The 16th Directions in Engine-Efficiency and Emissions Research (DEER) Conference

# Electrochemical $NO_x$ Sensors for Monitoring Diesel Emissions

September 30, 2010

Leta Y. Woo and R. S. Glass, Lawrence Livermore National Lab
R. F. Novak and J. H. Visser, Ford Motor Company

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

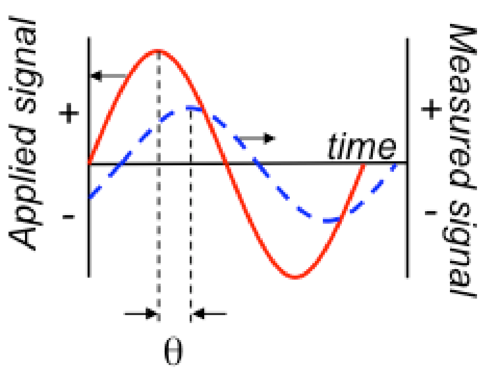
LLNL-PRES-451711

# Outline

- Approach – Impedancemetric sensing
- $NO_x$ sensitivity
- Stability and ammonia tolerance
- Cross-sensitivity and accuracy
- Summary

# Low-cost solid-state electrochemical $NO_x$ sensor addresses drawbacks of other technologies

- Unlike conventional amperometric or potentiometric (mixed-potential) operation, relies on **impedancemetric** operation
  - Correlates $NO_x$ with impedance-based signal, electrical response to alternating current (ac)
  - Improves stability by preventing electrically driven changes caused by direct currents (dc) in conventional operation
  - NO and $NO_2$ sensitivity (total $NO_x$) to < 5 ppm
  - Simple device using $O^{2-}$ conducting electrolyte, yttria-stabilized zirconia (YSZ)




# Sensing mechanisms: rates of electrochemical reaction at the electrode/electrolyte interface

***electrolyte* | *electrode***

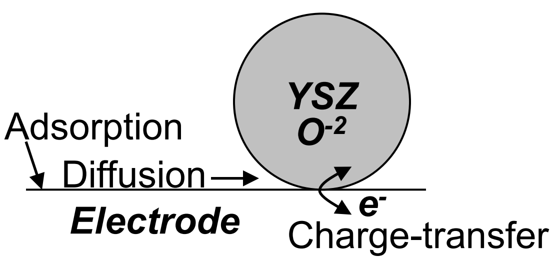
$$O^{2-} \longleftrightarrow \quad \frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}$$

$$NO_2 + 2e^- \leftrightarrow NO + O^{2-}$$

- Impedance measures reaction rates with different frequency dependencies
  - $NO_x$ and $O_2$ influence reaction rates at typically < 1 kHz

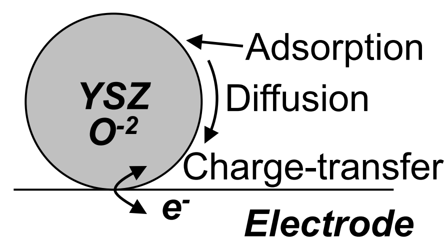
- Control electrode microstructure and composition to limit $O_2$ reaction rate and resolve ppm $NO_x$ signal in 2-21% $O_2$ background

***Low sensitivity***




Enhanced $O_2$ reaction rate, electrode surface dominates reaction paths

***High sensitivity***




Limited $O_2$ reaction rate, electrolyte surface dominates reaction paths

Woo, et al., *J. Electrochem. Soc.*, 154, 2007 & 155, 2008

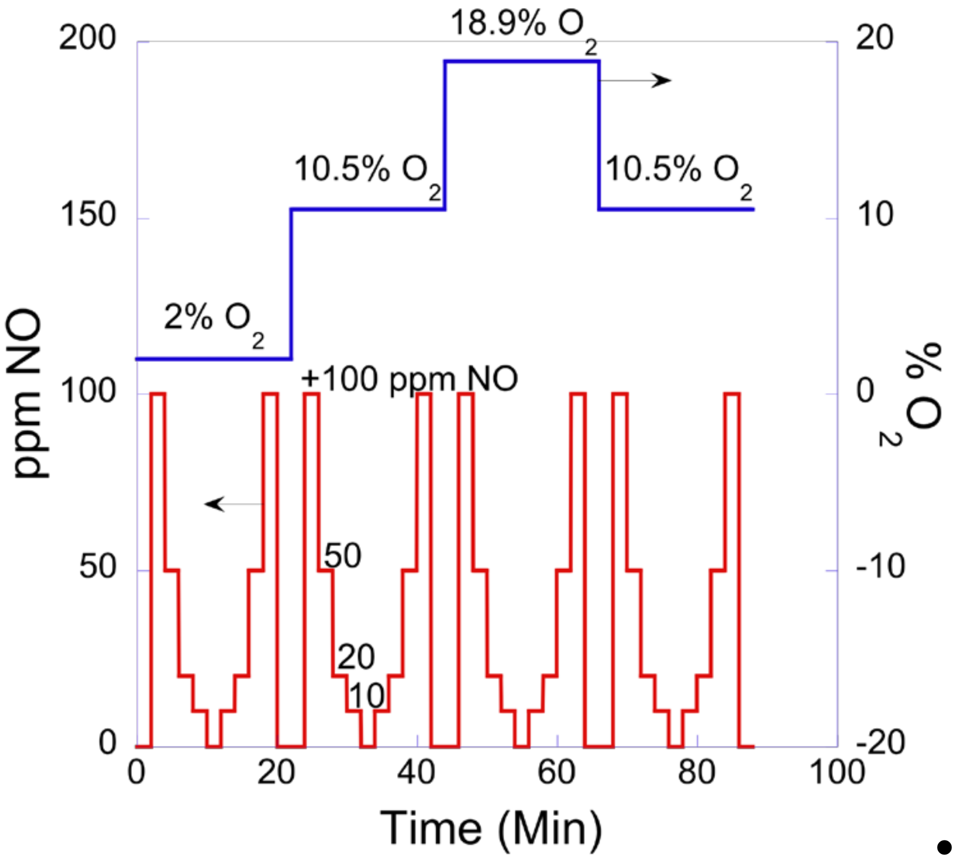
# Sensor operation: Response signal chosen at specified operating frequency (5 Hz) and excitation (100 mV)

- Complex impedance (Z) includes magnitude and phase angle
  - Phase angle signal: better sensitivity, stability, and reliability; measured directly or related to corresponding voltage using simple electronics
  - Optimum frequency and excitation: tradeoff between sampling rate and $NO_x$ sensitivity


Martin, et al., *J. Electrochem. Soc.*, 154, 2007

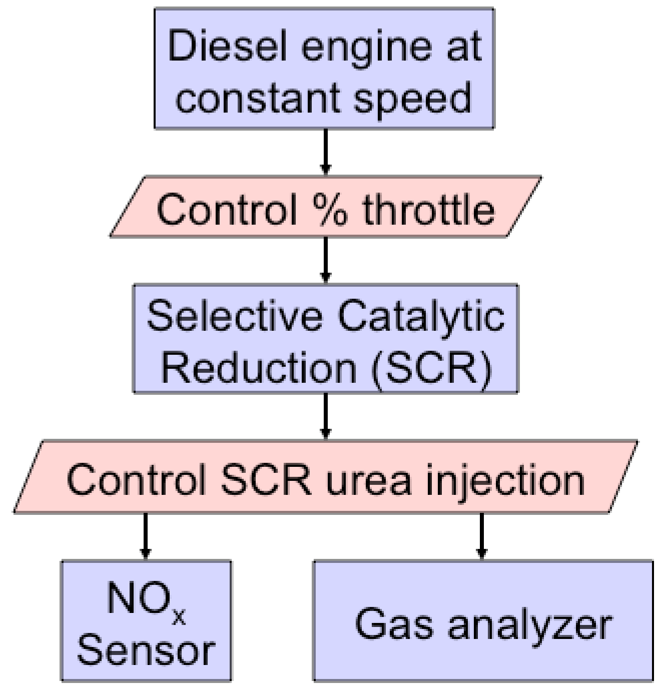
# Laboratory tests with defined gas concentrations and diesel engine dynamometer testing with real exhaust

## Laboratory



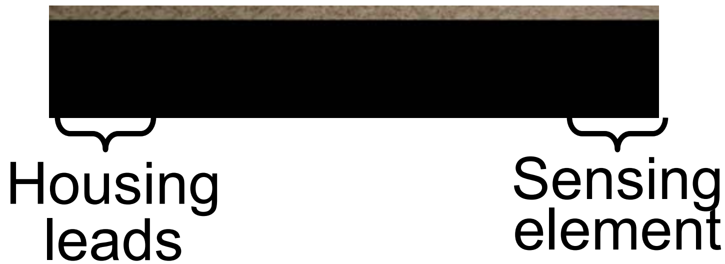

- Defined range of controlled gas concentrations

## Dynamometer

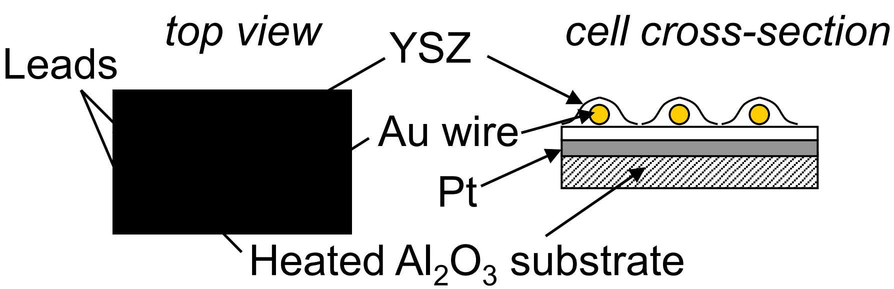



- Diesel exhaust: controlled engine parameters; measured concentrations with gas analyzer

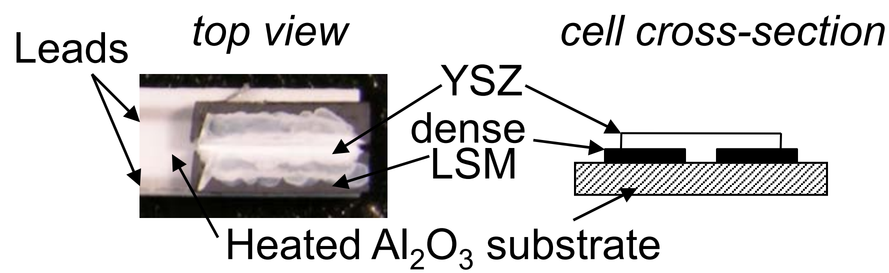
# Flexible single-cell designs, either metal or metal oxide sensing electrode, can be packaged into protective housing




*Au wire design*
*(one sensing electrode)*



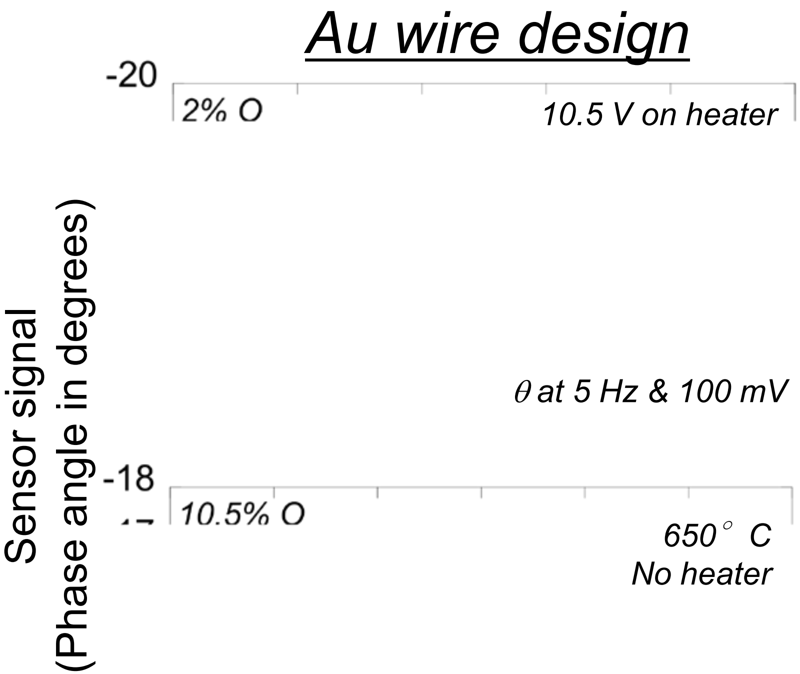

*Dense LSM design*
*(two sensing electrodes)*

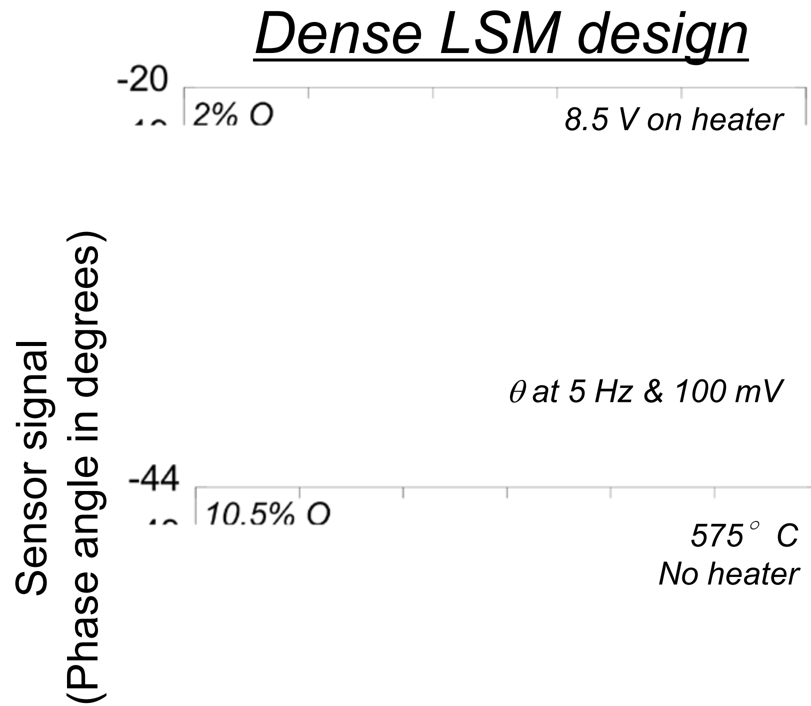



- Designs using either one or two sensing electrode(s)
  - (left) Au wire sensing electrode and Pt non-sensing electrode
  - (right) 15 mol% Sr-doped $LaMnO_3$ (LSM) sensing electrodes

Woo, et al., *J. Electrochem. Soc.*, 157, 2010

# Sensitivity to less than 5 ppm NO

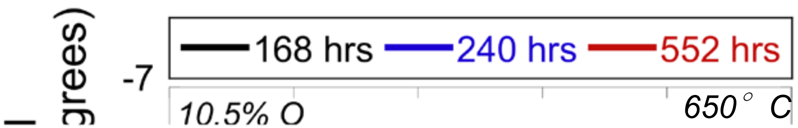



- LSM design required lower heater voltage/temperature to further limit $O_2$ reaction rate and achieve similar $NO_x$ sensitivities as Au

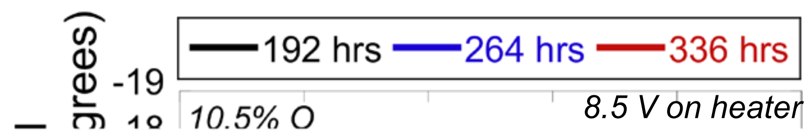
# Laboratory evaluations to over 500 hrs of aging indicated stable, reproducible sensor response

## *Au wire design*




*θ at 5 Hz & 100 mV*

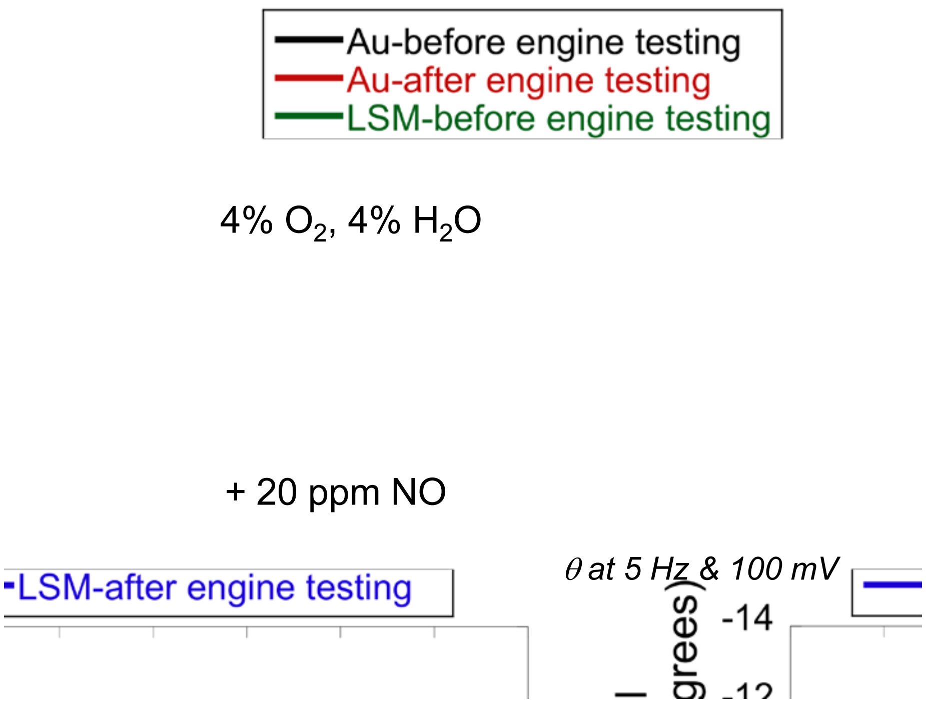
## *Dense LSM design*




*θ at 5 Hz & 100 mV*

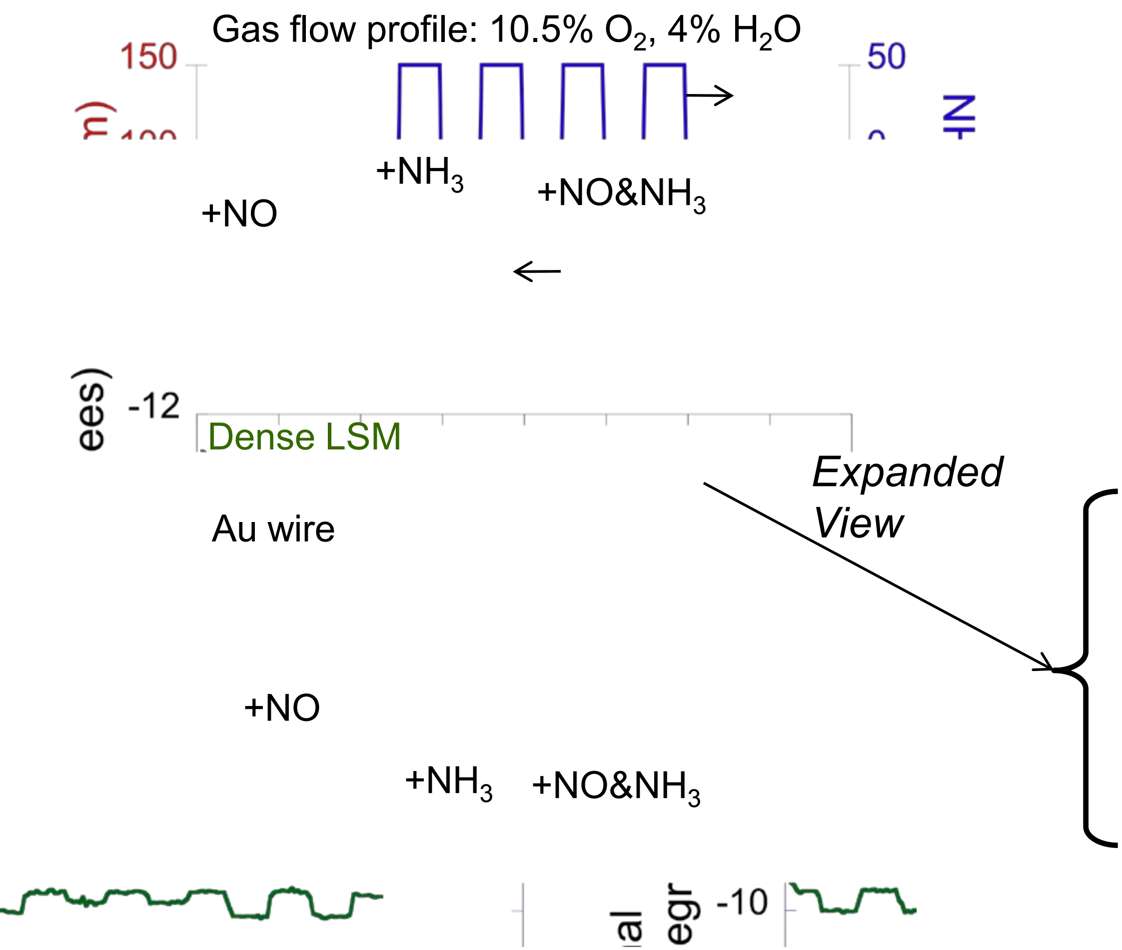
# Diesel engine dynamometer testing of packaged designs indicated good mechanical stability and robustness

- Mounted directly into manifold; simulating real-world operation, including engine vibrations and cold-start conditions
- Evaluated on high-flow test stand (30000 sccm) before and after engine testing: 30 sec pulses of 20 ppm NO

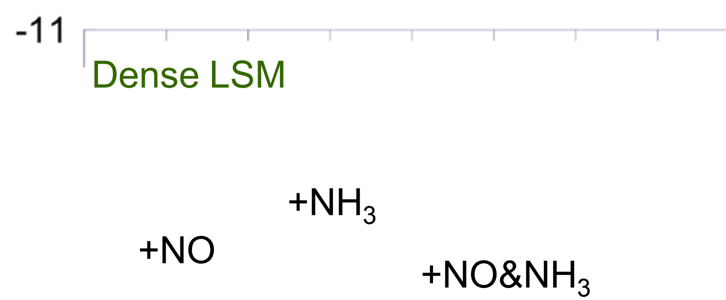


# High-flow test stand: LSM design had better ammonia ($NH_3$) tolerance than Au design

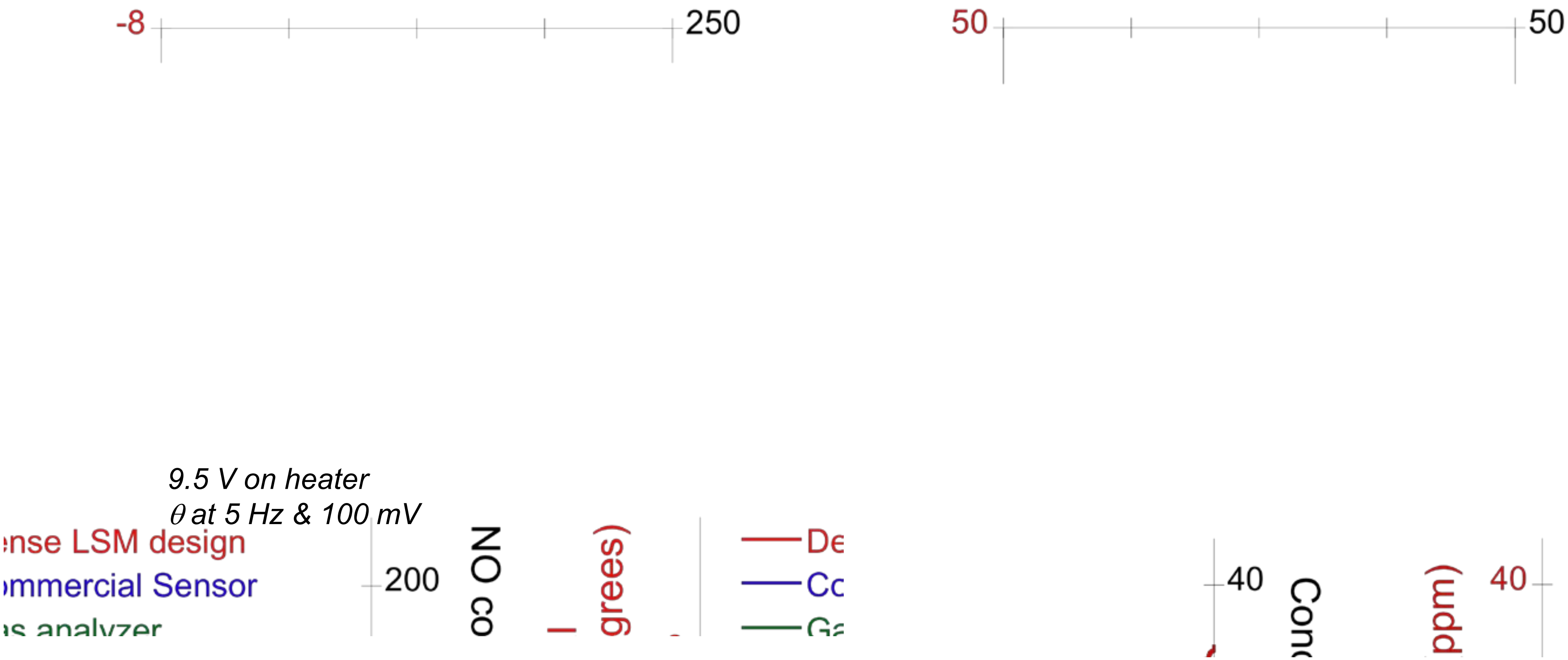
30 sec pulses: 50 ppm NO, 50 ppm $NH_3$, and 50 ppm NO + 50 ppm $NH_3$




- Au design more selective to $NH_3$
- LSM design more selective to NO with low cross-sensitivity to $NH_3$



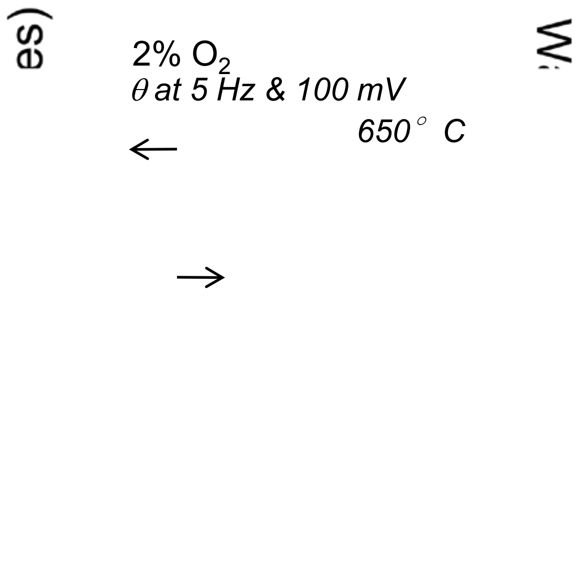
# Engine dynamometer test of packaged LSM design: reasonable agreement with expensive commercial sensor



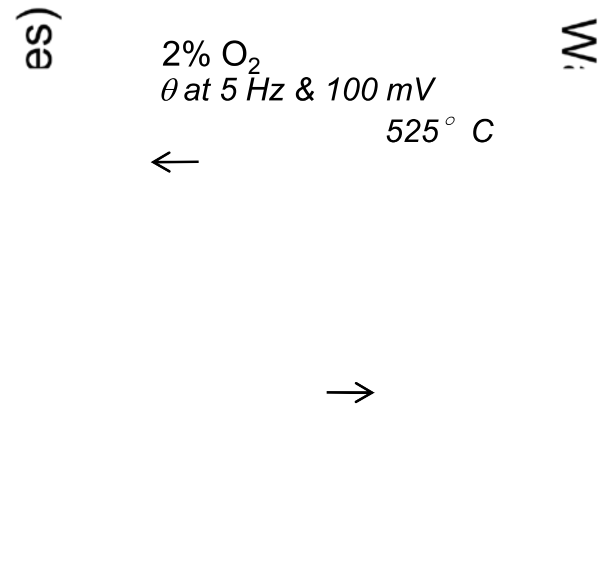

- Ammonia ($NH_3$) slip: non-steady state, increased during test
- LSM design had better tolerance towards up to ~35 ppm $NH_3$ compared to commercial sensor

# Au design had minimal water cross-sensitivity after the initial introduction of water

## Au wire design



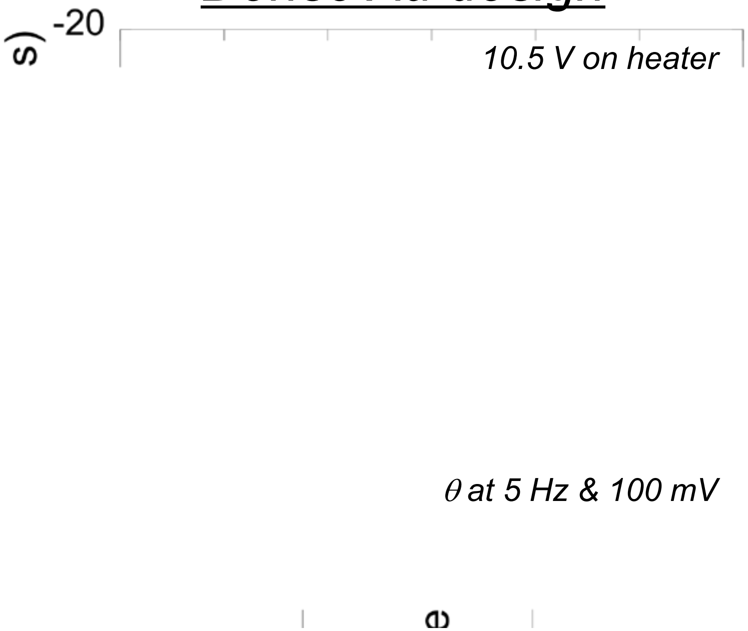

## Dense LSM design




- Signal decreased after initial introduction of water
  - Au design: low water cross-sensitivity with minimal response to additional changes in water concentration
  - LSM design: larger water cross-sensitivity with continued response to changes in water concentration

# Au design: measured cross-sensitivity to $O_2$, $H_2O$, and temperature used to reduce interferences

*Dense Au design*




- Test conditions: 2-18.9% $O_2$, 10-100 ppm NO, 2-6% $H_2O$, and 625-675ºC
  - $H_2O$ cross-sensitivity minimized at 650ºC
  - Three-step strategy to reduce interferences

- Step 1: Measure temperature (±1ºC) and $O_2$ (±4%) using higher frequency (1 kHz) signal that only responds to $O_2$
- Step 2: Calculate zero $NO_x$ (ideal signal without $NO_x$) using measured $O_2$ and temperature
- Step 3: Calculate ppm NO using difference between measured and calculated zero $NO_x$ signal

# Algorithm equations, using measured cross-sensitivities, for three steps to reduce interferences

1. Measure temperature, $T_{meas}$, ($\pm$1ºC) and $O_2$ ($\pm$4%): Method for measuring $O_2$ with higher frequency (1 kHz) signal, $\theta_{1kHz}$

650ºC
2% $H_2O$
*only responds to $O_2$ changes

$$\%O_2 = \frac{\theta_{1kHz} + 6.0754}{0.030542}$$

2. Calculate zero $NO_x$ signal ($\theta_{0NOx}$) using measured $O_2$ and temperature

$$\theta_{0NOx} = \theta_{O2} + \left(\frac{\Delta\theta}{\Delta T}\right)_{O2} \Delta T$$

$$\Delta T = T_{meas} - 650ºC$$

$$\theta_{O2} = -14 + 1.2(\%O_2) - 0.035(\%O_2)^2$$

$$\left(\frac{\Delta\theta}{\Delta T}\right)_{O2} = 0.069 - 0.0019(\%O_2)$$

650ºC

3. Calculate ppm NO using difference between measured and calculated zero $NO_x$ signal

$$\Delta\theta = \theta_{0NOx} - \theta_{meas}$$

$$\left(\frac{\Delta\theta}{\Delta NO}\right)_{O2} = 0.0551 - 0.00501(\%O_2) + 0.000143(\%O_2)^2$$

$$\Delta NO = \frac{\Delta\theta}{\left(\frac{\Delta\theta}{\Delta NO}\right)_{O2}}$$

650ºC

# Au design: accuracy assessed by determining noise introduced by fluctuations in temperature and water


- Signal changes with respect to interferences related to values for signal changes with respect to ppm NO
- Less noise at lower $O_2$ concentrations
  - ± 1ºC temperature noise decreased accuracy by ~1.5-3 ppm
  - ± 1% $H_2O$ noise decreased accuracy by ~1.2-2.2 ppm

# Summary

- Novel high-sensitivity, low-cost $NO_x$ sensor to meet cost and operational requirements and address drawbacks of other technologies
- Flexible single-cell design, alumina substrates with heaters, packaged into protective housing
- Sensitivity to < 5 ppm, engine dynamometer testing with real diesel exhaust in reasonable agreement with expensive commercial sensor
- Long-term sensor aging (>500 hrs): reproducible and stable sensor response
- Potential strategy using measured cross-sensitivity data developed to reduce interferences and improve accuracy

# Acknowledgements


- Numerous individuals at Ford Research and Innovation Center including David Kubinski and Richard Soltis
- Department of Energy, Office of Vehicle Technologies, Propulsion Materials (Jerry Gibbs)


Thank you for your attention!


Leta Woo

woo21@llnl.gov