Electrochemical NO_x Sensor for Monitoring Diesel Emissions

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in collaboration with

Ford Research and Innovation Center

2008 DOE Vehicle Technologies Merit Review

February 25, 2008

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This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

Outline

- Purpose of Work
- Barriers
- Approach
- Performance Measures and Accomplishments
- Technology Transfer
- Plans for Next Fiscal Year
- Summary
- Publications/Patents

Inexpensive NO_x emission sensors will accelerate the widespread introduction of diesel vehicles in North America

January, 2008

…if 33% of U.S. drivers switched…reduce oil consumption by about **1.5 million barrels per day**.

- Advantages of diesel technology:
  - Provides exceptional fuel economy
  - Completely compatible with biodiesel

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Estimate diesel light-vehicle penetration to increase from 3% (2007) to 14% by 2017

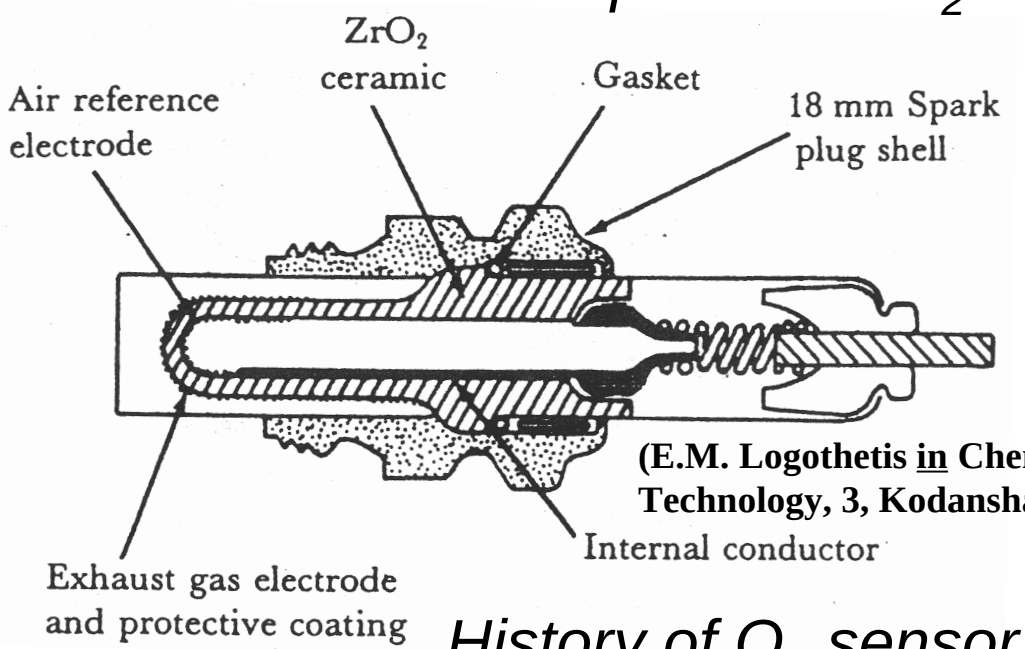
- Problem: Diesel technology is unable to meet stringent California Air Resources Board and U.S. EPA emission requirements for NO_x
- Goal: Develop new, low-cost, durable sensor technology for NO_x measurement and control

The technical performance requirements for NO_x sensors present significant development barriers

- Meeting California and U.S. EPA emission requirements will require a low-cost durable NO_x sensor
  - Performance requirements:
    - Sensitivity: < 5 ppm
    - Stability to achieve ± 1 ppm accuracy
    - Durability: 10 years/150,000 miles
    - Response time: $\tau_{10\text{-}90\%} \leq 2$ seconds for 10 to 50 ppm
    - Low cross-sensitivity to O_2, H_2O, and CO
    - Operating temperatures from 150-650°C with potential excursions to 900°C
  - Suitable sensor platform for manufacturability and commercialization

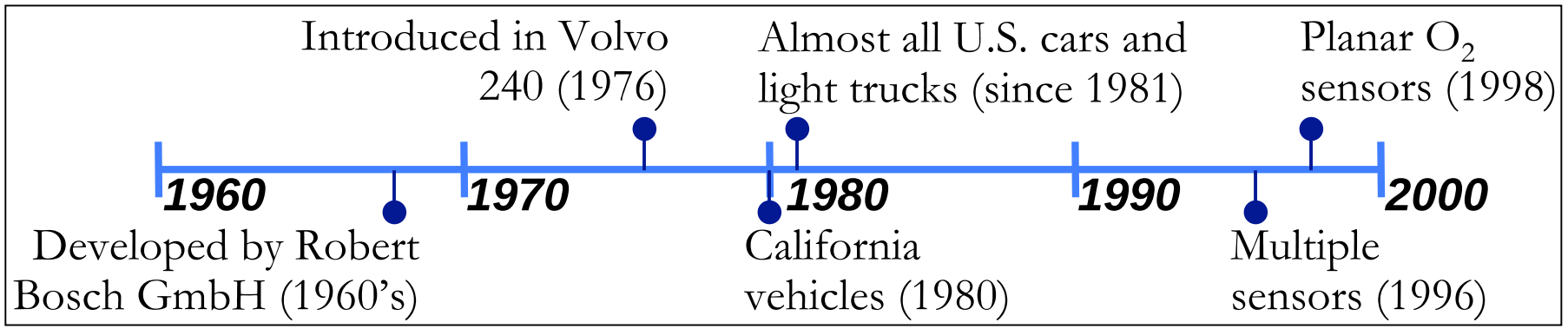
Solid-state electrochemical sensors are a proven robust technology for measuring exhaust emissions (O_2)—NO_x sensors build upon this technology

Schematic and picture of O_2 sensor for air/fuel control



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

History of O_2 sensor development



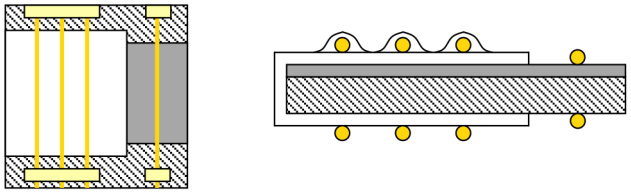
At the present time, available NO_x sensors do not meet cost and performance requirements

- Only one type of electrochemical NO_x sensor is commercially available
  - Based on Ford patent
  - Developed for lean-burn gasoline and diesel systems
  - Expensive due to design and operation
    - Complicated multiple-chamber design
    - Amperometric operation: measures dc current and requires complex electronics
  - Does not meet present or future diesel emission requirements

The solution is a new design and measurement strategy developed at LLNL

Prototype NO_x sensor

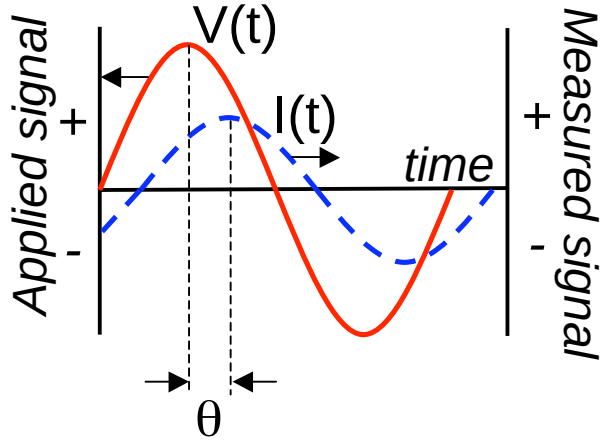
top view *side view*



- Based on proven robust electrochemical technology
- Unique measurement strategy uses complex ac impedance—electrical response to low-amplitude ac signal input

- Advantages over conventional dc voltage (potentiometric) and dc current (amperometric) operation:
  - *Higher sensitivity* - demonstrated < 5 ppm NO_x
  - *Better stability* - low-amplitude ac signal may prevent aging effects
  - *Better selectivity* - proper configuration provides total-NO_x sensing (potentiometric sensors give canceling signals)
  - *Inexpensive, simple device structure* - suitable for commercialization and manufacturability

In our impedancemetric measurement strategy, the phase angle (**θ**) is correlated with the level of NO_x in the exhaust



- Both magnitude (|Z|) and phase angle (θ) affected by ppm changes in NO_x
- Phase angle (θ) gives better stability and sensitivity at higher frequencies (10 Hz)

Measure response to low-amplitude (≤ 25 mV) alternating signal:

$$\underline{\textit{Complex Impedance:}}\ Z(\omega) = \frac{V(t)}{I(t)}$$

$$Z(\omega) = \mathrm{Re}(Z) + j\mathrm{Im}(Z)$$

$$\underbrace{\mathrm{Re}(Z)}_{\textbf{Real impedance}} = |Z|\cos\theta \qquad \underbrace{\mathrm{Im}(Z)}_{\textbf{Imaginary impedance}} = |Z|\sin\theta$$

$$\textbf{Magnitude:}\ |Z| = \sqrt{(\mathrm{Re}(Z))^2 + (\mathrm{Im}(Z))^2}$$

$$\textbf{Phase angle:}\ \theta = \tan^{-1}\left(\frac{\mathrm{Im}(Z)}{\mathrm{Re}(Z)}\right)$$

Performance measures and accomplishments: significant progress has been made satisfying sensor requirements

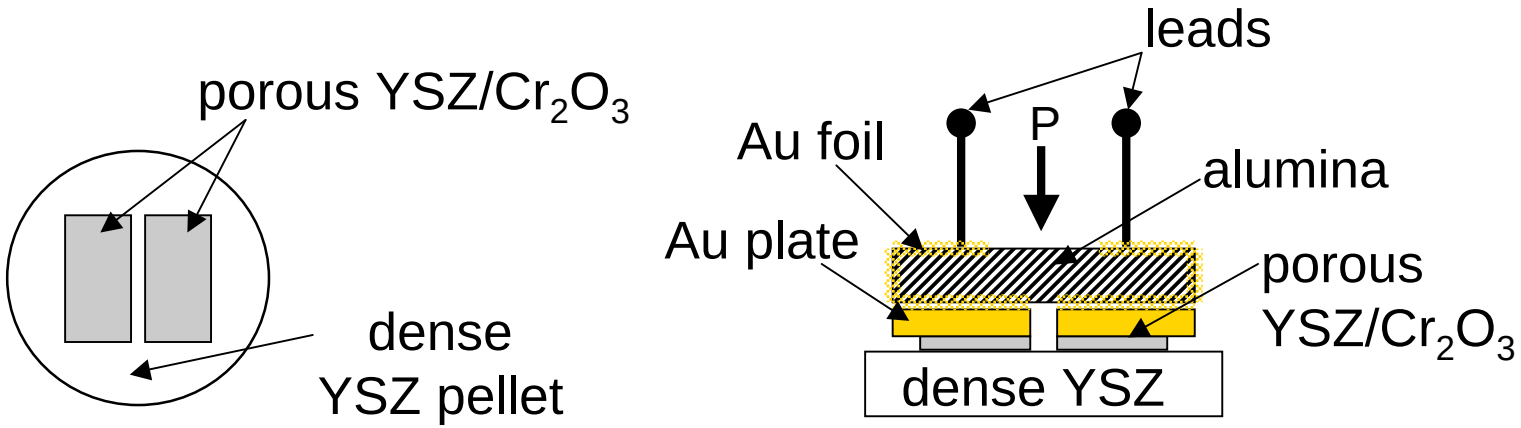
Low-cost materials and processing	✓
Sensitivity to ppm NO_x	✓
High-temperature operation	✓
Stability and durability	✓–
Low cross-sensitivity to interfering gases	✓–
Manufacturability	✓–
Response time	✗

✓: satisfied

✓–: partially satisfied

✗: not satisfied

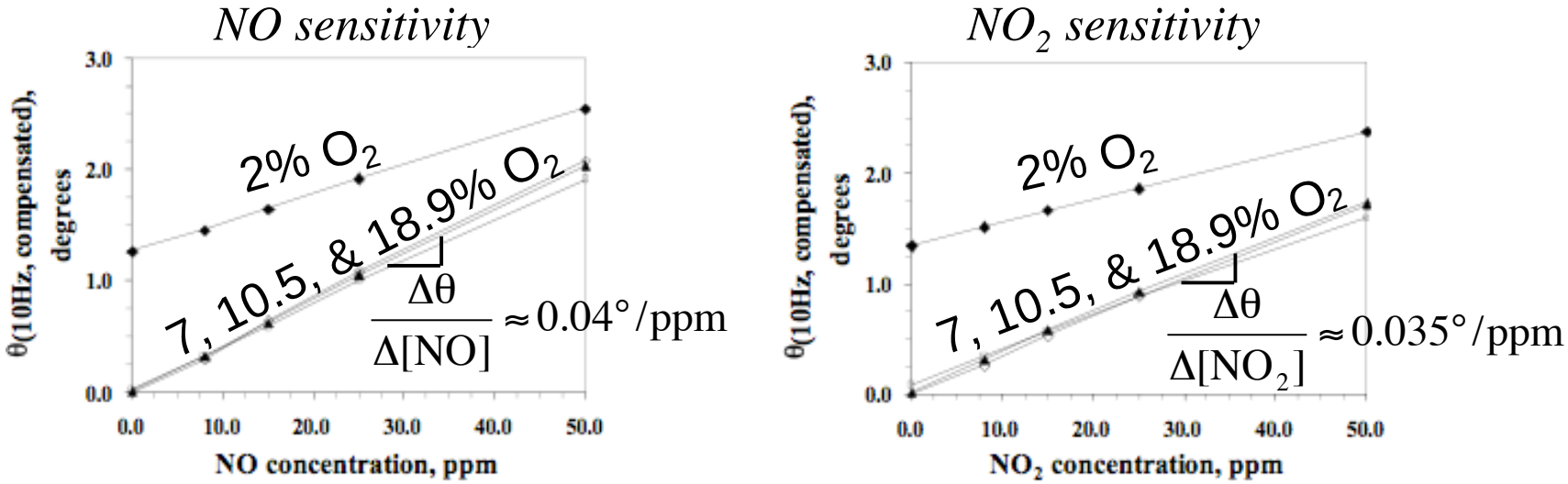
Early laboratory prototype sensor demonstrated feasibility of impedancemetric sensing



- Symmetric electrochemical cell:
  - Dense YSZ pellet and Au plate with porous YSZ/Cr_2O_3 composite between Au and YSZ
  - Simple design, well-studied materials
- Configuration requires constant spring-loaded pressure—not suitable for commercialization

*Martin, et al., *J. Electrochem. Soc.*, **154**, J97 (2007)

Using multiple frequency measurements, we have been able to compensate for O_2 cross-sensitivity in the range of 7-18.9% O_2



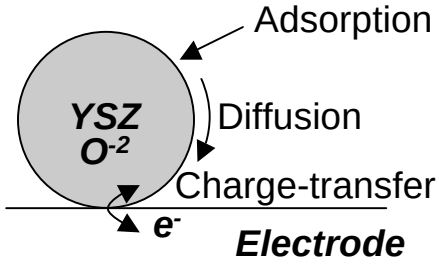
- θ sensing signal at 10 Hz compensated with 1 kHz signal
  - Deviation of 2% O_2 data due to slow O_2 response
- Similar sensitivity to NO and NO_2: Detection limit < 8 ppm NO_x
- 10-90% response time ($\tau_{10\text{-}90\%}$) for NO_x < 6 sec
  - NO_x response at least three orders of magnitude faster than O_2 response
  - Slow O_2 response due to presence of Cr_2O_3

Understanding the sensing mechanism(s) is key to developing an improved sensor

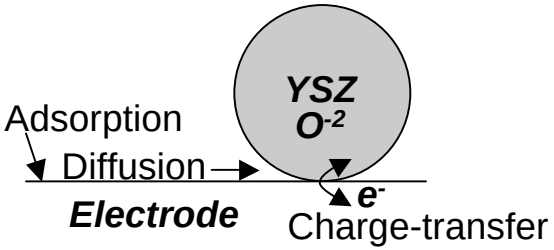
Parallel contributions of O_2 and NO_x reactions at porous YSZ/electrode interface:

$$R_{total} = \left(\frac{1}{R_{O_2}} + \frac{1}{R_{NO_x}} \right)^{-1}$$

High NO_x sensitivity



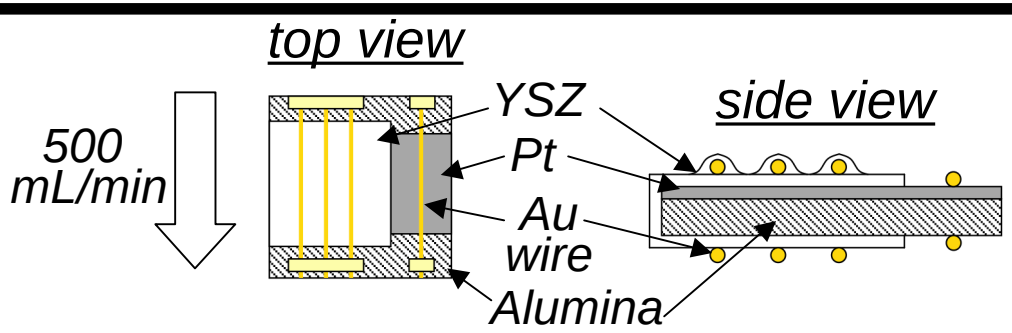
Low NO_x sensitivity



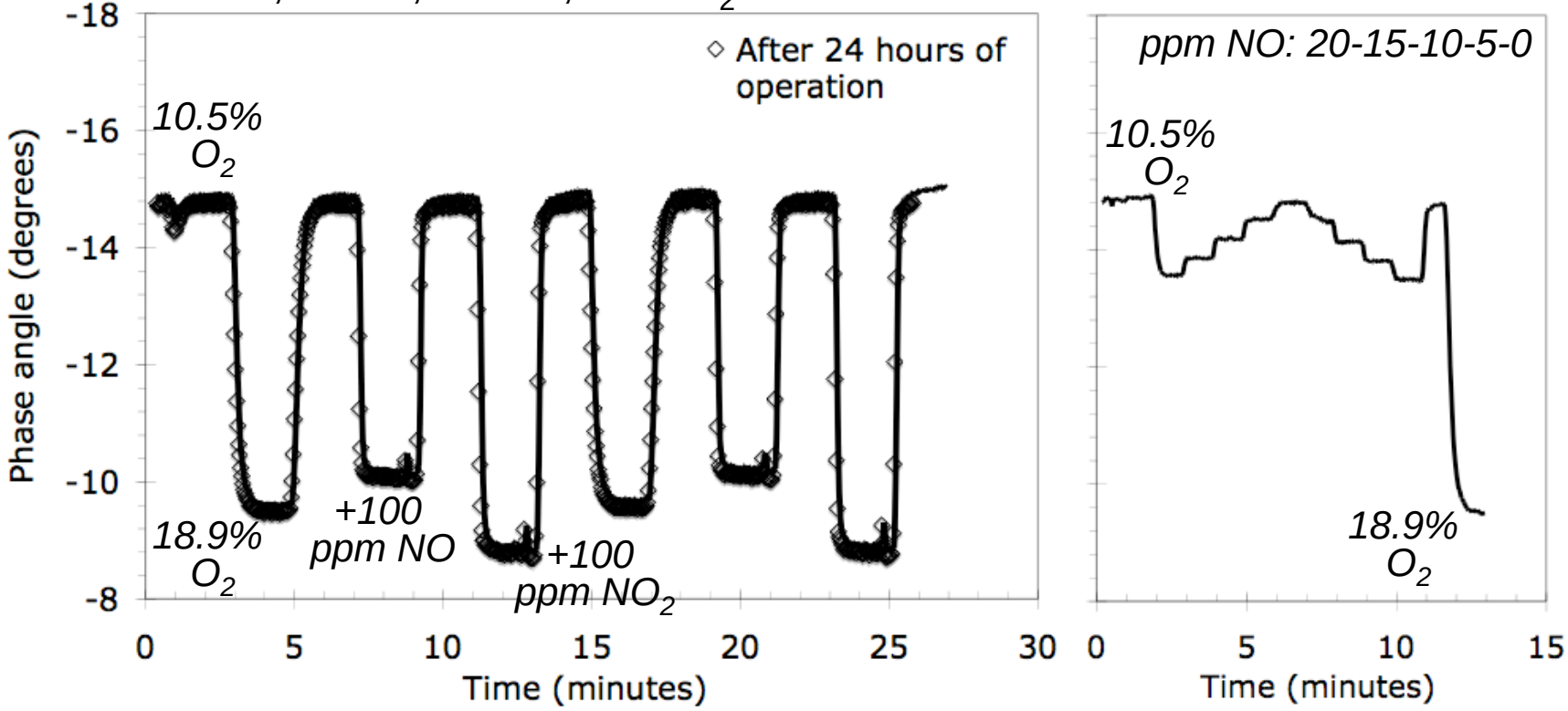
- Processes proceed on electrodes with better O_2 catalytic activity
- Much larger contribution of O_2 to electrode polarization compared to NO_x

- Sensing relies on electrodes with poorer O_2 catalytic activity so rate-limiting processes occur on YSZ
- More comparable contributions from O_2 and NO_x
  - Equivalent circuit analysis suggests likely rate-limiting steps:
    - O_2 surface diffusion on YSZ
    - NO_x adsorption on YSZ

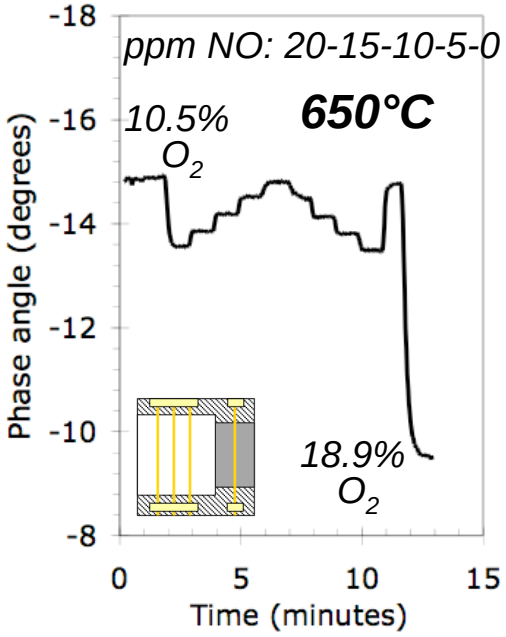
Recent prototype using an alumina substrate has focused on a more commercializable design

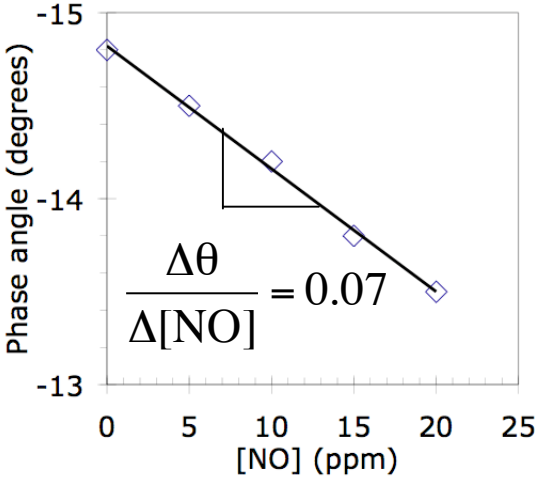


650°C, 10 Hz, 25 mV, ~3% H_2O



Alumina substrate prototype has large cross-sensitivity to O_2, but better NO_x sensitivity than early prototypes





- Large cross-sensitivity to O_2
  - 1 kHz signal too small to be useful for O_2 compensation
  - NO sensitivity of θ at 10.5% O_2:

$$\frac{\Delta\theta}{\Delta[NO]} = 0.07^\circ/\text{ppm}$$

- Sensitivity down to < 5 ppm NO
- Similar response time for O_2 and NO
  - 10-90% response time: $\tau_{10\text{-}90\%}$ < 10 sec.

Currently discussing with Ford several options for O_2 compensation

Performance measures and accomplishments: significant progress has been made satisfying sensor requirements

Low-cost materials and processing	✓
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Technology transfer: our collaborators at Ford have taken the lead to interface with suppliers

- Development will be completed within three years:
  - Characterize sensor performance with interfering gases
    - Implement strategies to reduce cross-sensitivity, increase sensor accuracy, and reduce response time
  - Compile long-term stability data
  - Evaluate sensor configurations and platforms suitable for commercialization
  - Evaluate readiness of sensor performance/platform for approaching suppliers
- Obtain feedback from potential commercialization entity/automotive supplier

Plans for next fiscal year (slide 1 of 2)

- Continue detailed electrochemical evaluation of mechanisms
  - Use impedance spectroscopy to identify important species and rate-limiting steps
    - *Milestone:* Refinement of criteria for suitable materials and configurations based upon mechanistic understanding
- Continue exploring stable electronically-conducting oxides for electrodes
  - Potentially have better stability at high temperatures and better processing flexibility (lower cost) than metal electrodes
    - *Milestone:* Evaluation of of oxide electrodes
    - **Decision point:** Down select to metal or electronically-conducting oxide electrodes

Plans for next fiscal year (slide 2 of 2)

- 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
  - ***Milestone:*** Dynamometer testing of prototype sensors
- Evaluate configurations and platforms suitable for commercialization
  - Explore processing techniques for a manufacturable sensor platform
    - ***Milestone***: Select promising manufacturing platform(s) and Ford will take the lead to discuss with commercialization entity

Summary (slide 1 of 2)

- Diesel technology will play a crucial role in reducing petroleum usage—potentially by ~1.5 million barrels per day if 33% of U.S. drivers were to switch
- High sensitivity, low-cost NO_x sensor in conjunction with appropriate exhaust after-treatment, i.e., lean NO_x trap or urea selective catalytic reduction, is necessary for meeting emission requirements and enabling widespread use of diesel vehicles in U.S.
- We are developing a novel sensor with the potential to meet OEM cost and operational requirements, which current technology does not:
  - High sensitivity (< 5 ppm NO), low cost, improved stability, similar responses to NO and NO_2, and ability to compensate for cross-sensitivity to other gases
  - Materials (in part) derived from proven O_2 automotive sensor
  - Unique impedancemetric measurement strategy

Summary (slide 2 of 2)

- Sensing mechanism depends on porous YSZ/dense electrode interface and relies on the poor O_2 catalytic activity of the electrode
- Prototypes more suitable for manufacturing and commercialization have been developed using an alumina substrate
- Strong collaboration with Ford Motor Company enables on-vehicle testing and pathway to commercialization
  - Ford is taking the lead on finding potential suppliers and will provide feedback on supplier's needs
- Plans for the next fiscal year focus on optimizing sensor materials and operation and developing a manufacturable platform

Publications, Presentations, and Patents (slide 1 of 2)

- Presentation made at the 32nd International Conference & Exposition on Advanced Ceramics and Composites, Jan. 27 - Feb. 1, 2008, in Daytona Beach, FL:
  - "Sensing Mechanism of Impedancemetric NO_x Gas Sensors Based on Porous YSZ/Dense Electrode Interfaces"
- "Investigating the Stability and Accuracy of the Phase Response for NO_x Sensing 5% Mg-modified $LaCrO_3$ Electrodes," *ECS Transactions*, accepted, (2008).
- "Effect of Electrode Composition and Microstructure on Impedancemetric Nitric Oxide Sensors Based on YSZ Electrolyte," *J. Electrochem. Soc.*, **155**(1):J32-J40 (2008).
- "Impedance Characterization of a Model Au/Yttria-stabilized Zirconia (YSZ)/Au Electrochemical Cell in Varying Oxygen and NO_x Concentrations," *J. Electrochem. Soc.,* **154**(4):J129–J135 (2007).
- "Impedancemetric NO_x Sensing Using YSZ Electrolyte and YSZ/Cr_2O_3 Composite Electrodes," *J. Electrochem. Soc.,* **154**(3):J97–J104 (2007).

Publications, Presentations, and Patents (slide 2 of 2)

- Presentations made at the 211th Electrochemical Society Meeting, May 6 - 11, 2007 in Chicago, IL:
  - "Investigating the Stability and Accuracy of the Phase Response for NO_x Sensing 5% Mg-modified $LaCrO_3$"
  - "Role of Electrode Composition and Microstructure in a YSZ-Based Impedancemetric NO_x Sensor"
- U.S. Patent 7,153,401 B2 entitled "Current biased potentiometric NO_x sensor for vehicle emissions," by L.P. Martin and A.Q. Pham was awarded December 26, 2006.
- Presentations/published conference proceedings from the Fall Meeting of the Materials Research Society, Nov. 27 – Dec. 1, 2006 in Boston, MA:
  - "Impedancemetric Technique for NO_x Sensing Using a YSZ-Based Electrochemical Cell"
  - "Impedance Analysis of Electrochemical NO_x Sensor Using a Au/Yttria-Stabilized Zirconia (YSZ)/Au cell"