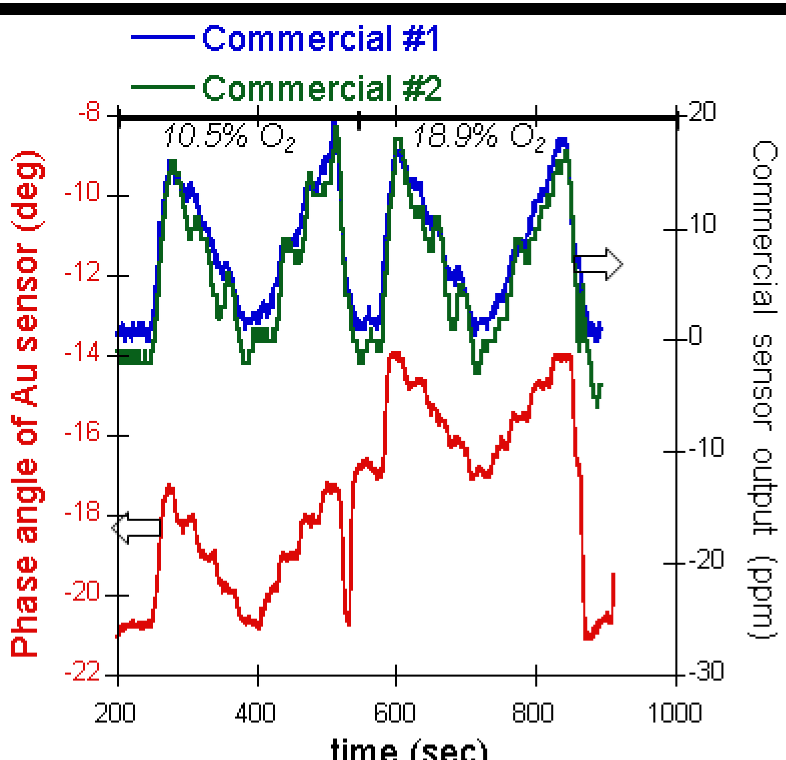


- Au prototype sensor tested alongside commercial amperometric NO_x sensors (same design, two different suppliers) in various NO (30 second steps), O_2, and H_2O concentrations (good tolerance to water)
  - Low NO concentrations: 20 to 0 to 20 ppm in 5 ppm increments
  - High NO concentrations: 100 to 0 to 100 ppm in 25 ppm increments
  - O_2 concentrations of 10.5 and 18.9% and H_2O concentrations of ~4 and ~8%

Technical accomplishment: Demonstrated excellent performance in both high (up to 100 ppm) and low (less than 20 ppm) NO concentration alongside commercial NO_x sensors



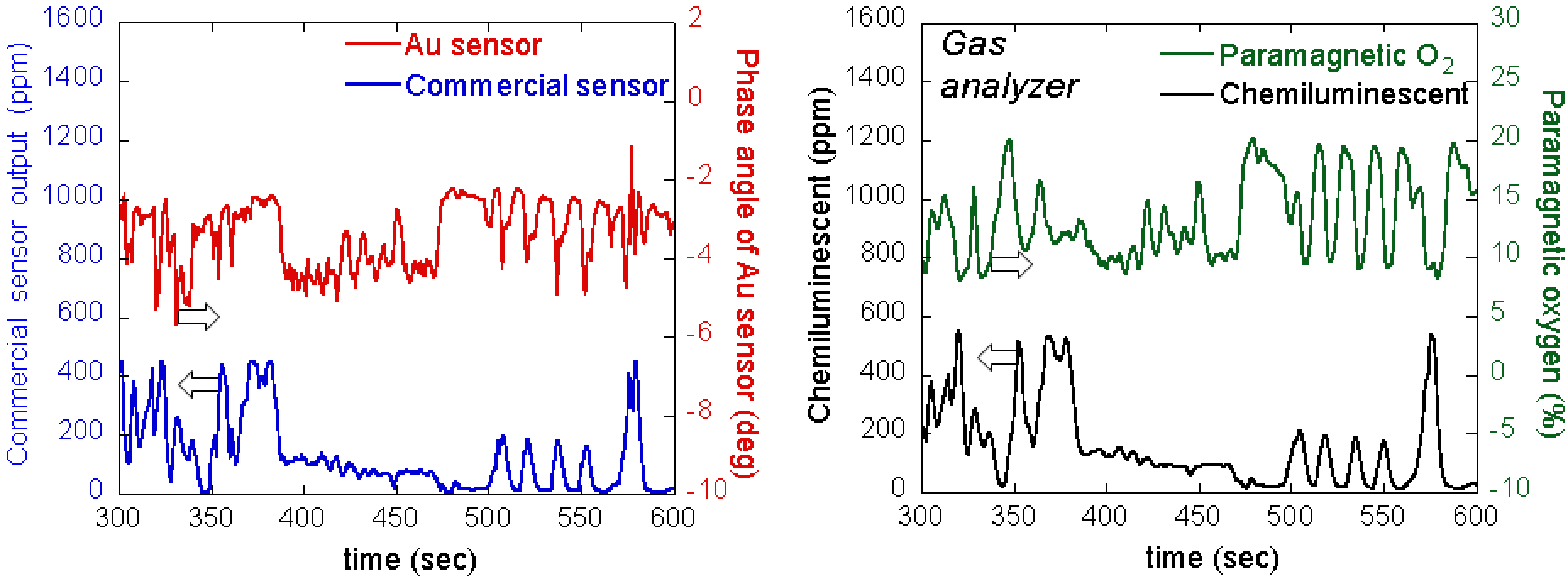
Full NO range up to 100 ppm (25 ppm steps) at 4% H_2O



Lower NO range less than 25 ppm (5 ppm steps) at 4 % H_2O

- Au prototype had similar behavior, but better resolution, as commercial NO_x sensors (same design, two different suppliers), and also similar good tolerance to water with expected larger effect of oxygen – multiple frequency technique has previously been demonstrated in prototypes to remove oxygen interference
- Commercial sensors incorporate complicated electronics, leading to undesirably high costs
- Prototype data shown are raw output; however, algorithms have been developed for corrections

Technical accomplishment: Performed FY12 dynamometer test in real diesel exhaust at Ford using packaged prototypes directly mounted in the tailpipe



- Above FY12 data show new result from a portion of EPA US06, a high acceleration aggressive dynamometer driving schedule
  - Au prototype sensor signal also responded to O_2 as expected
  - Even without the incorporation of any electronics and corrections (used extensively in commercial sensors), demonstrated good performance of prototype in reasonable agreement with commercial sensor
- Confirmed previous results of robust and durable performance when mounted directly in the engine manifold during dynamometer testing

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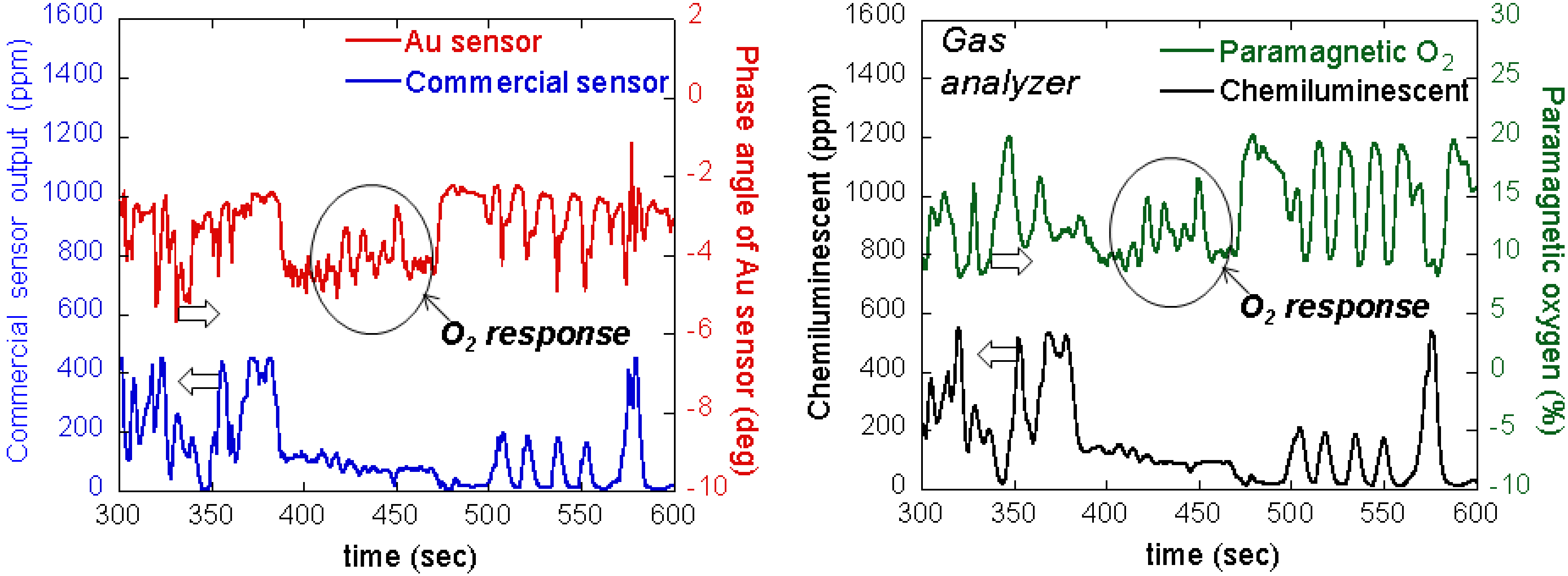

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Collaboration

- 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; enable advanced packaging of sensors with U.S. automotive supplier
- Commercialization pathway:
  - Ford is OEM in need of supplier/manufacturer for NO_x sensor technology
  - EmiSense Technologies, LLC
    - Exclusive Patent License Agreement for LLNL NO_x technology (June 2011)
    - CRADA executed March 6, 2012
    - Conference calls and onsite visits

Proposed Future Work: Remainder of FY 2012

- Refine fabrication processing methods for incorporating active components in collaboration with EmiSense – methods include tape casting, slurry painting, spin coating, and photolithography/sputtering
- Refine sensing strategy and electronics (in collaboration with EmiSense and Ford) – multiple frequency method with updated electronics
- Down-select for improved materials and design/platform – develop imbedded heaters using strategy with alumina coated on YSZ
- 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
- Development of long-term and accelerated testing protocol

Proposed Future Work: FY 2013

- Down-select fabrication processing methods
- Down-select electronics and circuit designs
- Complete laboratory testing and evaluation of improved prototypes including long-term aging and drift
- Perform cross-validation and engine/vehicle performance evaluation
- 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.
- EmiSense Technologies, LLC has obtained an Exclusive Patent License Agreement and a CRADA was executed on March 6, 2012.
- Our technical accomplishments in the last year include:
  - Laboratory long-term aging (up to 1000 hours) confirmed previously measured minimal drift in Au prototype, but indicated variance in LSM prototype
  - Demonstrated acceptable solution to optimize the tradeoff between micro-crack formation and drift in LSM prototype by modifying substrate composition
  - Demonstrated excellent performance of Au prototype in both high (up to 100 ppm) and low (less than 20 ppm) NO concentration alongside two commercial amperometric sensors (same design, two different suppliers)
  - Additional advanced engine testing in real diesel exhaust and aggressive conditions continued to show good results including sensor durability and robustness
- Future plans include working with EmiSense to refine fabrication/processing and sensing strategy/electronics to prepare for a down-select and to perform cross-validation and engine/vehicle testing of more advanced prototypes.