NO_x Sensor Development (CRADA w/ Ford Motor Company)

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PM_9118
Armstrong

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NO_x Sensor Development (CRADA with Ford)

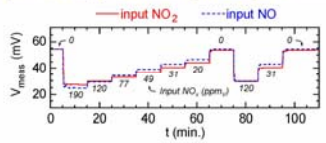
21CTP Technical Goal: Develop and demonstrate an emissions compliant engine system for Class 7-8 highway trucks that improves the engine system efficiency from ~42% today to 50% by 2010.

Project Objectives
Develop NO_x sensors suitable for OBD (remediation and/or monitoring) of diesel engine exhausts.

FY 2005 Focus
1. Stability of electrode materials.
2. Cross-sensitivity.

Planned Duration
October 2001 to September 2006

DOE Funding/Industry Cost Share
FY04: $200K/$200K; FY05: $175K/$175K



"Total NO_x" (similar response to NO and NO_2) sensing behavior of ORNL sense element at 600 °C with 7% O_2.

Principal Investigator(s)
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Accomplishments
1. Developed electrochemical total NO_x sensor (January 04).
2. Developed electrochemical NO-selective sensor (September 04).
3. Eliminated electrode stability issues in steam (July 05).

Significant Future Milestones
Characterize cross-sensitivity and performance of new electrode compositions in real (dyno) exhausts (Dec. 05).

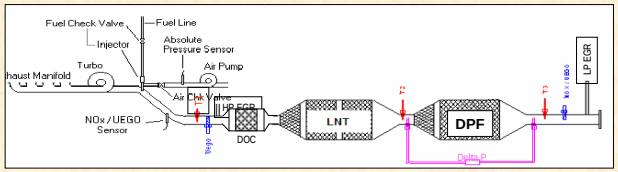
Project ID/Agreement ID	Program Structure	Sub-Program Element	R&D Phase	Date
PM_9118	Materials Technology	HV Propulsion Materials	Applied Research	8-11-05

Objective

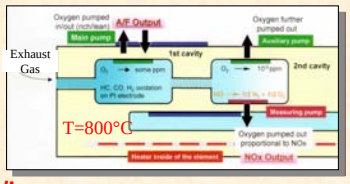
- **Development of NO_x sensor for use with Lean NO_x Trap (LNT) and Selective Catalytic Reduction (SCR) systems**
  - ***Sensors are needed to control trap regeneration (LNT) and reagent injection (SCR)***

Use environment / requirements

- **T ~ 600 °C**
- **$[NO_x]$ 10-1000 ppm**
- **"NO_x" a mixture of NO and NO_2 ($[NO]:[NO_2]$ unknown)**
- **Varying $[O_2]$ and $[H_2O]$**
- **Other redox gases (CO and C_yH_z) *may* be present**



NO_x Sensor



Amperometric, dual-cell
Ford US Patent in 1992

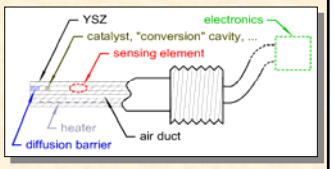
Status/Issues:

- Only production NO_x sensor available for MY2010
  - only 2 suppliers worldwide: NGK Locke / Siemens, NTK (Market Study w/Ford Purchasing)
  - not from Bosch, Delphi or Denso for MY2010
- Main issues
  - cannot currently meet specification
  (at best: ±10-20 ppm w/o noise factors)
  -cost (~$75-$100)

- Industry-wide (EMA) consensus that current NO_x sensors are not accurate enough, this is especially supported by those that are attempting to meet T2B

NO_x Sensor Development CRADA

- **Oak Ridge National Laboratory**
  - T. Armstrong, **F. Montgomery, D. West**
    - **Materials development**
    - **Sensor response measurements (I-V characteristics…)**
- **Ford Motor Company**
  - J. Visser, **R. Soltis, D. Kubinski, R. Novak, E. Murray**
    - **Electrode adhesion/mechanical stability**
    - **Sensor design / thermal management**
- **Lawrence Livermore National Laboratory**
  - R. Glass, **L. P. Martin, S.-w. Song**
    - **Sensing mechanisms**
    - **Impedance Spectroscopy**



- **Ford in discussion with 2 diesel engine manufacturers to join project**

Technical Approach

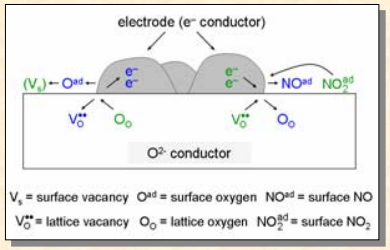
- Investigate use of DC electrical biasing to enhance the NO response of solid electrolyte-based NO_x sensing elements
  - ⇒ Co-planar sensing elements based on YSZ
  - ⇒ Survey electrode materials, look for commonalities
  - ⇒ Vary electrode geometry and T, study effect(s) on response magnitude and speed

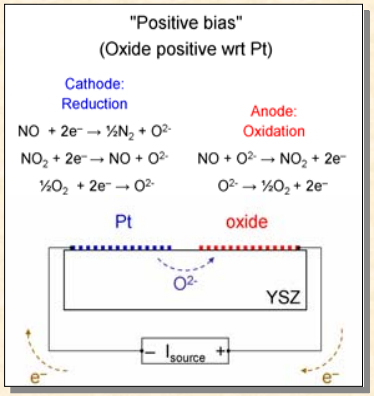
- Substrates fabricated in-house
- Screen-print & fire electrodes
- Furnace testing simulates high temperature
- Use electrical stimulus ("bias")
- Sensing signal = voltage developed between electrodes
- Measure NO_x response
  - NO *vs.* NO_2
- Study effect of varying $[O_2]$, H_2O, impurities

Oxide/Pt sensing element

All-oxide sensing element

Sensing Approach: Biased Electrode

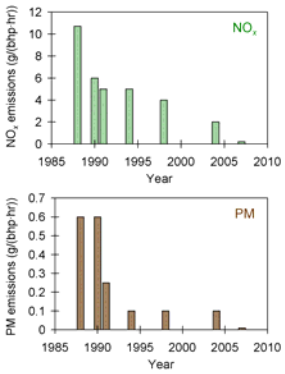




- Bias current driven between oxide/Pt electrodes, monitor voltage (V_{meas}).
- Presence of NO_x causes change in V_{meas} (ΔV).

Relevance to 21 CT Goals

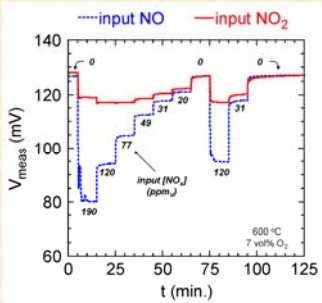
- **Development of a NOx sensor supports the approaches to emissions management in Engine Systems**
  - **LNT, SCR, or fuel-rich operation will be required to meet NO_x standards**
  - **NO_x sensors enable control and OBD of LNT and SCR technologies**
- **Past 21 CT**
  - **Application to lean burn engine technology**
- **Discussions ongoing with 2 21CT partners to join program**



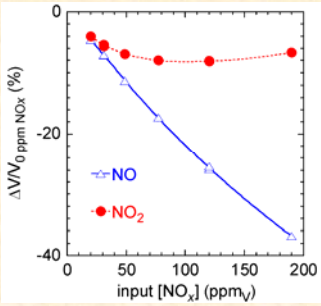
EPA Emission Standards for Heavy-Duty Diesel Engines (www.dieselnet.com/standards/us/hd.html)

Technical Accomplishment I: NO-selective sensing elements

V_{meas} = f(t) w/ varying [NO_x]



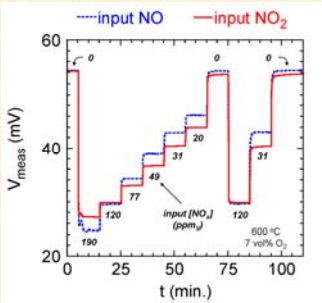
ΔV = f([NO_x])



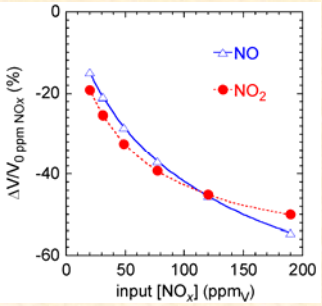
- **Response to NO stronger than response to NO_2.**
- **Enables measurement of [NO] in mixtures of varying NO:NO_2.**
  - **Ratio not known with certainty in application.**

Technical Accomplishment II: "Total NO_x" sensing elements

V_{meas} = f(t) w/ varying [NO_x]



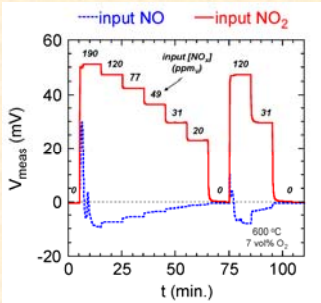
ΔV = f([NO_x])



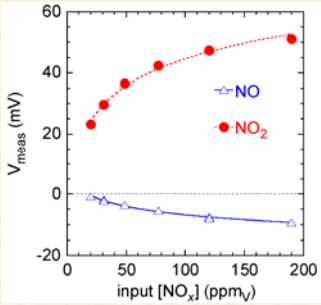
- **Approximately equal response to NO and NO_2.**
- **Enables measurement of [NO] + [NO_2] irrespective of [NO]:[NO_2].**

ORNL elements behave differently than "mixed-potential" elements†

V_{meas} = f(t) w/ varying [NO_x]



ΔV = f([NO_x])



- **No electrical stimulus applied in "mixed-potential mode".**
- **NO_2 response larger and opposite in sign to that for NO.**
- **Unfortunately NO dominant NO_x species above ~500 °C.**

†Garzon *et al.*, *Solid Sate Ionics* **136-7**, 2000;
Lu *et al.*, *J. Mater. Chem.* **7**[8], 1997.

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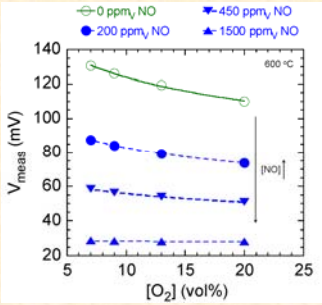
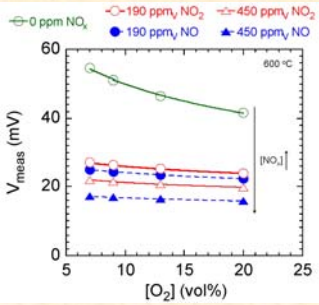
[O_2] sensitivity is a decreasing function of [NO_x]

V_{meas} = f([O_2]) ("NO-selective")



V_{meas} = f([O_2]) ("total NO_x")



- **Diesel exhaust [O_2] is about 10-15 vol% O_2.†**
- **Currently plan in-situ [O_2] measurement in sensor design.**

†Kaspar *et al.*, *Catalysis Today* **77**, 2003.

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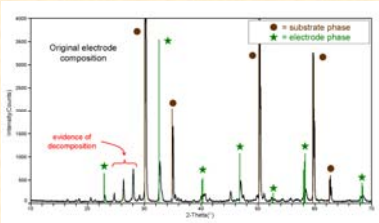
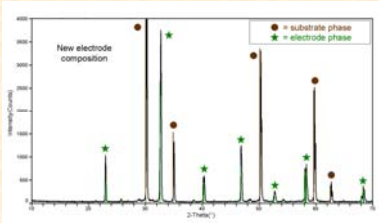
Technical Accomplishment III: Stability in steam

Θ–2Θ (Cu K_α) XRD original electrode matl.



Θ–2Θ (Cu K_α) XRD new electrode matl.



- **XRD's after simulated "long-term" (~1 month) use in wet gas.**
- **As-fabricated elements were phase pure in both instances.**
- **New and original electrode compositions both quaternary oxides.**

Technology Transfer Status

- "NO" sensing element is focus of go forward effort
- CRADA partner (Ford) is designing prototype sensors that incorporate these elements
- ORNL will have input into materials selection and processing methods
- Third party manufacturer (e.g. Honeywell, Delphi) is being sought to manufacture sensor
- Additional engine manufacturers being sought as CRADA advisors

Future Work-I

- **Detailed understanding of sensing mechanism.**
  - Important as ease of fabrication and cost may dictate changes in materials or electrode geometry when element is incorporated into final design
  - Collaborating with GA Tech on DRIFTS investigation of surface species during operation
  - Collaborating with LLNL and Northwestern on impedance spectroscopy
  - Expect results beginning of FY 06
- **Cross-sensitivity.**
  - Setting up to mix six gases at one time and vary [H_2O] from 1-10%.
  - Expect results middle of FY 06

Future Work-II

- **Evaluate stability of elements in real and simulated auto exhausts.**
  - Prototype sensors suitable for mounting will be assembled at Ford
    - Dynos available both at Ford and NTRC.
  - Plan to begin dyno testing first part of FY 06
- **Investigate use of time-varying electrical stimulus.**
  - May enhance signal stability
  - Will know efficacy by middle of FY 06.
  - Should only impact signal processing aspects of sensor.

Publications, Presentations, Patents

Publications

1. D. L. West, F. C. Montgomery, and T. R. Armstrong, "Total NO_x sensing elements with compositionally identical oxide electrodes," accepted by Journal of the Electrochemical Society May 2005.
2. D. L. West, F. C. Montgomery, and T. R. Armstrong. "NO-selective NO_x sensing elements for combustion exhausts," accepted by Sensors and Actuators B, Feb. 2005.
3. D. L. West, F. C. Montgomery, and T. R. Armstrong. "Electrically biased NO_x sensing elements with coplanar electrodes," Journal of the Electrochemical Society, 152 [6], H74–9, 2005.
4. D. L. West, F. C. Montgomery, and T. R. Armstrong. "Use of $La_{0.85}Sr_{0.15}CrO_3$ in high-temperature NO_x sensing elements," Sensors and Actuators B, 106[2], pp. 758-765, (2005).

Presentations

1. D. L. West, F. C. Montgomery, and T. R. Armstrong, "All-oxide "total NO_x" sensing elements," 207th Meeting of the Electrochemical Society, Quebec City, Canada, 2004.
2. D. L. West, F. C. Montgomery, and T. R. Armstrong, "DC electrical-biased, all-oxide NO_x sensing elements for use at 873 K," 29th International Cocoa Beach Conference on Advanced Ceramics and Composites, Cocoa Beach, FL, 2005.
3. D. L. West, F. C. Montgomery, and T. R. Armstrong, "High-T NO_x sensing elements using conductive oxides and Pt," Proceedings of ICEF: Engines for Mobile, Marine, Rail, Power Generation and Stationary Applications, Long Beach, CA, 2004.
4. D. L. West, F. C. Montgomery, and T. R. Armstrong, "NO-selective NO_x sensing elements for combustion exhausts," Eurosensors XVIII, Rome, Italy, 2004.
5. D. L. West, F. C. Montgomery, and T. R. Armstrong, "Electrically biased NO_x sensing elements with co-planar, multi-layered electrodes," 205th Meeting of the Electrochemical Society, San Antonio, TX, 2004.
6. D. L. West, F. C. Montgomery, and T. R. Armstrong, "Electrode materials for mixed-potential NO_x sensors," 28th International Cocoa Beach Conference on Advanced Ceramics and Composites, Cocoa Beach, FL, 2004.

Patents

1. F. C. Montgomery, D. L. West, T. R. Armstrong, and L. C. Maxey, "NO_x Sensing Devices Having Conductive Oxide Electrodes," submitted to USPTO November 2004.