Electrochemical NO_x Sensor for Monitoring Diesel Emissions

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in collaboration with

Ford Research and Innovation Center

2009 DOE Vehicle Technologies Merit Review

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LLNL-PRES-411402

Overview

- **Timeline**
  - Start: FY 2002
  - Finish: FY 2011
  - 75% Complete
- **Budget**
  - Total project funding
    - DOE:$2292K
    - Ford (in kind):$711K
  - Funding received
    - FY08: $250K
    - FY09: $360K
  - Funding for FY10 (requested): $400K
- **Barriers**
  - Lack of technologies for emission regulation compliance in light-duty compression-ignition, direct-injection (CIDI) engines that have dramatically higher fuel economies
  - Cost disadvantages of emission control technology
- **Partners**
  - Ford Motor Company

Objectives

- 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 sensors which are a proven technology for measuring O_2 in the exhaust to control automobile emissions and maximize engine efficiency
  - Characterize and understand sensing mechanisms in order to optimize materials composition/microstructure and sensor configuration/operation
  - Demonstrate suitable sensor platform for commercialization

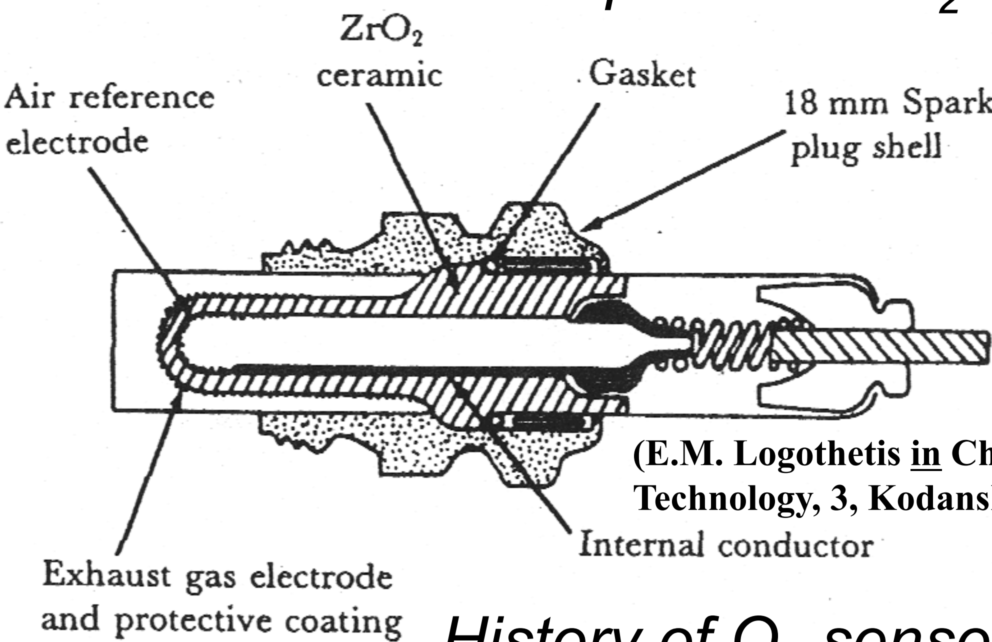
At the present time, commercially available NO_x sensor technology does not meet cost and performance requirements

- Only one type of electrochemical NO_x sensor is commercially available: based on a Ford patent and developed for lean-burn gasoline and diesel systems
  - Expensive due to complicated multiple-chamber design and amperometric operation which requires complex electronics to measure nanoamp current
  - Does not meet present or future diesel emission requirements
- 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

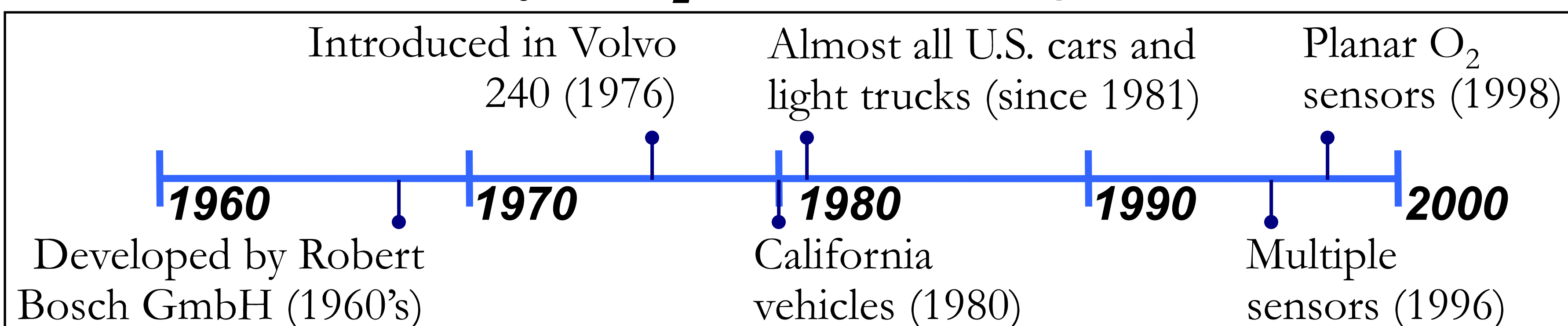
Solid-state electrochemical sensors are a proven robust technology for measuring O_2 in exhaust to control emissions—NO_x sensors build upon this technology

Schematic and picture of O_2 sensor for air/fuel control



(E.M. Logothetis <u>in</u> Chemical Sensor Technology, 3, Kodansha Ltd.: 1991, p. 89)

History of O_2 sensor development



Major milestones for fiscal year (FY) 2008 and 2009

- **FY 2008**
  - Refined criteria for sensor materials and configurations
  - Performed engine dynamometer test of FY 07 prototypes
  - Evaluated performance of electronically conducting oxides
  - Investigated cross-sensitivity to interfering gases
  - Improved sensor platform to consider commercial design constraints
- **FY 2009**
  - Received initial feedback from potential commercialization entities, with Ford leading the discussions
  - Perform engine dynamometer test of next generation prototypes
  - Complete longer-term test for stability of FY 08 prototypes and initiate testing with integrated heater substrates
    - Decide whether to focus efforts on metal or oxide sensing electrodes
  - Evaluate methods for compensating for cross-sensitivity
  - Narrow focus to most promising strategies to improve accuracy
  - Continue discussions with potential commercialization entities

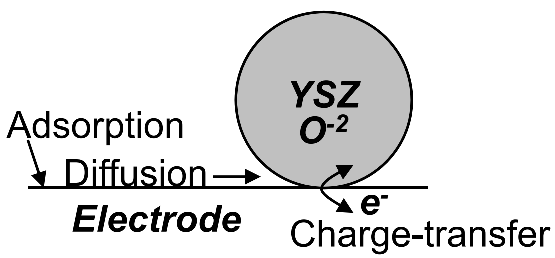
Approach: LLNL developed unique design and measurement strategy leverages proven robust solid-state electrochemical technology

- 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)

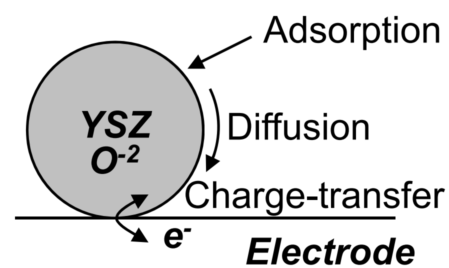
- Understanding sensing mechanisms is key to sensor development: parallel contributions of O_2 and NO_x reactions at porous YSZ/electrode interface

Low sensitivity



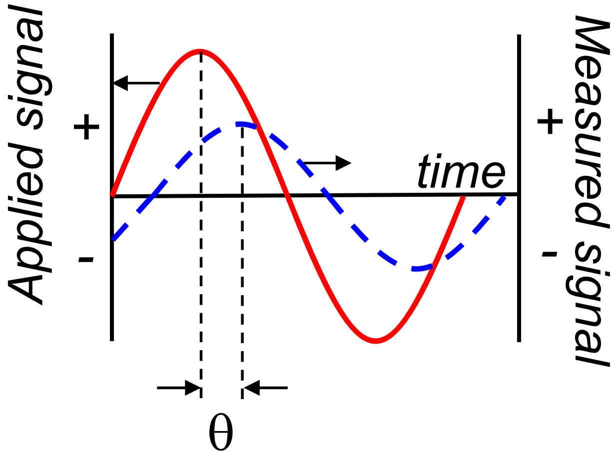
Minimal NO_x response when electrode surface dominates

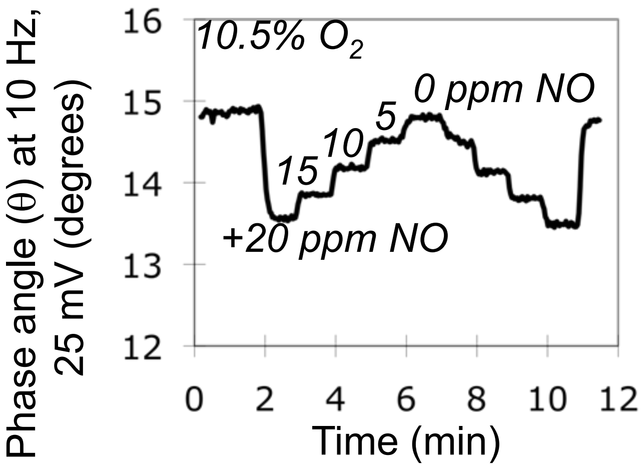
High sensitivity



Larger NO_x response: controlling microstructure and composition is essential

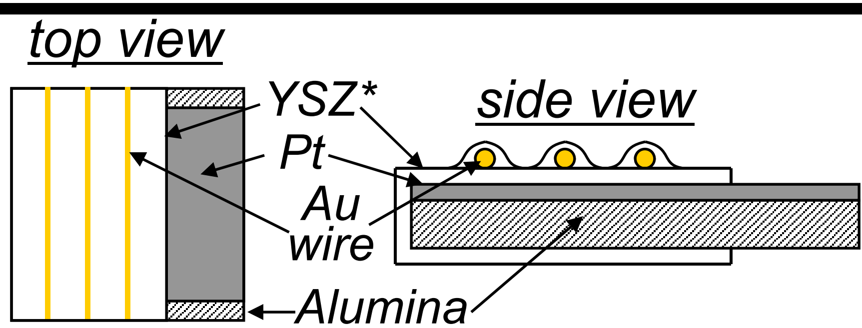
In our alternating current (ac) measurement strategy, the phase angle (θ) is correlated with the level of NO_x in the exhaust





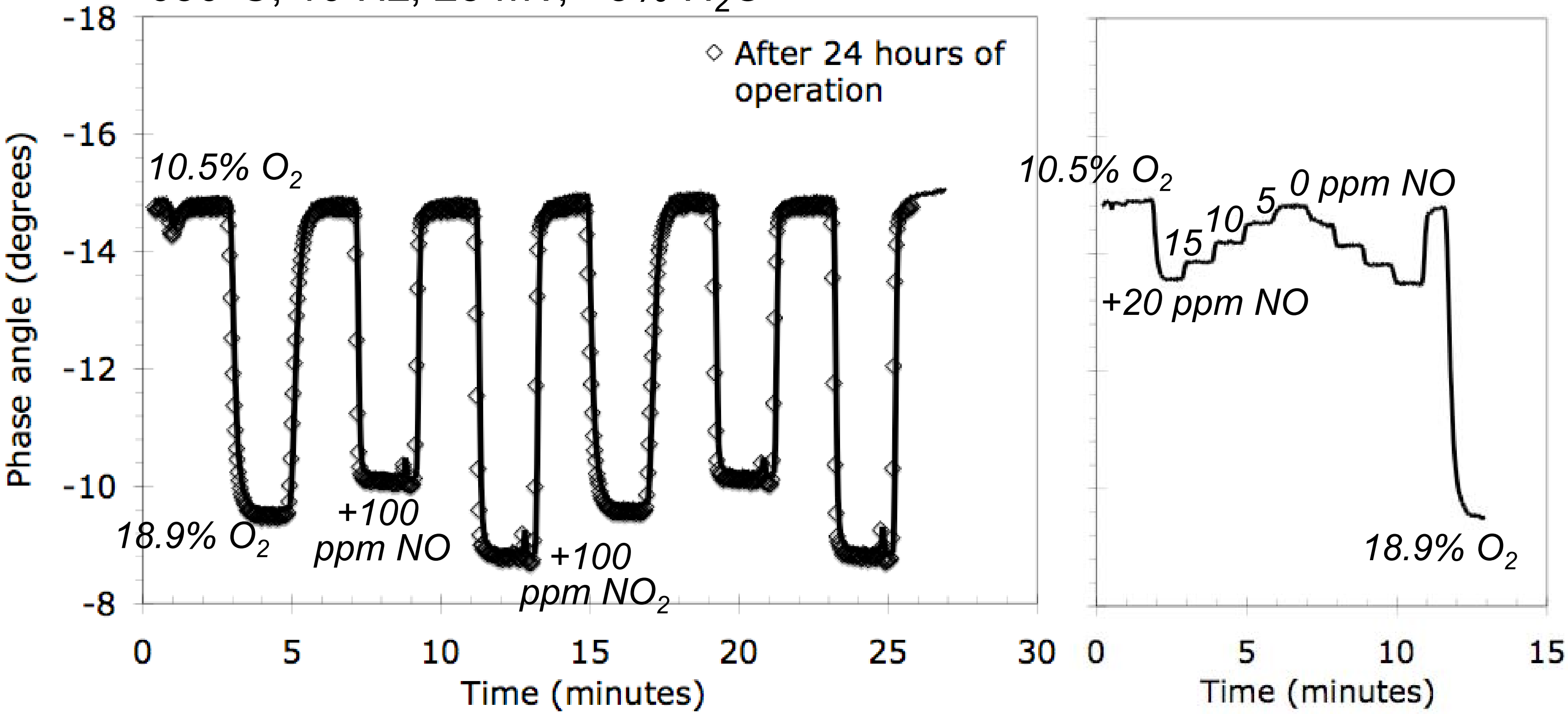
- Similar to electrical resistance, which measures the opposition to an electrical current, impedance measures the opposition to a time-varying current (i.e., alternating current, ac)
  - Impedance is a complex quantity with both magnitude and phase angle (θ) information
- For the electrochemical LLNL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

Technical accomplishment: Last year, presented promising results for a laboratory prototype using an alumina substrate that focused on a more commercializable design

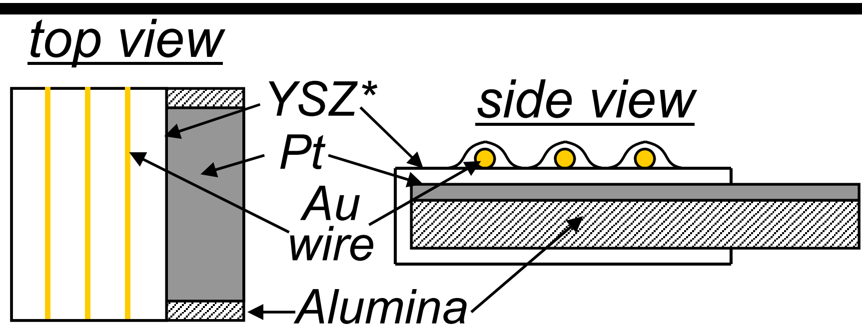


*yttria-stabilized zirconia: oxygen-ion conducting ceramic

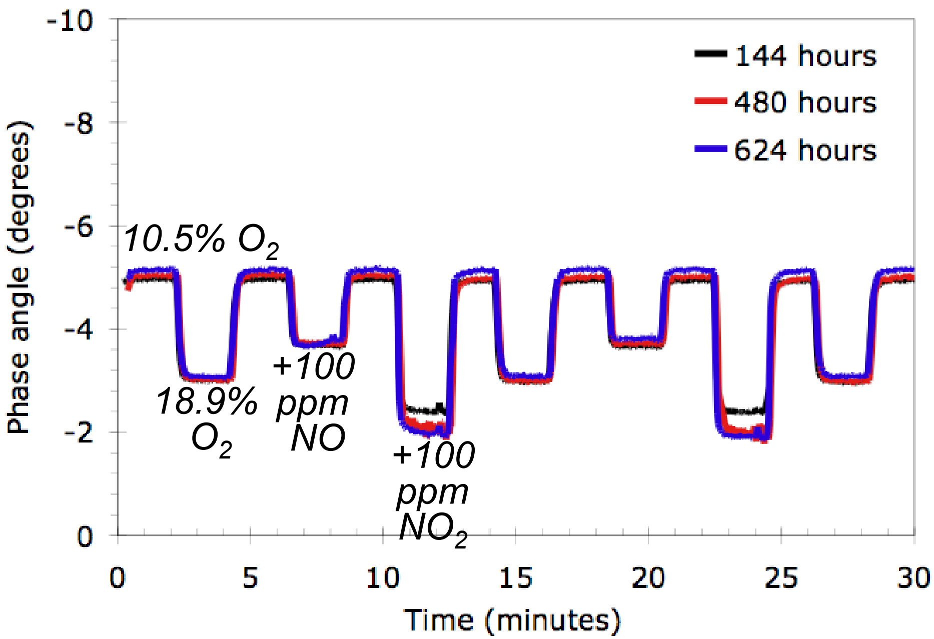
650°C, 10 Hz, 25 mV, ~3% H_2O



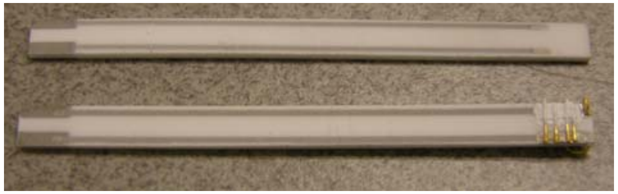
Technical accomplishment: Recently, achieved crucial milestone by demonstrating longer-term (more than 600 hours) stability at operating temperatures of 650°C

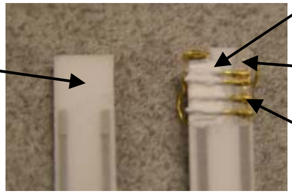


*yttria-stabilized zirconia: oxygen-ion conducting ceramic



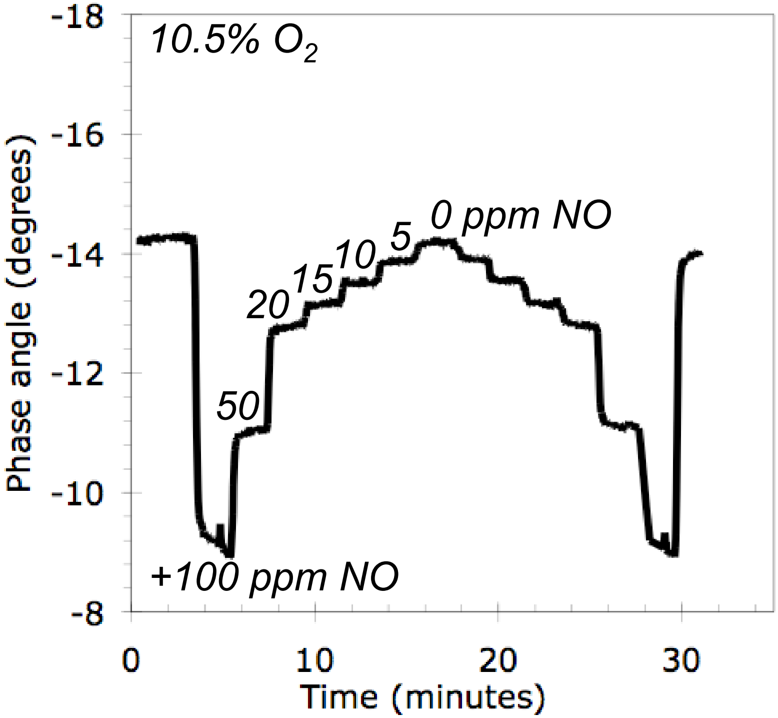
Technical accomplishment: Met another milestone by developing a more advanced prototype, taking a further design step towards future commercialization



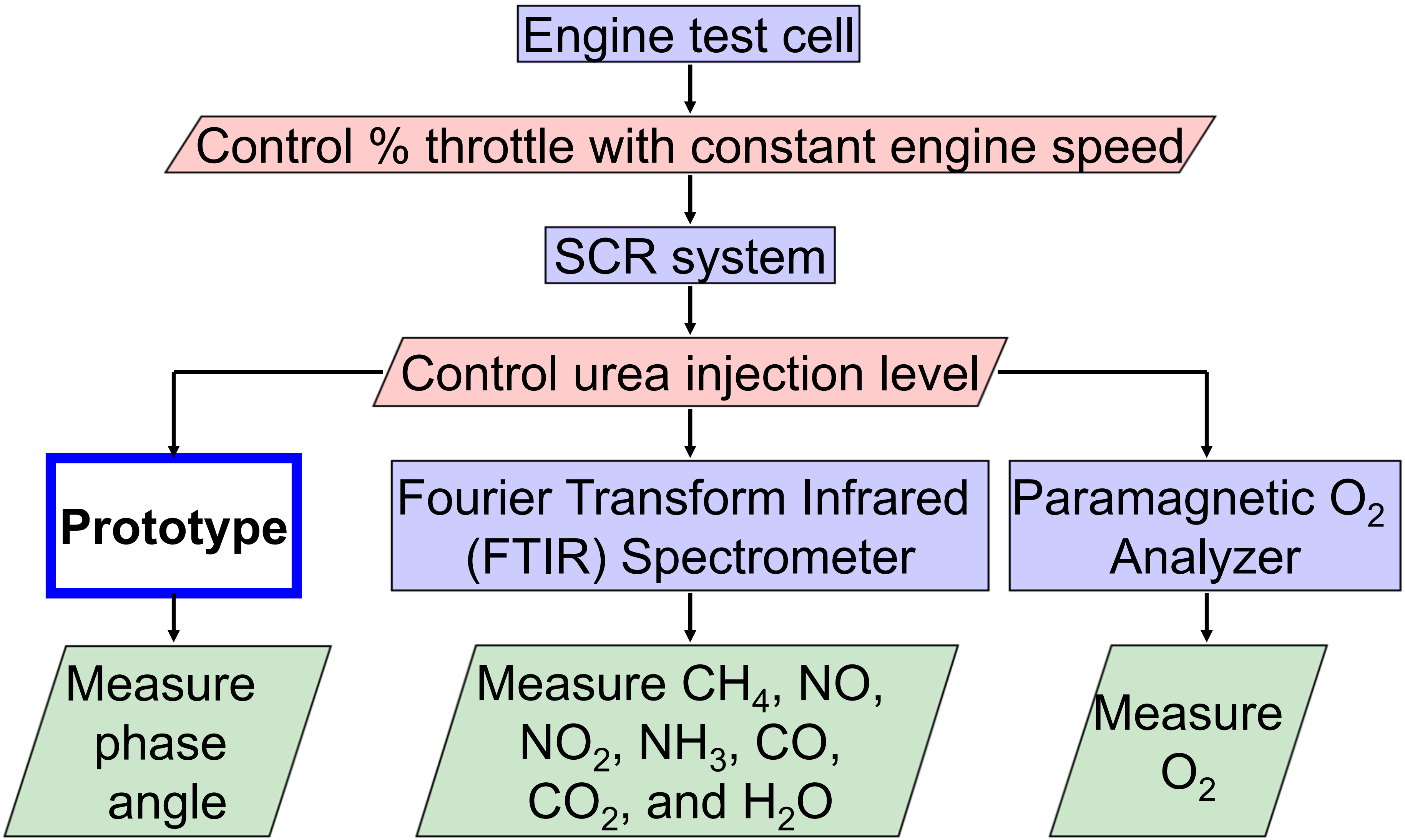


*yttria-stabilized zirconia

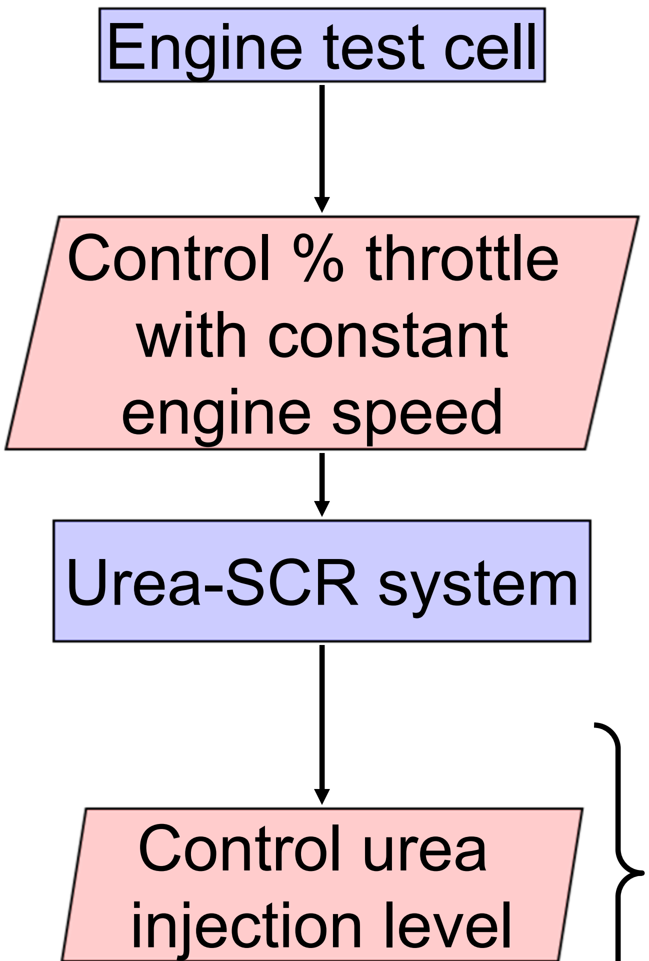
- More advanced prototype built on an alumina substrate, provided by Ford, with an integrated heating element
- Substrate packaged by U.S. automotive supplier into a commercial sensor housing



Technical accomplishment: Successful diesel engine dynamometer test at Ford Research Center using a urea-based selective catalytic reduction (SCR) system



Engine test cell: Use two different test sequences, one to isolate the NO_x response and another to investigate oxygen cross-sensitivity



<u>Test Sequence 1:</u>

*Isolating NO_x response

Constant 30% throttle

Initially minimize NO_x, then step to lower urea (higher NO_x concentrations)

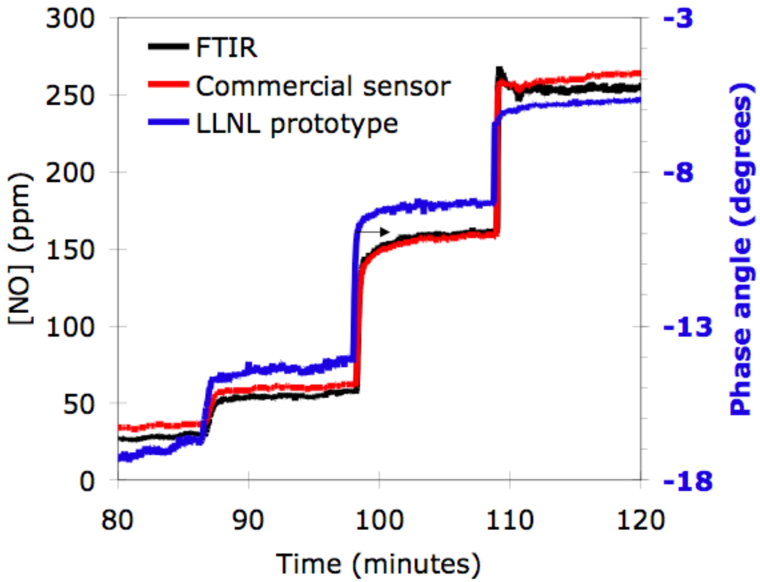
<u>Test Sequence 2:</u>

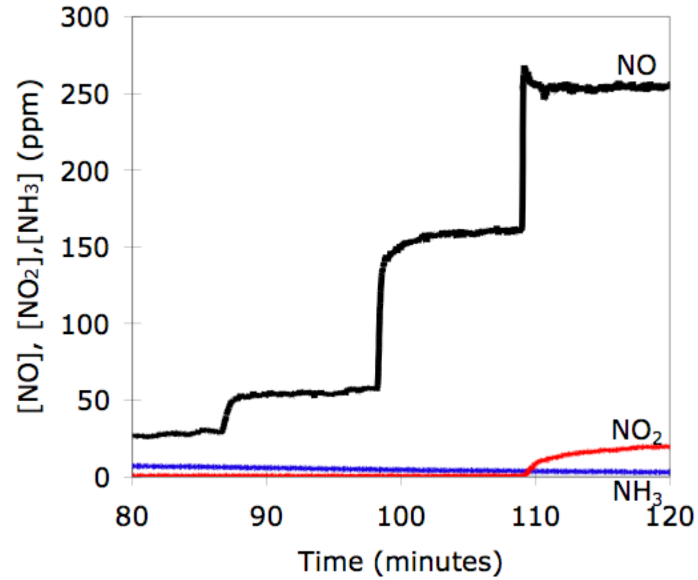
*O_2 cross-interference

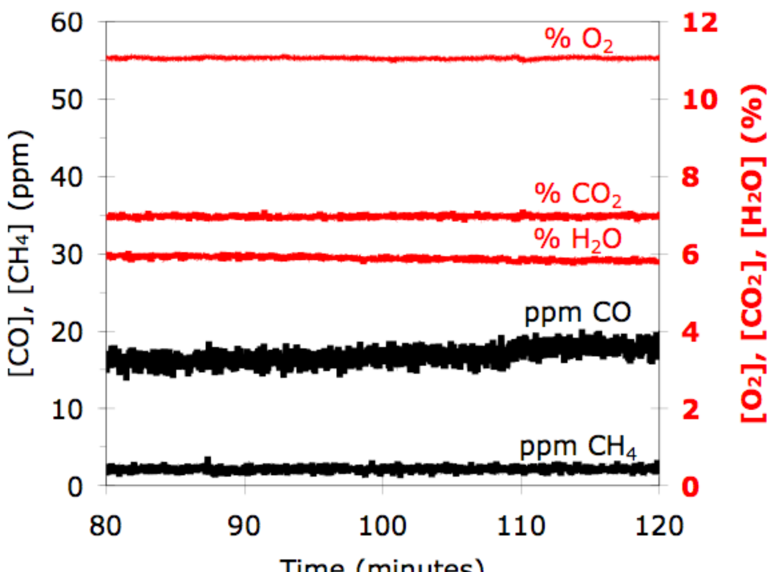
Initially 30% throttle, then step 40-35-32.5-30%

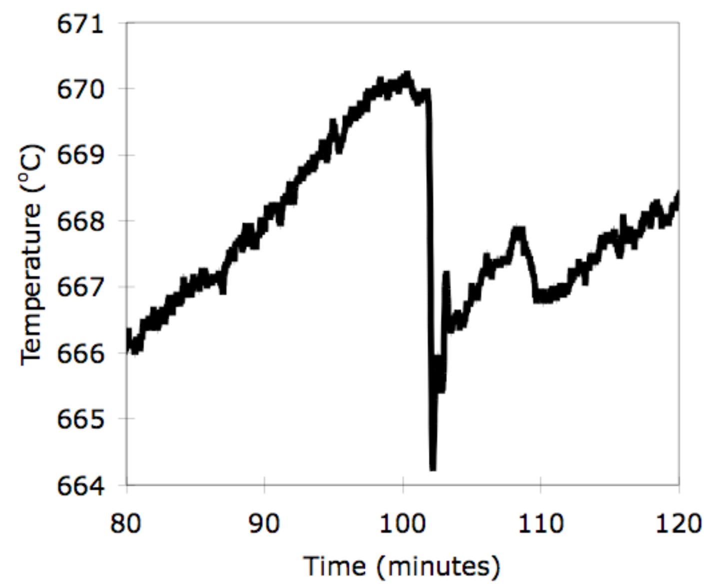
Constant urea to minimize NO_x at 30% throttle

Test sequence 1: Prototype detects NO_x in the exhaust, with a signal that agrees with a commercial sensor

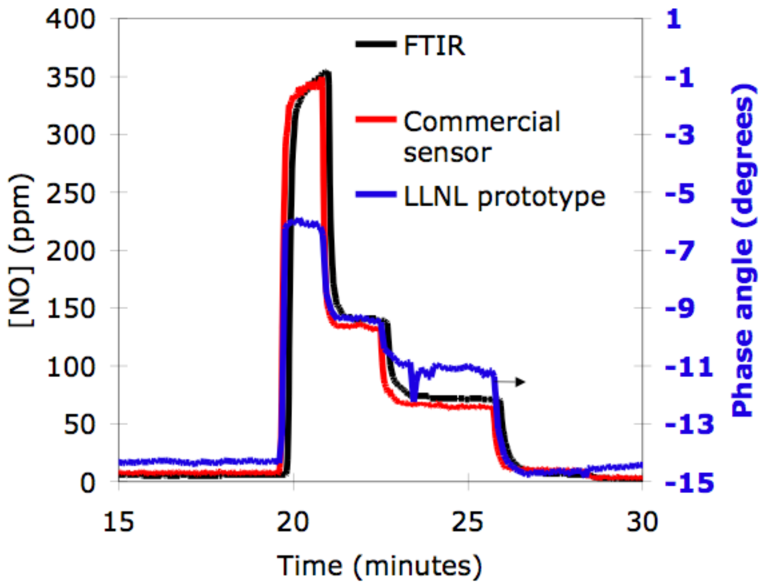


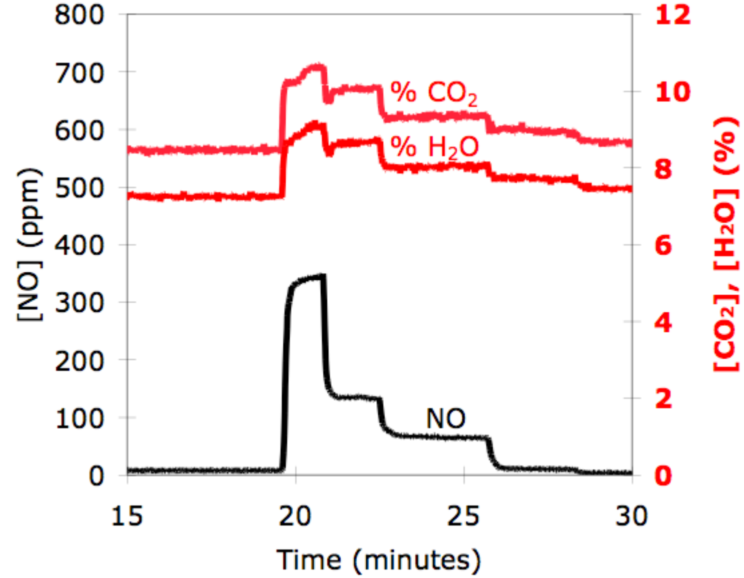


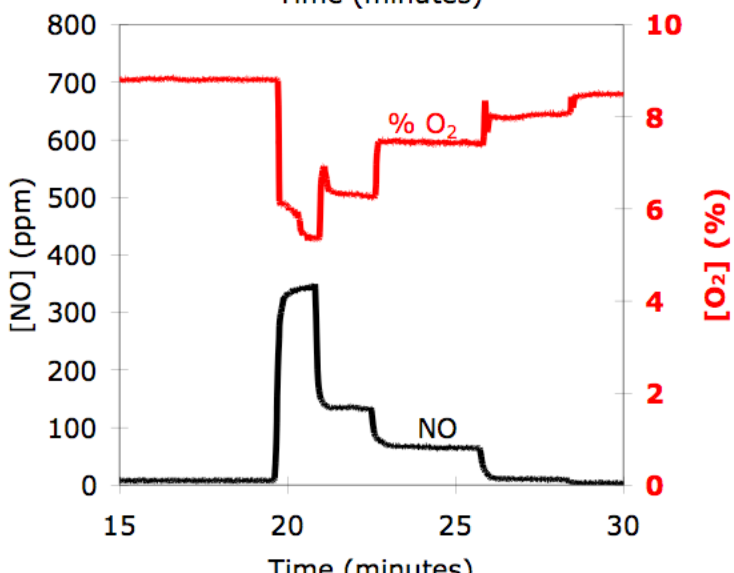


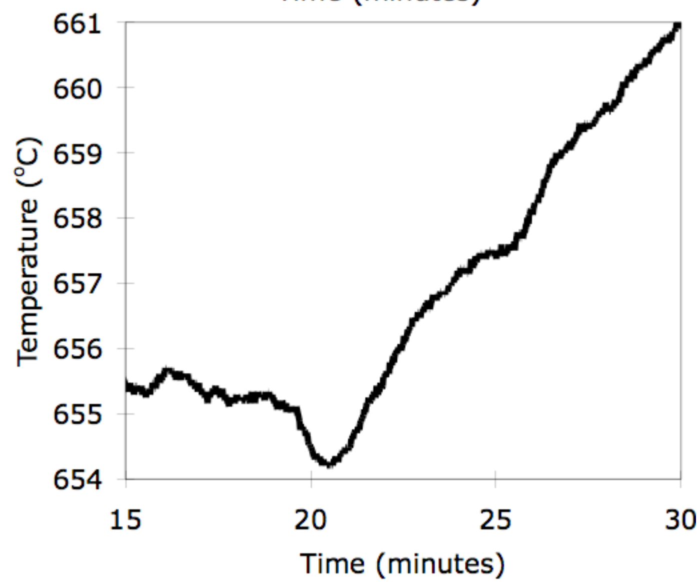


Test sequence 2: Prototype has same trend as a commercial sensor, but different relative response magnitude due to oxygen interference

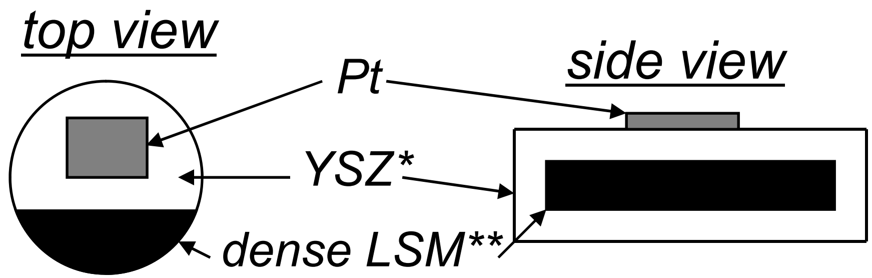






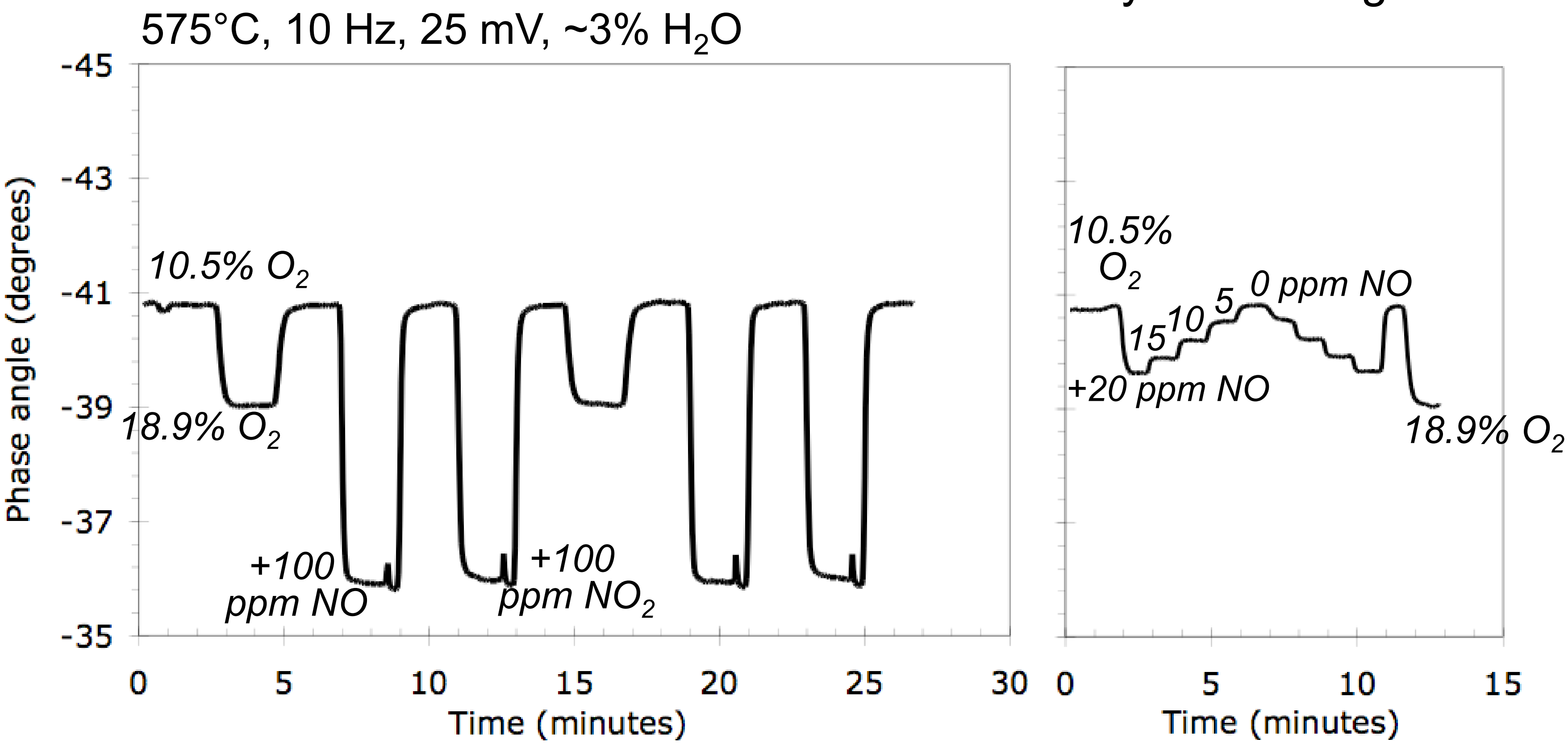


Technical accomplishment: Last year, showed prototype with high-temperature materials for lower cost processing and thermal expansion matching for improved stability

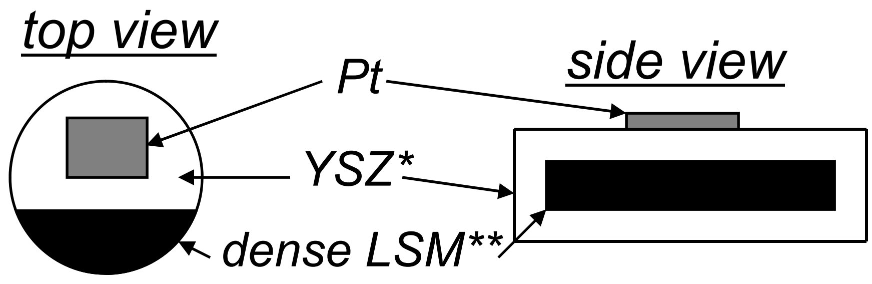


*yttria-stabilized zirconia: oxygen-ion conducting ceramic

**LSM ($La_{0.85}Sr_{0.15}MnO_3$): electronically conducting oxide



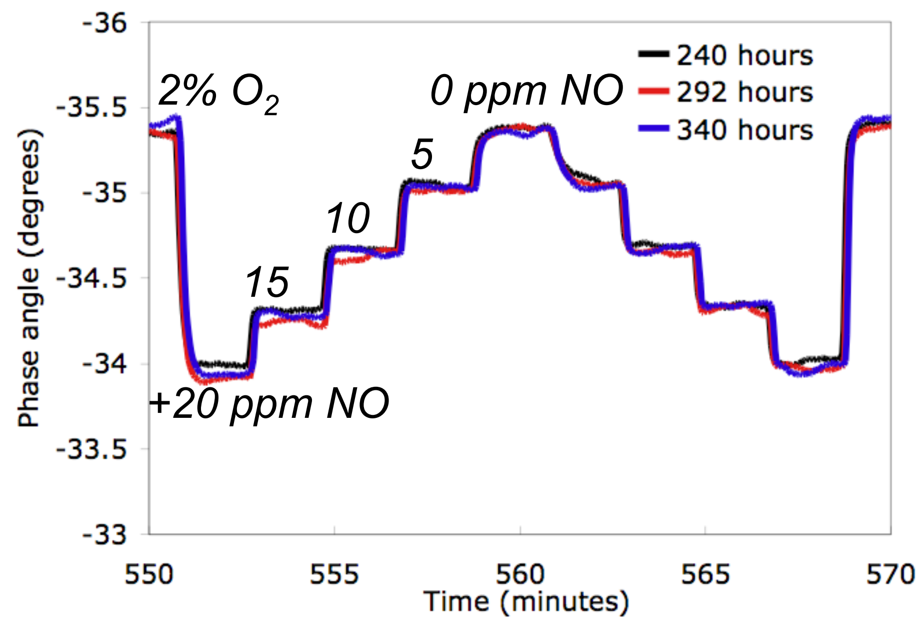
Technical accomplishment: Met recent milestone by completing initial longer-term stability testing



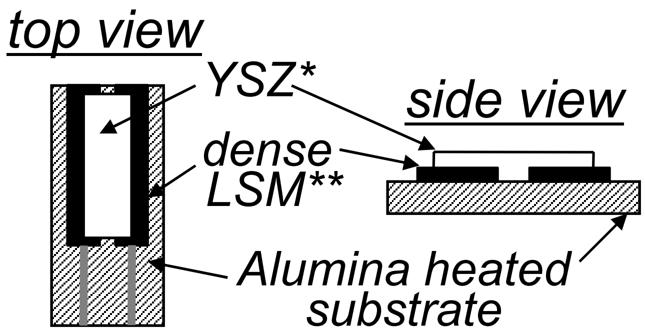
*yttria-stabilized zirconia: oxygen-ion conducting ceramic

**LSM ($La_{0.85}Sr_{0.15}MnO_3$): electronically conducting oxide

- Initial signal drifts up to ~ 240 hrs
- Stable for 100 hrs, then resumes drift
- Previous work has shown instabilities related to porous electrode



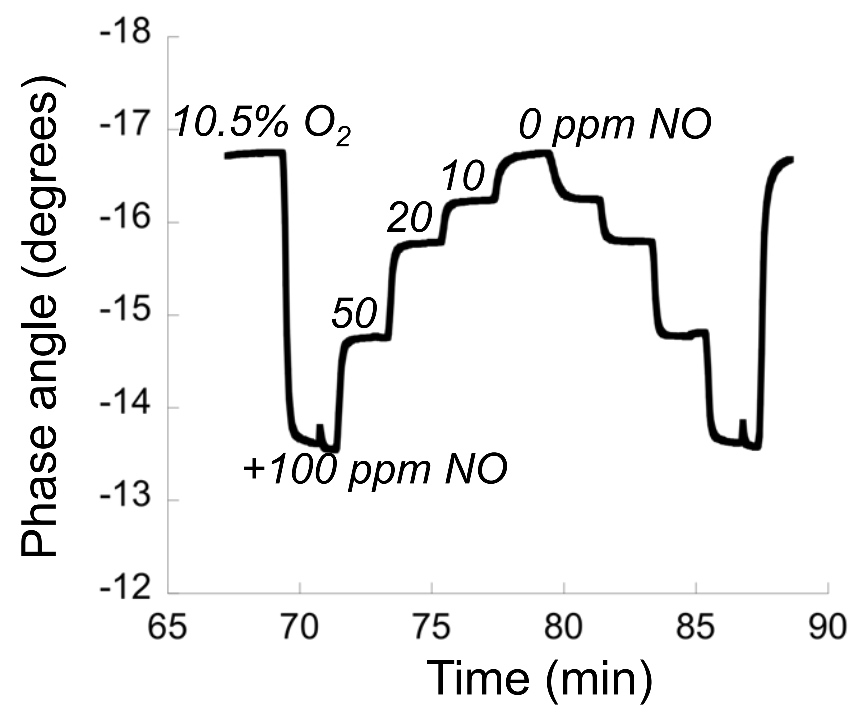
Technical accomplishment: Improved electronically conducting oxide prototype design and incorporated substrate with integrated heating element provided by Ford



*yttria-stabilized zirconia: oxygen-ion conducting ceramic

**LSM ($La_{0.85}Sr_{0.15}MnO_3$): electronically conducting oxide

- Similar to previous prototype replacing porous with dense materials
- Previous work has shown instabilities related to porous electrodes
- Advanced prototype built on an alumina substrate, provided by Ford, with an integrated heating element



Future Work: Remainder of fiscal year 2009

- Improve mechanical stability of current prototypes to improve reliability when packaging into a commercial sensor housing for longer-term testing on engines and vehicles
- Evaluate cross-sensitivity to interfering gases and temperature interference to determine ultimate accuracy levels that include noise factors
- Continue testing dense electronically conducting oxide electrodes with potentially better mechanical stability at high temperatures and processing flexibility (lower cost) than metal electrodes
  - *Milestone:* Completed evaluation of oxide electrodes
  - **Decision point:** Down select to metal or electronically conducting oxide electrodes

Future Work: Fiscal year 2010

- Continue electrochemical characterization of more advanced prototypes to refine criteria for optimizing and improving sensor design including evaluating configurations and platforms suitable for commercialization
  - Explore processing techniques for a manufacturable and robust sensor platform
  - **Decision point:** Select promising manufacturing platform(s) and techniques with Ford taking the lead to discuss with commercialization entity
  - *Milestone:* Dynamometer testing of more advanced prototype sensors
- Develop strategies to reduce cross-sensitivity and increase accuracy
  - *Milestone:* Compiled sensor data for interfering gases with operating parameters such as frequency and temperature
  - **Decision point:** Focus on intrinsic (dual-frequency) or extrinsic (separate O_2 measurement) for O_2 compensation

Future Work: Technology transfer

- Our Ford collaborators have taken the lead interfacing with potential commercialization entities, including two different 2nd Tier U.S. automotive suppliers, and will continue contacting other suppliers
- To aid in commercialization prospects and conversations with suppliers, extensive documentation of sensor performance and reliability are necessary
  - Strategies to increase sensitivity and accuracy and reduce cross-sensitivity and response time
  - Longer-term stability and performance data
  - Sensor configurations and platforms suitable for manufacturing
- Feedback from potential automotive supplier(s) will aid the sensor development pathway to commercialization

Summary

- High sensitivity, low-cost NO_x sensors are needed to meet emission requirements and enable widespread use of diesel vehicles with dramatically better fuel economies.
- We are developing a novel sensor with the potential to meet OEM cost and operational requirements, which available technology is currently unable to meet.
- In the past year, we have demonstrated more advanced prototypes with reasonable longer-term performance (> 500 hrs) and potentially more commercializable platforms using a substrate with an integrated heater that can then be packaged into sensor housings.
  - Our strong collaboration with Ford has enabled engine/vehicle testing and a pathway to commercialization with Ford contacting two different 2nd Tier suppliers and providing feedback about sensor development needs.
- Plans for next year focus on optimizing sensor materials and operation and developing a manufacturable platform to take the technology even further on the pathway to commercialization and attract potential suppliers.