Unclassified

Performance Evaluation of Mixed-Potential HC, NO_x, and NH_3 Sensors in Diesel and Lean Gasoline Exhaust

2015 DOE Crosscut Lean/Low-temperature Exhaust Emissions Reduction Simulation Workshop

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Talk Outline

- Research Motivations
- Ammonia sensor pre-commercial sensor development (briefly touched upon last year)
- FY15 Engine Evaluation at ORNL– multiple sensor evaluation in lean gasoline and diesel exhaust
- NH_3 sensor testing / NH_3 slip simulations during lean-stratified operation
- NO_x response with ammonia (λ switching, large PO_2 changes)
- Conclusions
- Acknowledgements

NO_x Sensors for lean burn engine applications

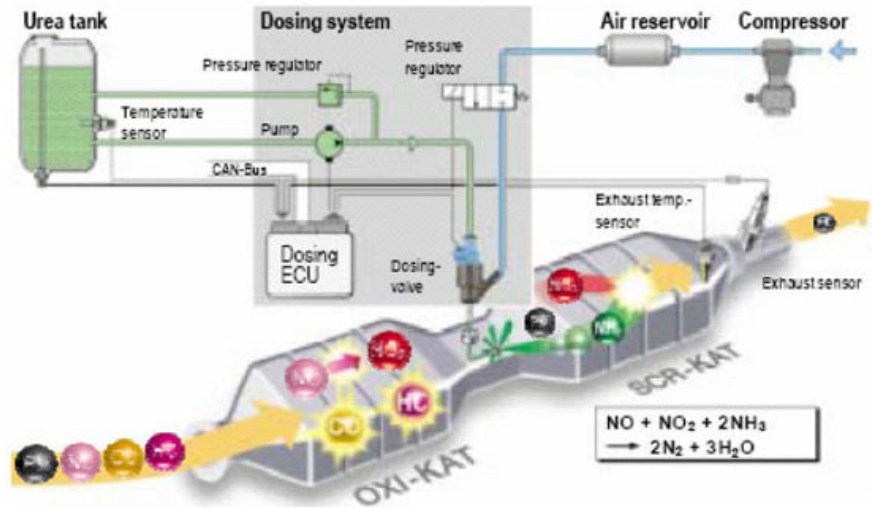
- Use of selective catalyst reduction (SCR) and exhaust gas recirculation (EGR) systems combined with regenerative particulate traps have reduced NO_x and PM tailpipe emissions from diesel vehicles in recent years of mandated use.

- Lack of a simple, robust and cost-sensitive exhaust gas sensor technology hampers efforts to monitor tailpipe emissions and to maintain optimized SCR and EGR efficiency over start-up and over the entire drive cycle.

- Availability of sensors would aid modeling and testing of new and advanced drive cycles/engine control modes.

- We are working towards developing robust and inexpensive sensors analogous to commercial Zirconia oxygen sensors.

  - Diesel *and* lean burn gasoline applications



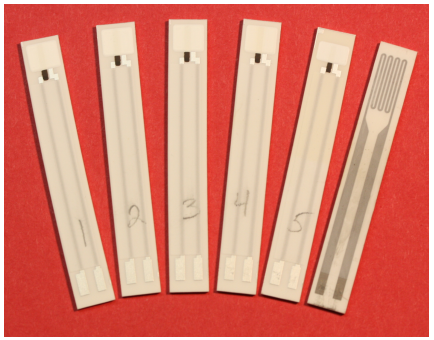
http://www.spatcodef.com/faqs/

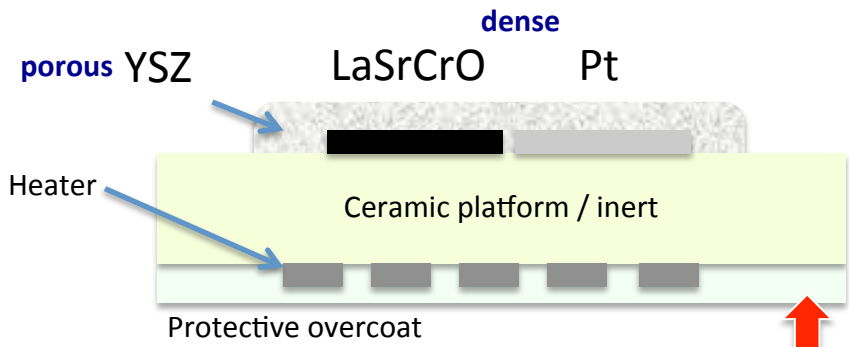
VDO/ NGK UniNOx Sensor
ZrO_2 -based multilayer sensor with 3 oxygen pumps
Complex expensive sensor is only commercial product today

http://www.vdo.com

LANL using ESL HTCC Approach for Mixed Potential NO_x/HC and NH_3 Sensors: a simplified device

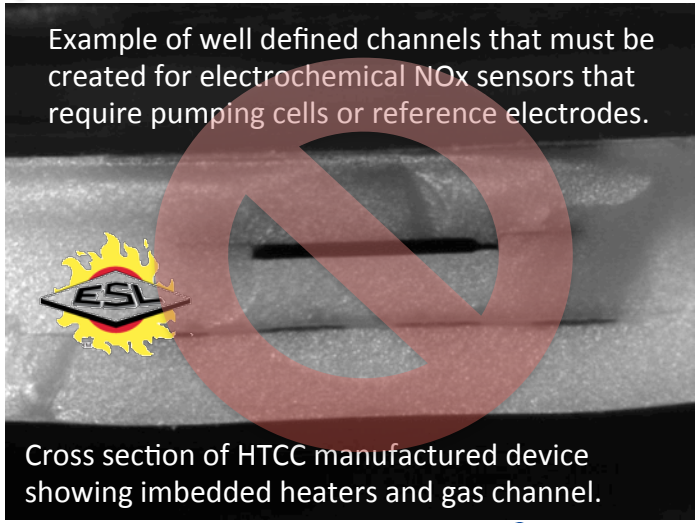
- **Devices as prepared by ESL->**
- **Good uniformity in performance between devices.**
- **Price is dropping even for R&D use.**





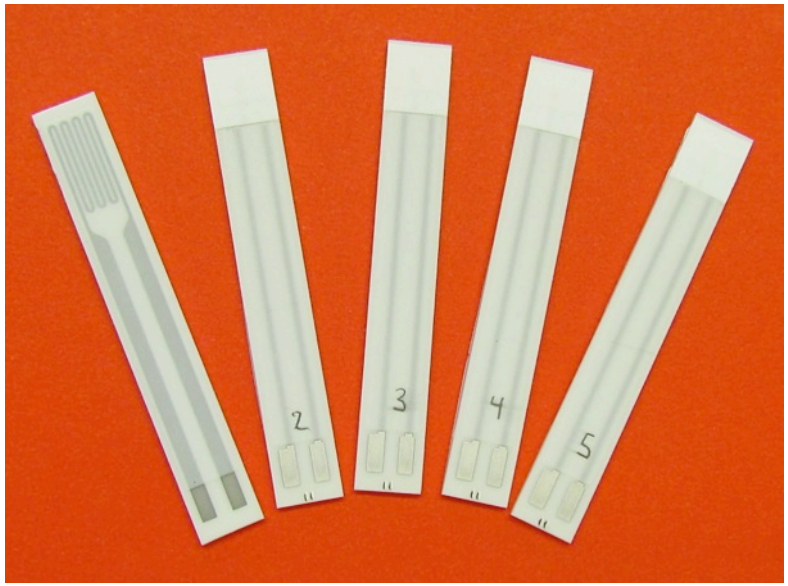
Both HTCC Approaches

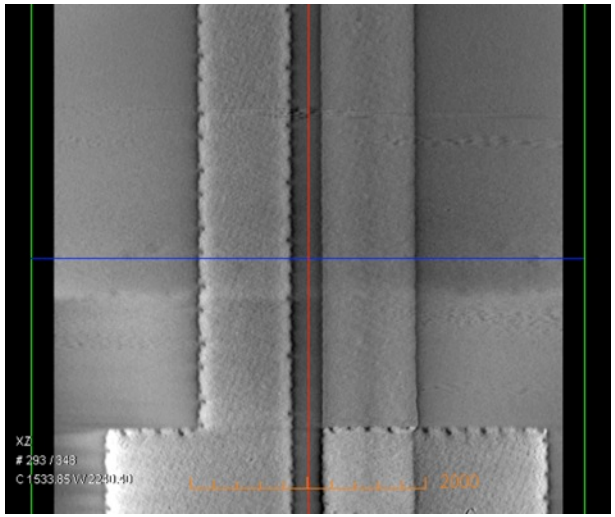
- Significantly less complex sensor design: lower cost to manufacture; less complicated design = lower reject rate
- No fugitive spacers needed to complicate the HTCC manufacturing process
- Air reference channel and internal oxygen pumping cells not required
- Faster turn-on during start-up; *no issues with water condensate initiating thermal shock and failure
- No pumping channels to become blocked
- Two electrode electrochemical device



2nd generation ESL NO_x – HC sensor: Addition of protective, porous overcoat

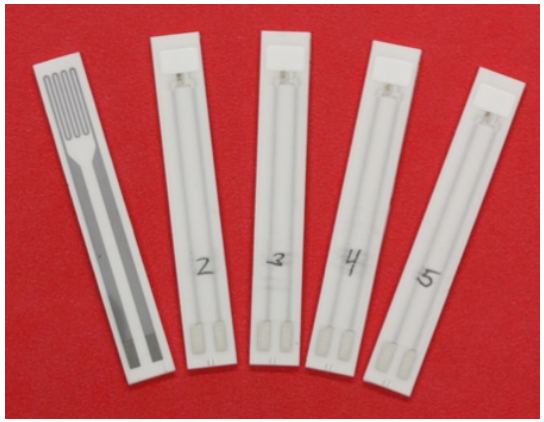
- In FY14, ESL prepared a batch of 10 NO_x sensors with a non-conductive (ionic *and* electronic) porous overcoat applied to protect sensor elements from particulate impingement and exhaust gas erosion.
- Results:
  - Excellent compatibility with HTCC process (negligible addition to fabrication costs) / CTE match
  - Does not affect sensor response characteristics
  - Does not act as a diffusion barrier to O_2 under bias
- Only substantive affect is to act as a thermal blanket to retain heat from the Pt resistive heater.
  - Reduces power consumption which is an advantage, otherwise the overcoat does not affect device response characteristics.

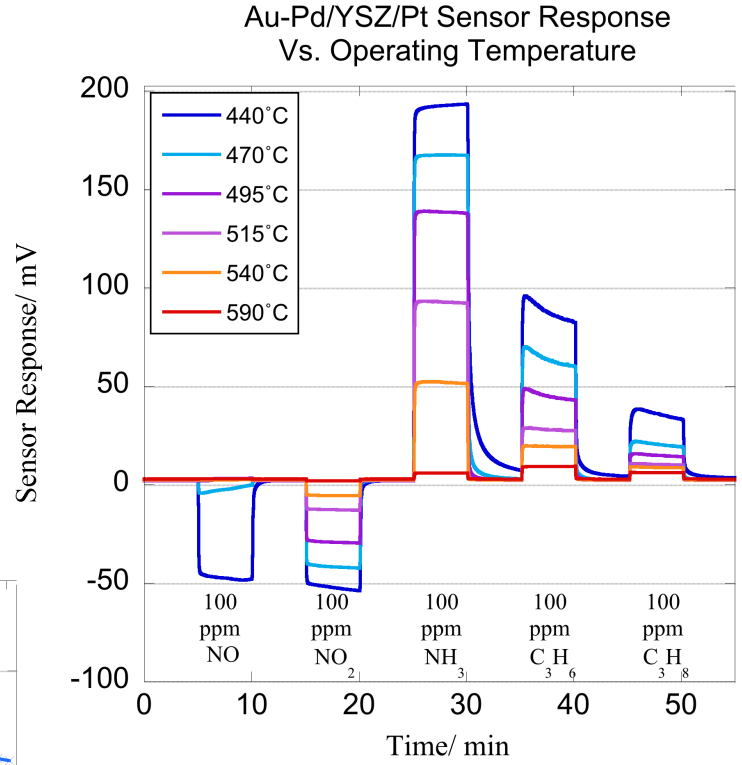




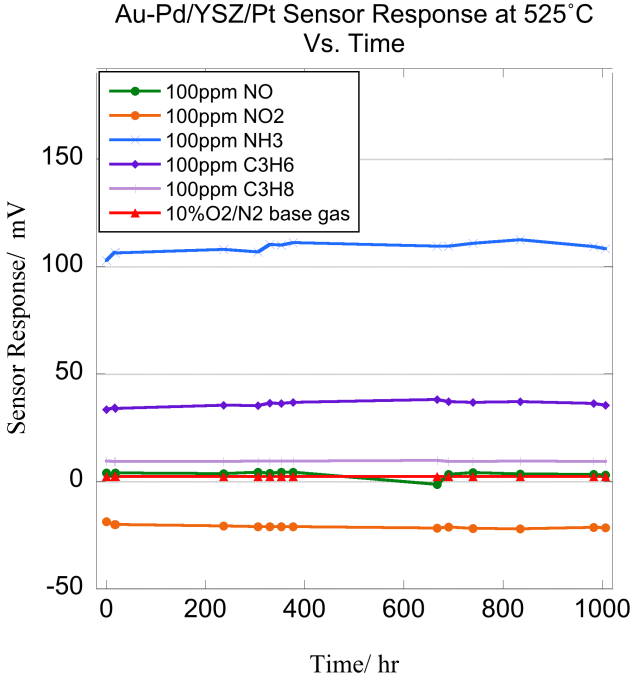
3D X-ray tomography showing nominal electrode structure, electrolyte layer, and generally crack and defect free device.

Characterization – Au/Pd Ammonia Sensors

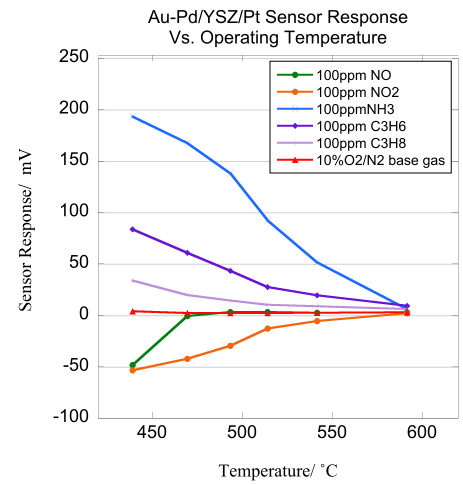




Optimal Temperature is ≈ 525 ºC

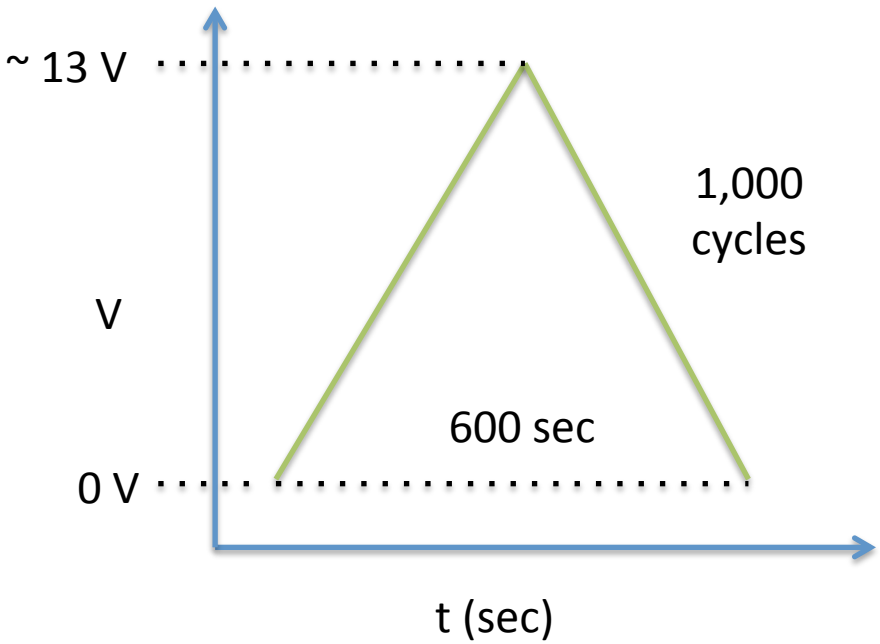


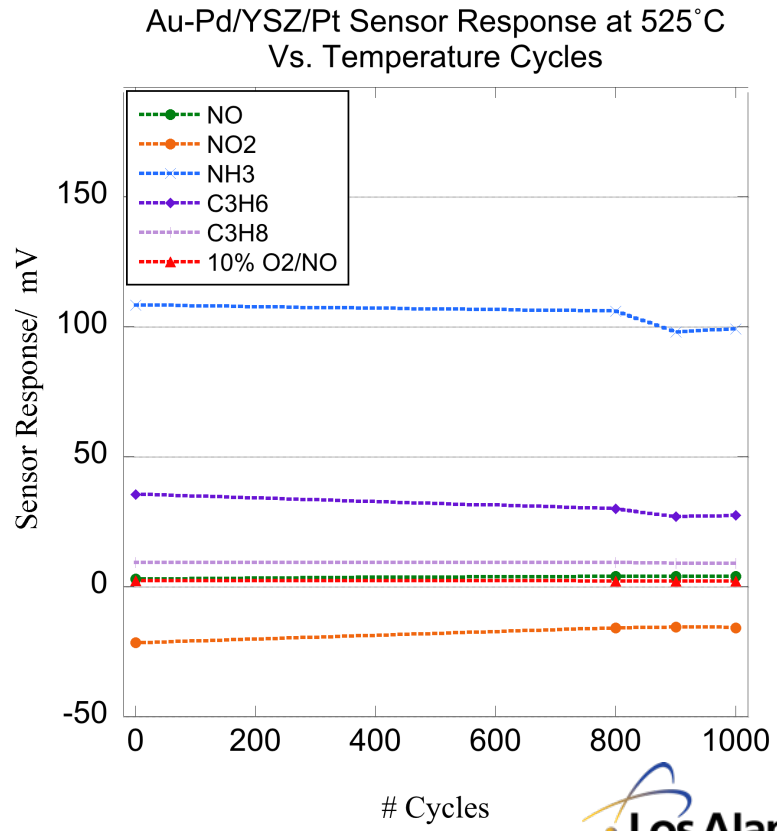
Response Stable for 1000 hours



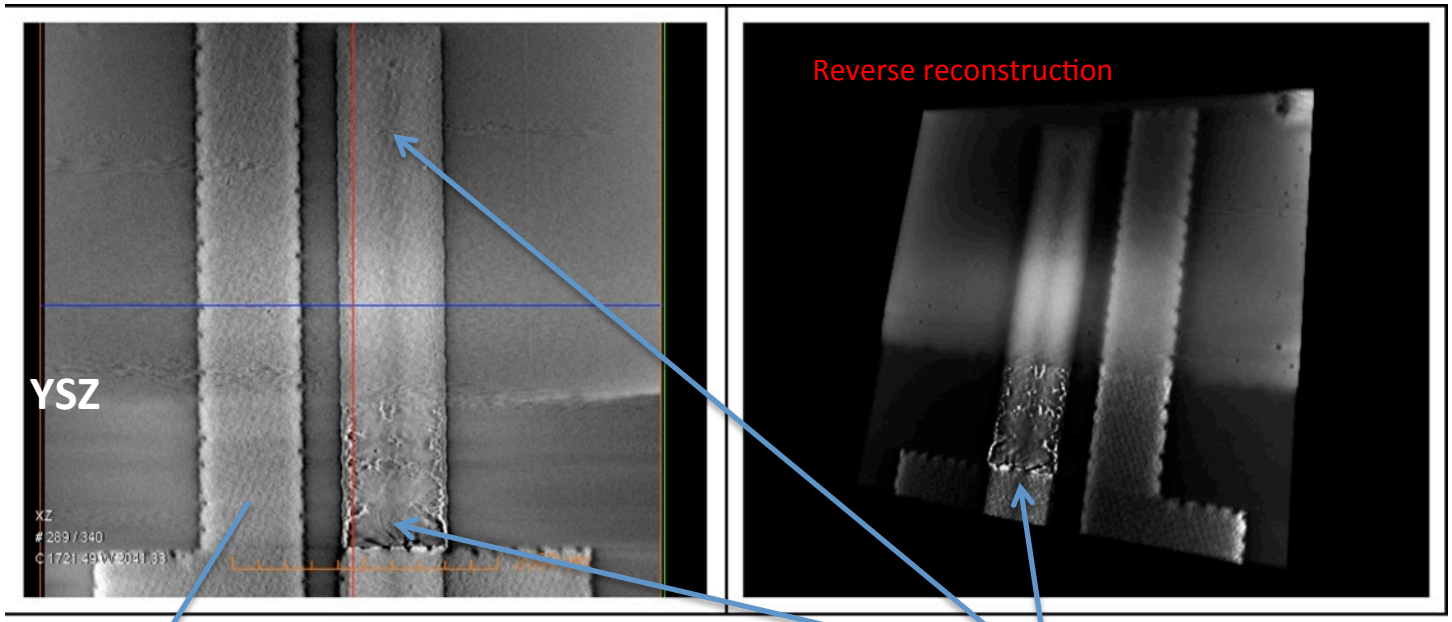
Durability Testing Results – Au/Pd Ammonia Sensors

- Automated heater voltage control program cycles sensor temperature at a desired rate for number of desired cycles.
- 1000 cycles to 550°C and back to RT
- Cycling had no effect on device response. Response to NH_3 and tested interferents were identical comparing as delivered device and after T cycling.





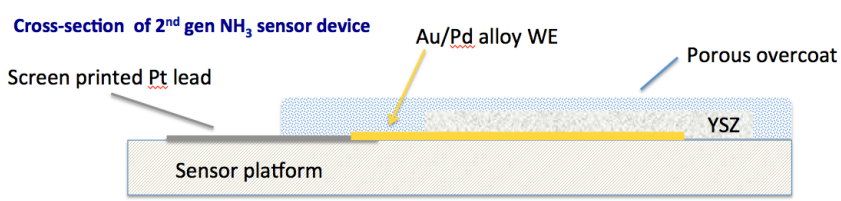
Durability Testing Results – Au/Pd Ammonia Sensors post 1000 Temperature Cycles



Pt counter electrode

Au/Pd working electrode

- Delamination of the electrode occurred in the exposed region only – <u>adhesion issue</u>.
- Pt electrode nominal – identical to NO_x/HC sensors
- Au/Pd alloy film under YSZ electrolyte appears normal. There is *no change* after T cycling.
- Indicates weaker adhesion to substrate than metal oxide or Pt counter electrodes.
- Should not be an issue.



Experimental: Sensor Evaluation in Diesel and Lean Gasoline Exhaust

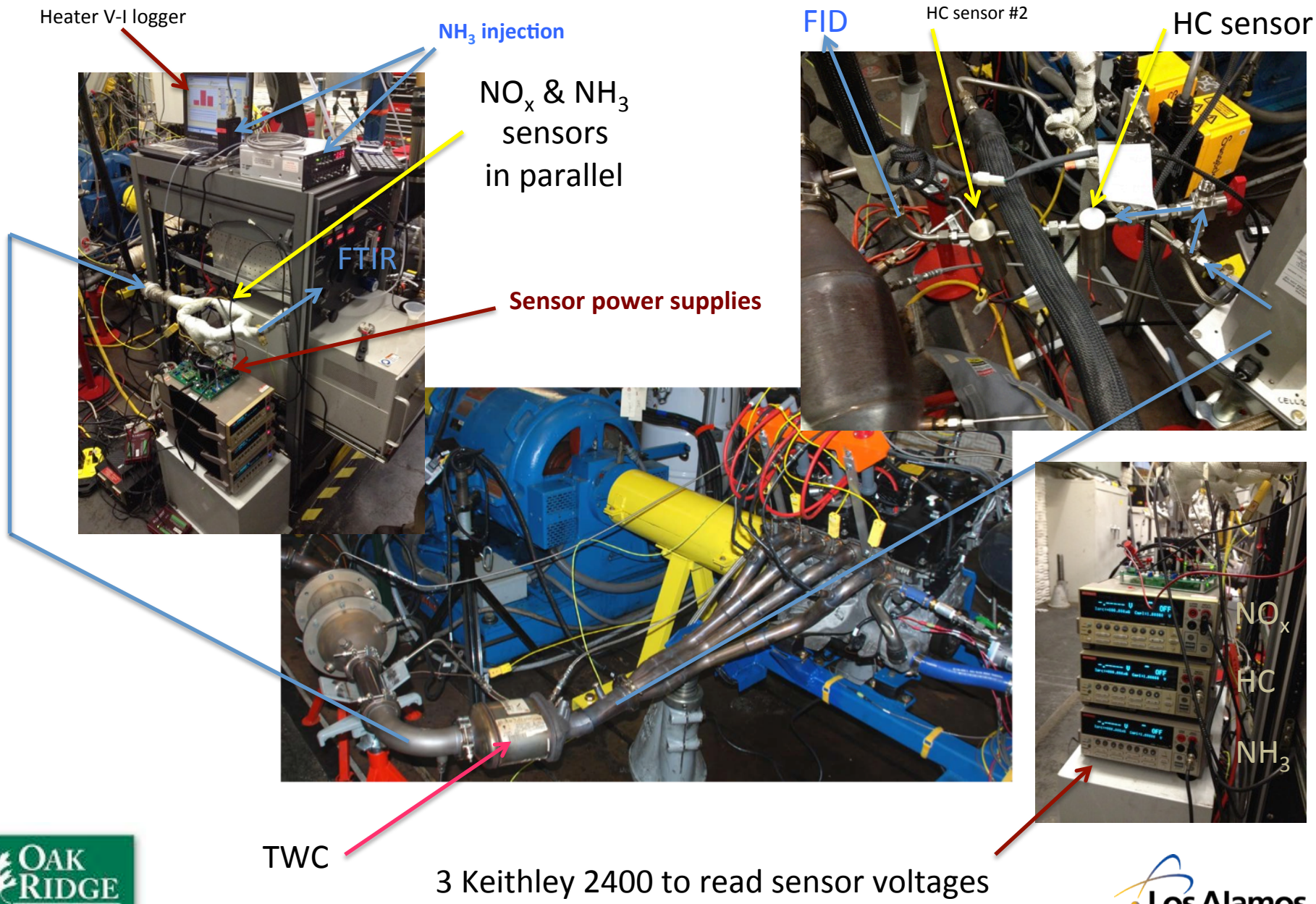
- ✓ **1st Campaign**: March 2013. (Diesel)
  - Primary focus, testing NOx response, sensor control electronics, data acquisition system, and sensor packaging
- ✓ **2nd Campaign**: January 2014. (Diesel)
  - Repeat NO_x, EGR experiments with improved sensor packaging
  - Perform cold-start experiments
    - Capture NO_x (post-DOC) and HC (post-DOC and engine out) data sampling configurations
  - Acquire data from sensor power supplies to understand behavior of sensor control systems
  - Perform EGR sweep experiments in NO_x and HC modes
- ✓ **3rd Campaign**: March 2015.
  - Simultaneous testing of NO_x, HC, and NH_3 sensors w/o attempting to repeat dyno runs.
  - Added 4th (HC) to measure impedance of YSZ electrolyte to measure how well heater resistance feedback and power supplies fix operating T.

- **Studies on BMW 120i lean gasoline engine platform with Drivven open controller**

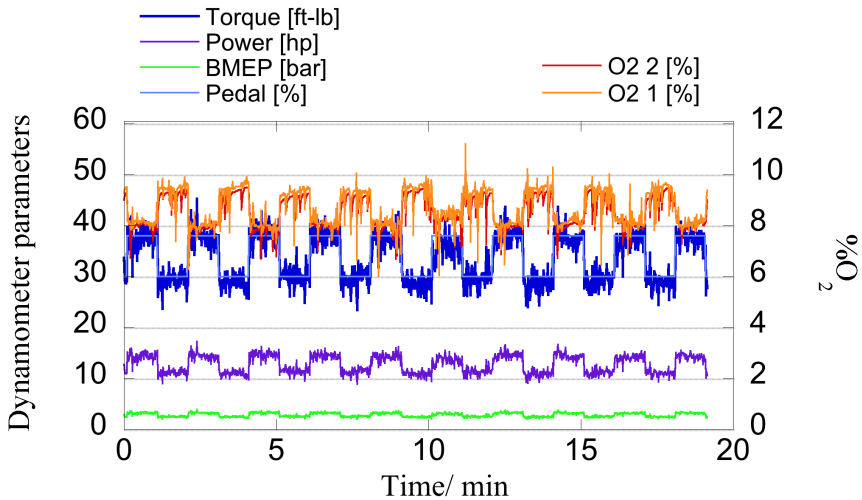
Experimental: Engine Experiments Performed in Week of Testing During 3rd Campaign

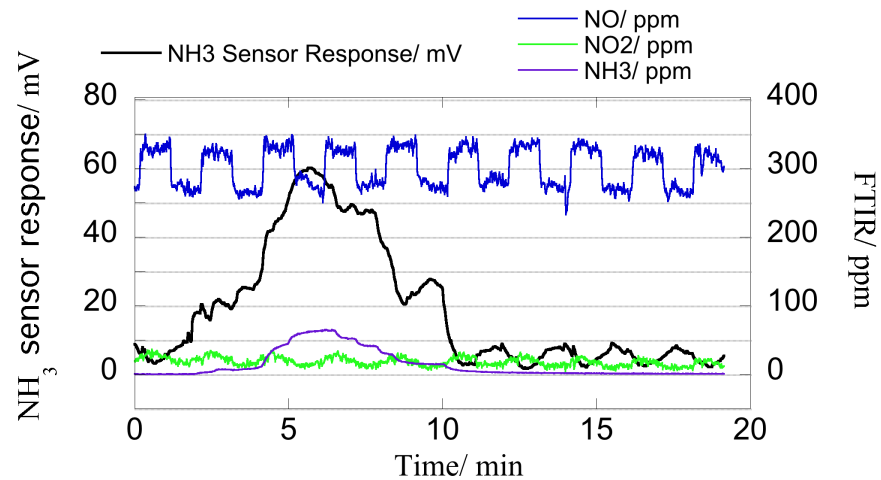
1. Start-up : collected HC, NO_x, and NH_3 data before and after TWC.
2. Vary NO_x emissions when operating in lean homogeneous and lean stratified operation.
   - Similar to EGR sweeps on the diesel engine in Campaigns 1 and 2.
3. Lambda sweeps ($0.98<\lambda<1.8$) to determine characteristics of individual sensors over large changes in background PO_2.
   - Large changes in exhaust gas constituents.
4. Inject known concentrations of NH_3 from bottle post TWC and upstream of NH_3 and NO_x sensors during lean operation (PO_2>5%) to simulate slip events from SCR.
5. Use Gamry Reference 600 portable impedance spectrometer to monitor HFR of YSZ electrolyte layer of a 4th sensor.
   - Understand how uniform T of sensor and CRPS is at controlling heater R.

Experimental: Engine Testing at ORNL NTRC

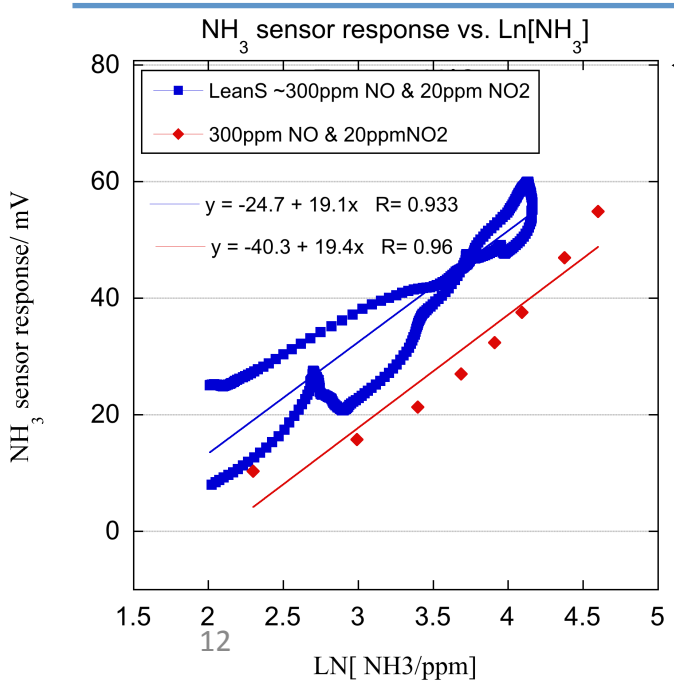


Engine testing: NH_3 sensor response



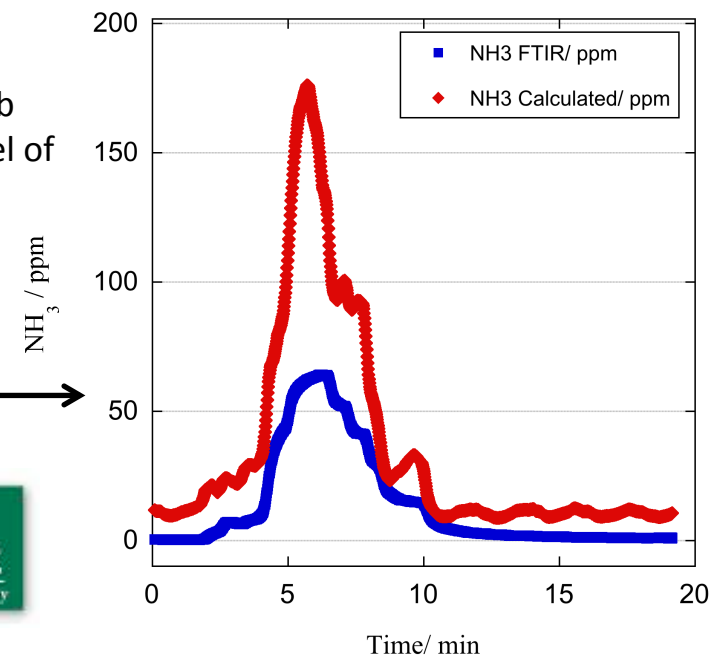


- Engine in lean-stratified mode, load varied to change $NO/NO_2/PO_2$
- Inject NH_3 into exhaust stream post TWC



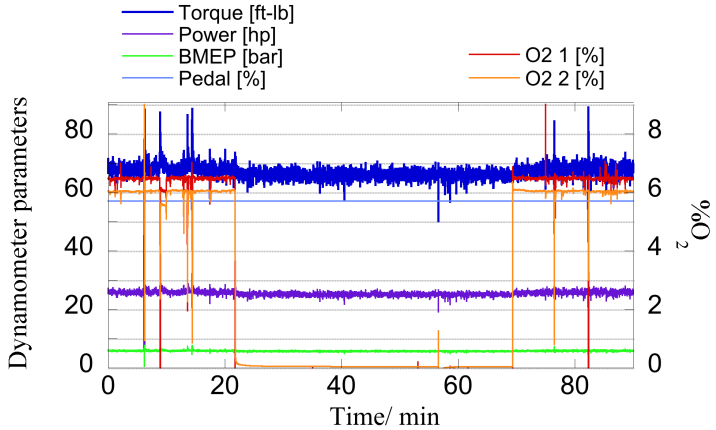
NH_3 sensor response vs. $Ln[NH_3/ppm]$ measured in dynamometer and from lab calibration using same level of NO & NO_2 interferents.

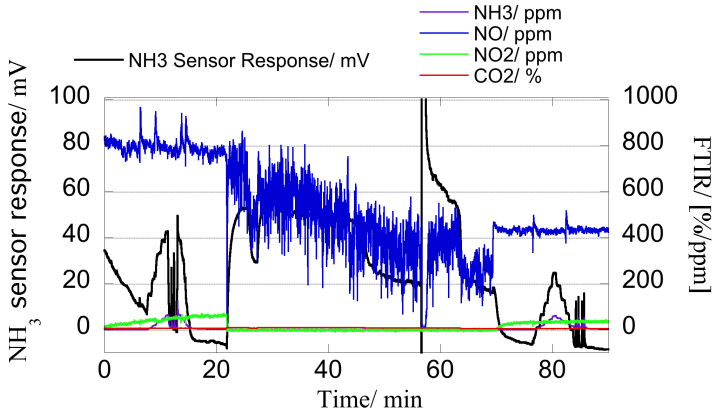
Comparison of FTIR $[NH_3]$ to $[NH_3]$ calculated from sensor response using lab calibration.



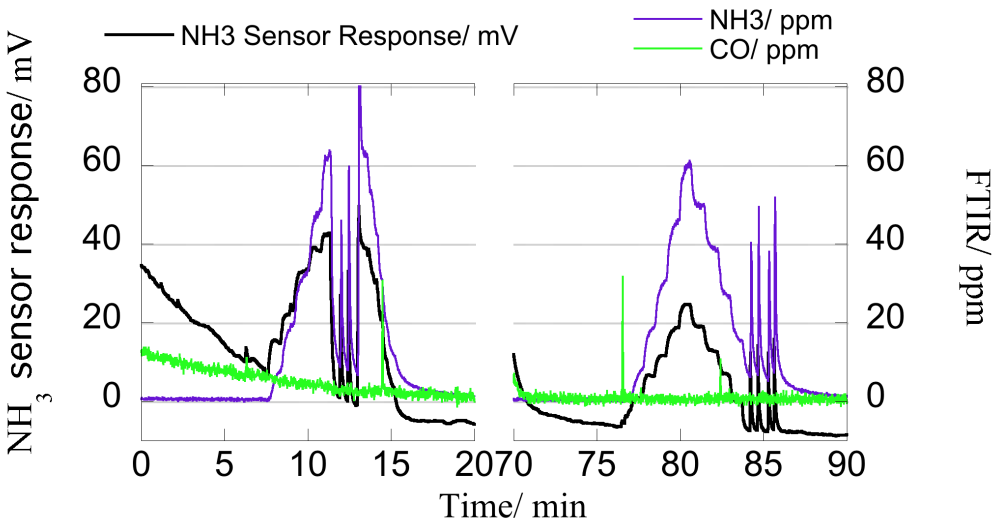
Engine Testing: Ammonia Injection to Simulate Slip in SCR System/Lean Burn

- Engine in lean-homogeneous mode (t<20 min and t> 70 min), vary load
- Inject NH_3 into exhaust stream post TWC





- NH_3 sensor response and NH_3/ppm measured via FTIR vs. time under lean engine conditions.
- Offset between two NH_3 staircases likely due to CO interference.



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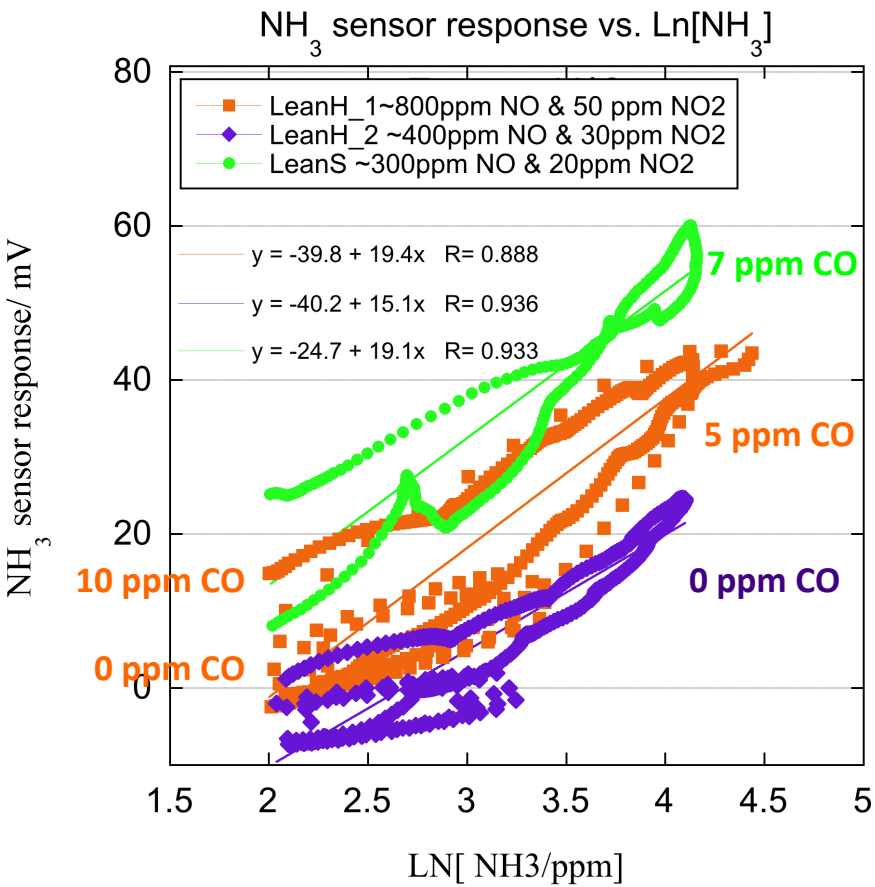
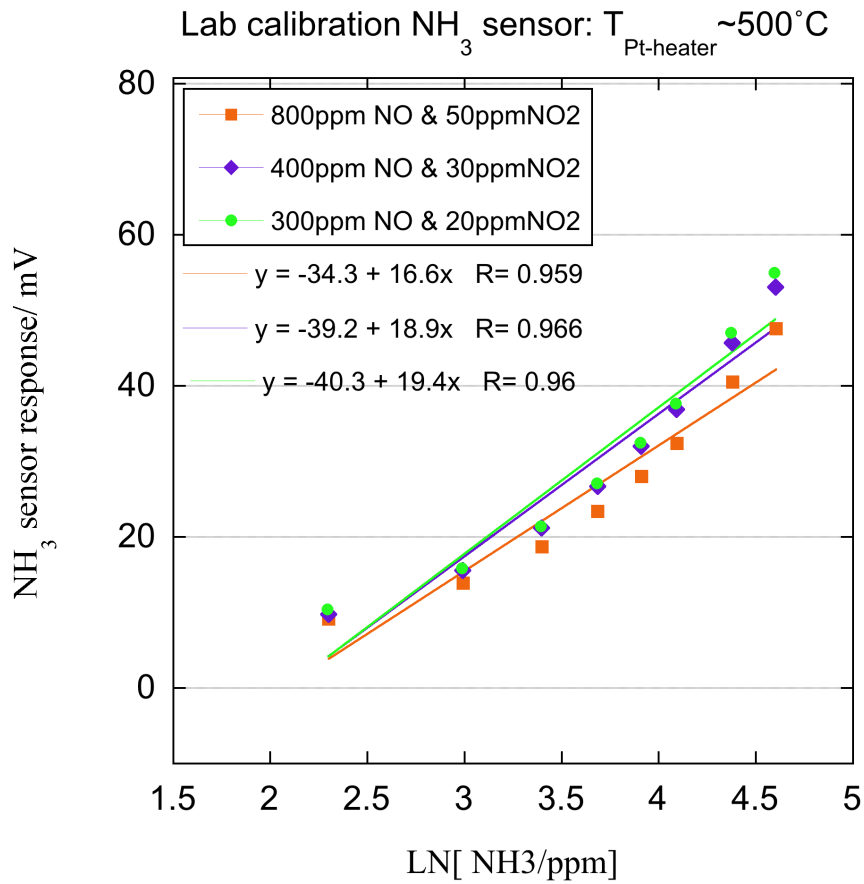
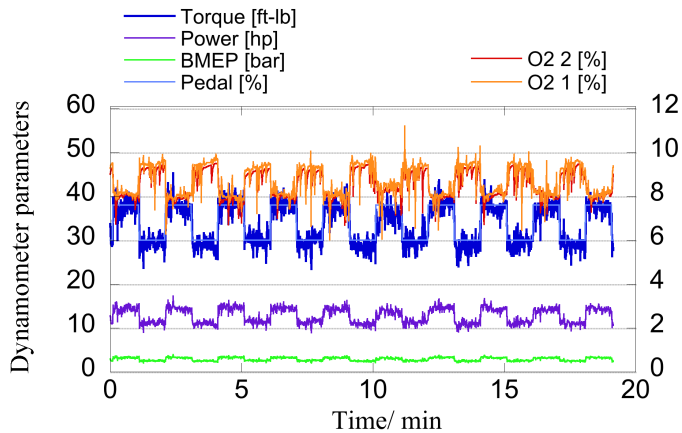


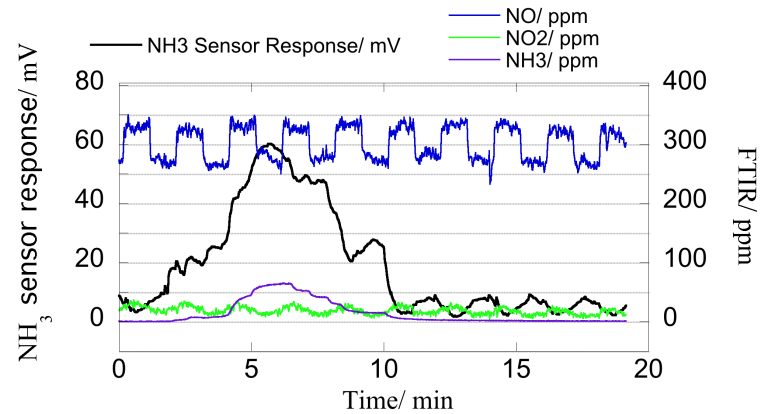


- Lab calibration reveals minimal influence of NO & NO_2 on NH_3 sensor response
- Dyno data shows significant "baseline" shift between varying NH_3 staircases: CO, even at low levels (<10 ppm), is likely the dominant interferent species.
- Presence of H_2O also influences sensor response with large difference between "dry" and humidified, but insensitive to %RH.

Results: Ammonia Injection to Simulate Slip in SCR System/ Lean Burn

- Engine in lean-stratified mode, vary load
- Inject NH_3 into exhaust stream post TWC





- NH_3 sensor response and NH_3/ ppm measured via FTIR vs. time under lean engine conditions.
- CO present at constant ~7 ppm

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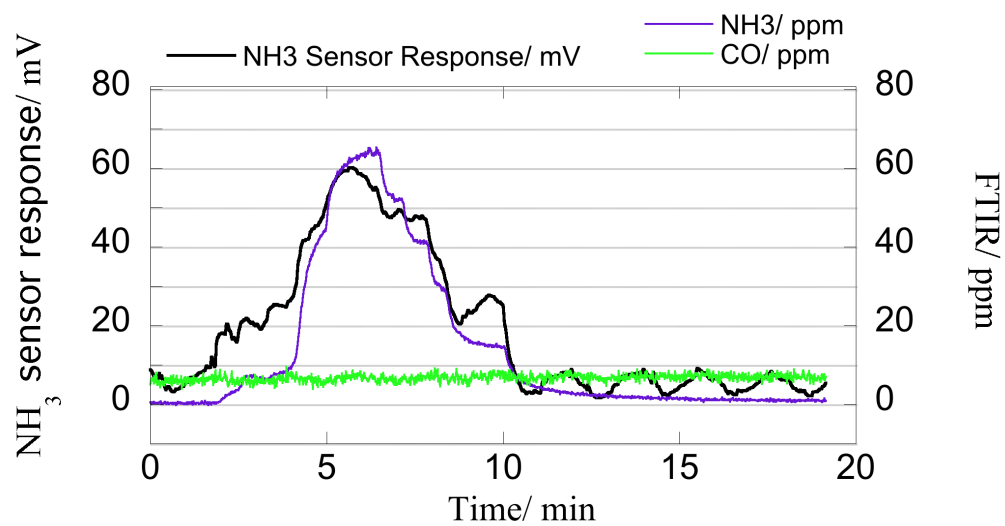
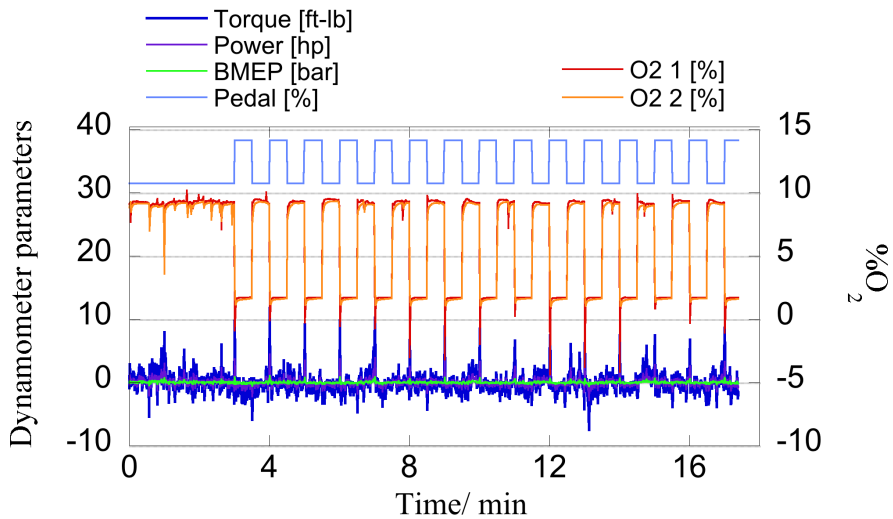
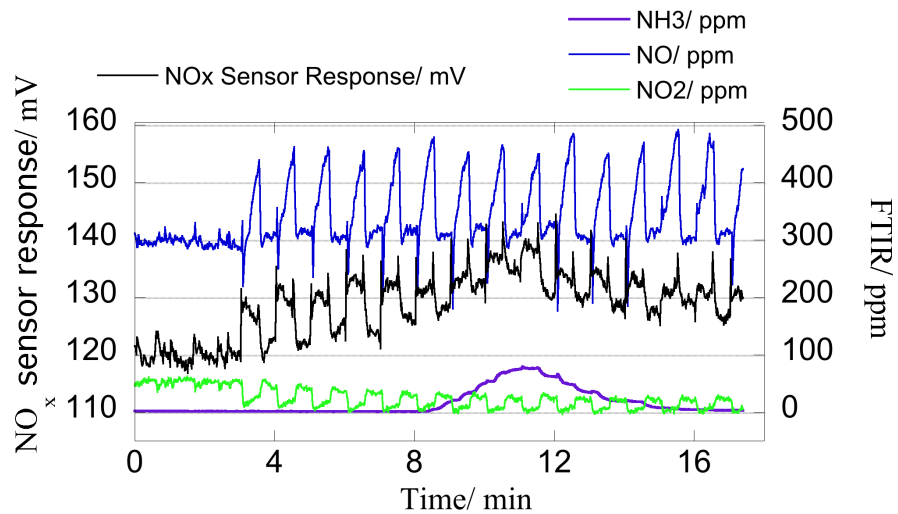


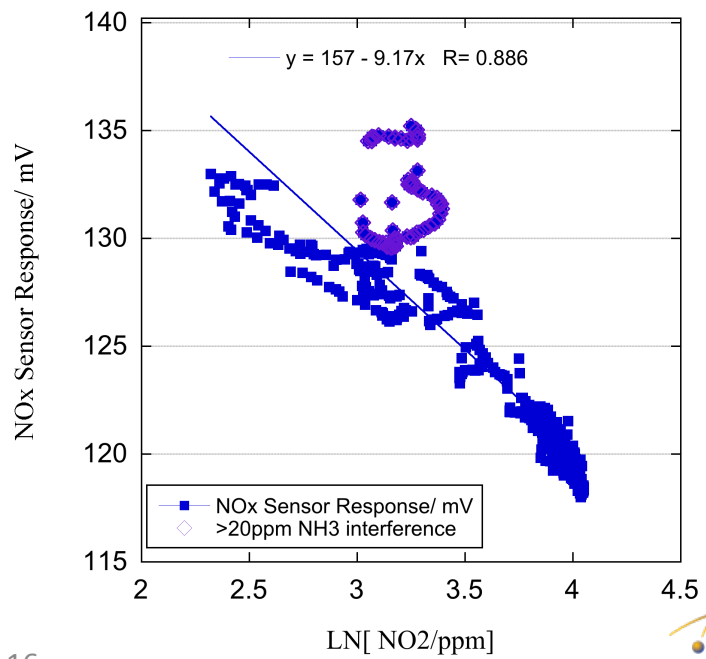
Engine testing: NO_x sensor response



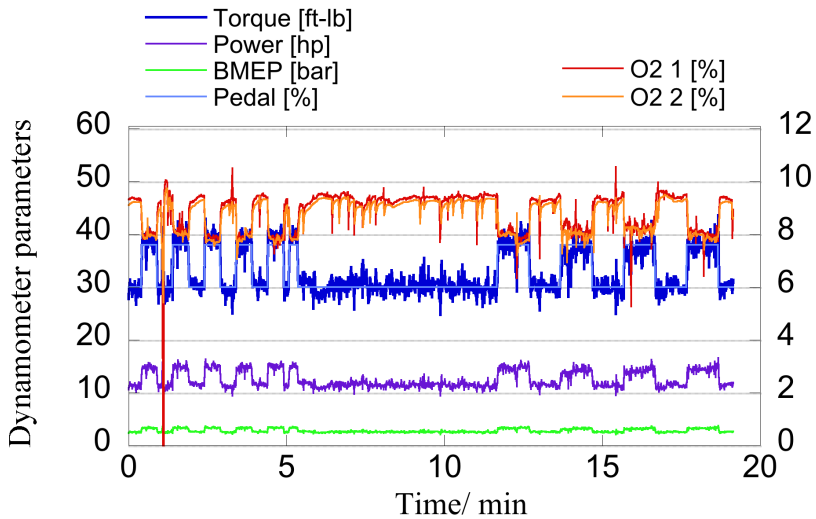


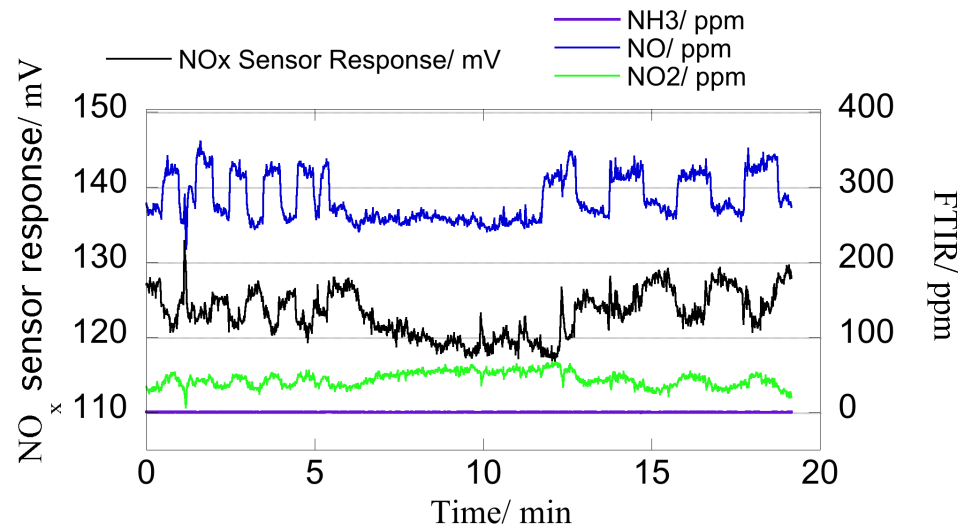
- λ switching 1.1 → 1.8
- Large variation in PO_2

- NO_x sensor exhibits log-linear correlation to $[NO_2]$ against large variation in PO_2 (1.5-9%) and P_{H_2O}. →
- Interference from NH_3>20ppm



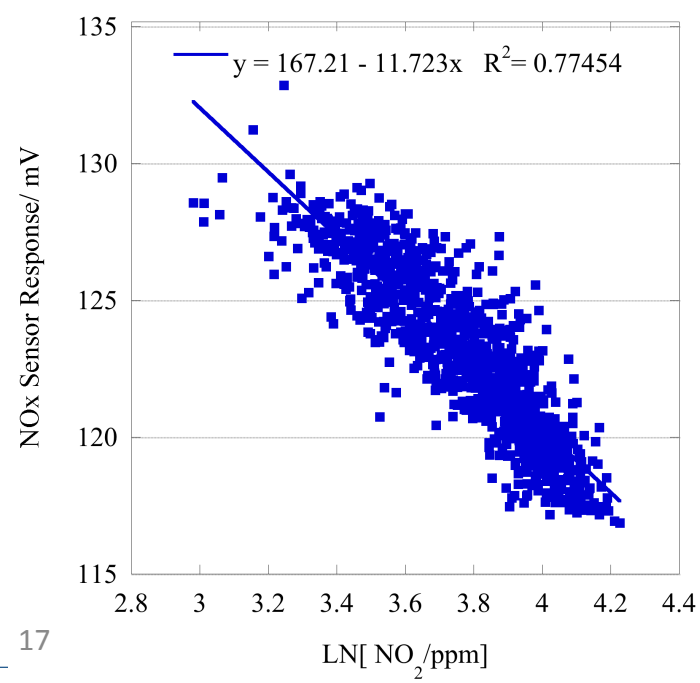
Engine testing: NO_x sensor response



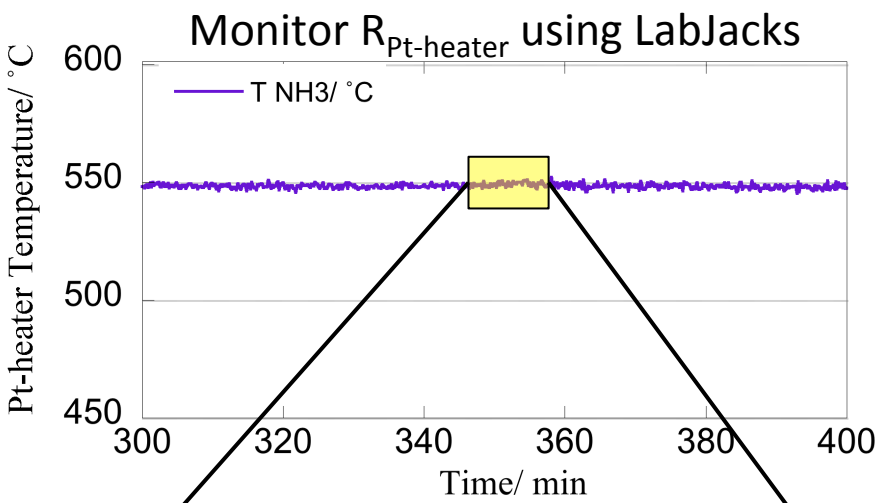


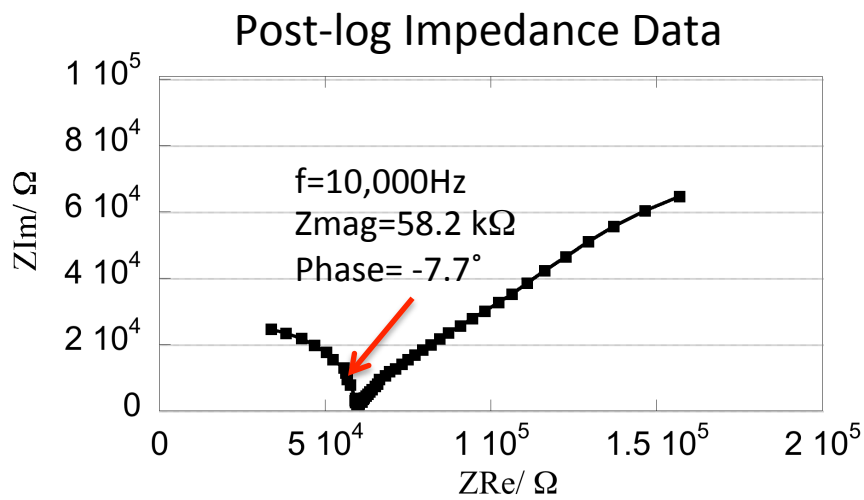
- λ adjusted from 1.86 to 1.62
- Vary engine load

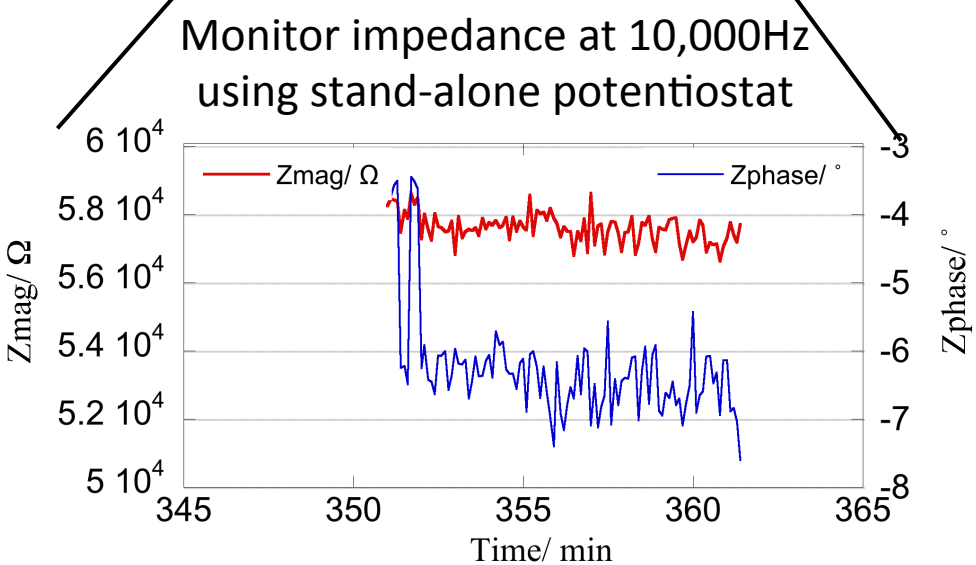
NO_x sensor exhibits log-linear correlation to $[NO_2]$. Similar relationship as that observed in λ switching conditions. →

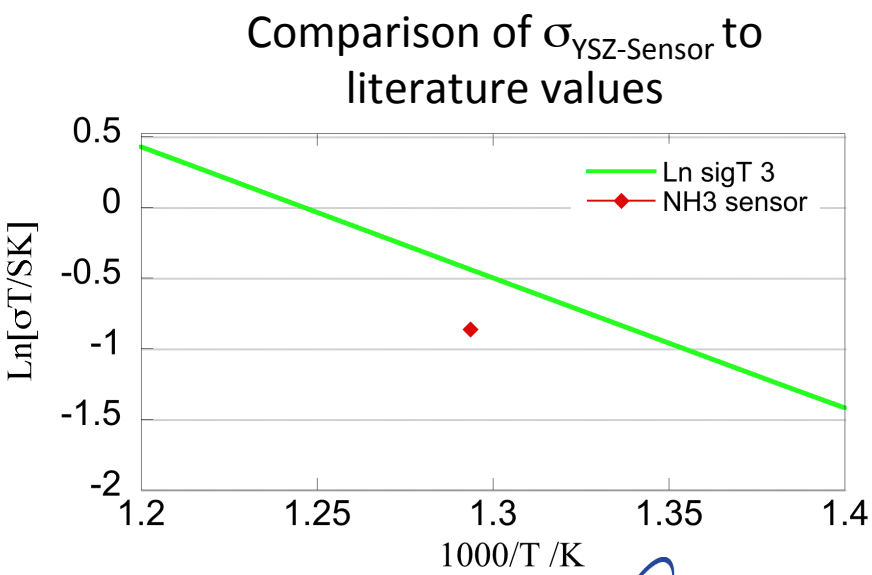


Results: Monitoring sensor element HFR and Pt-heater resistance simultaneously









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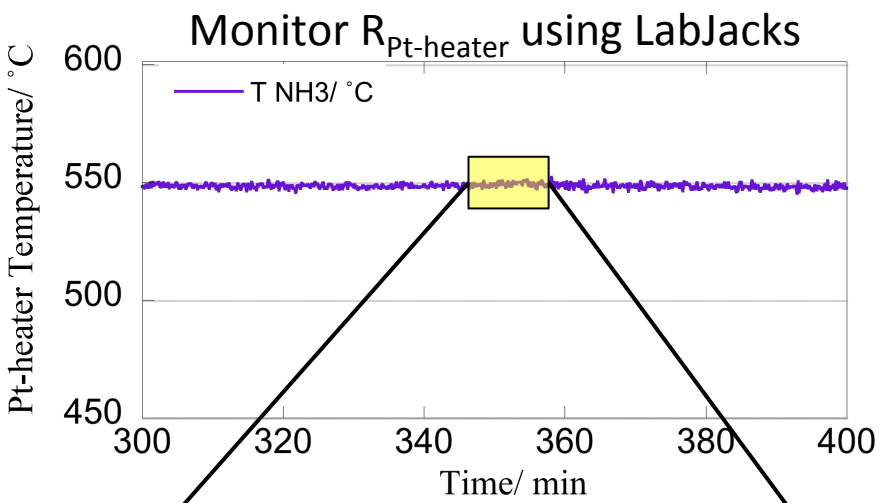
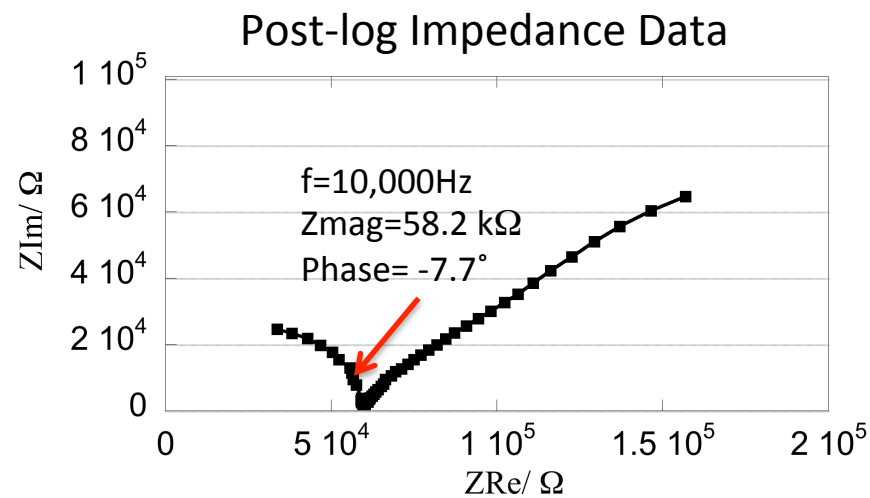
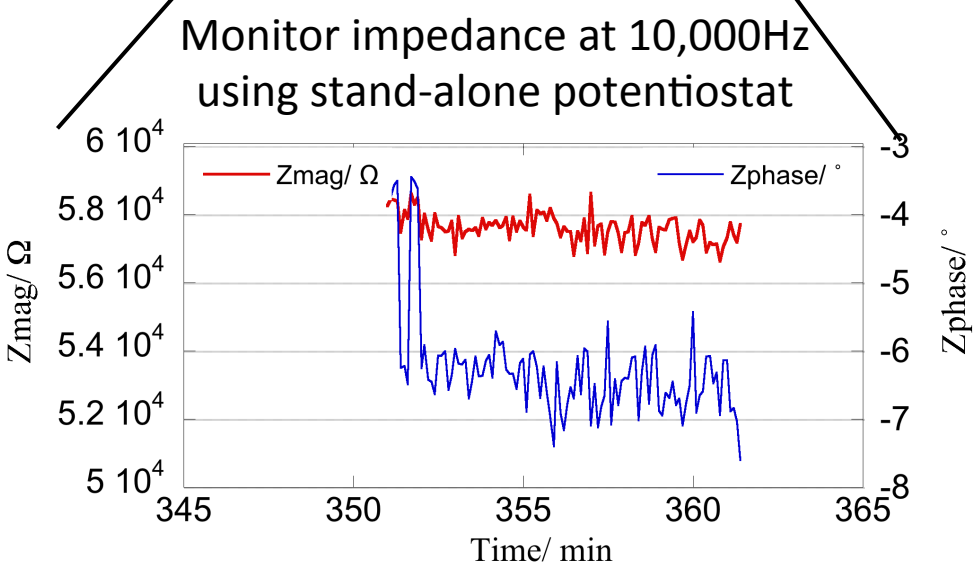
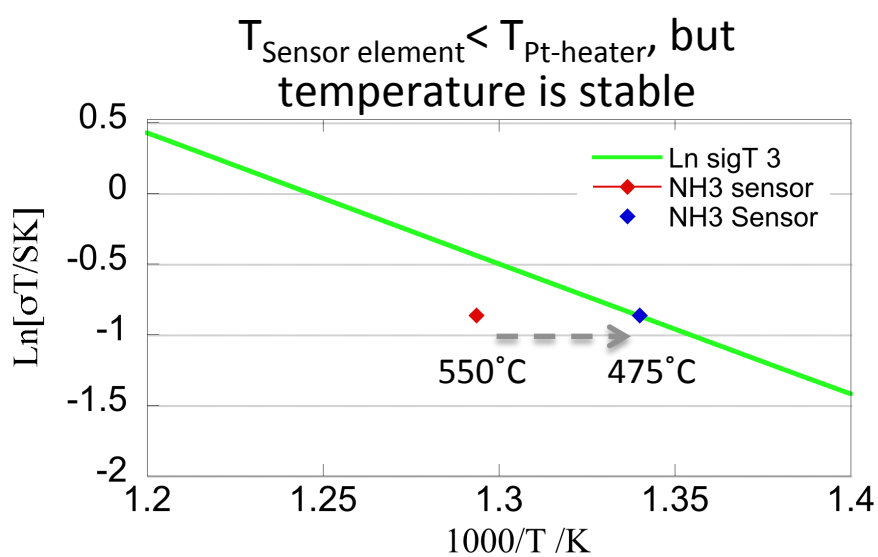








Summary

- Latest campaign (March 2015): 4 sensors, NO_x, NH_3, and HC (2) sensors logged independently upstream and downstream of the TWC respectively. Multiple sensors simultaneously tested under identical dyno conditions.
  - Collected data on BMW lean GDI 4 cyl engine (all 4 sensors)
  - Collected data on 1.9L GM diesel (NH_3 naked and w/ porous overcoat)
- GDI engine permitted first testing of MPES over wide Lambda ($0.98<\lambda<1.8$).
- New NH_3 sensor tested that shows strong promise to fulfill needs of a sensor to monitor slip from an SCR in lean burn gasoline/diesel applications.
  - Small amount of interference from NO_x but this can be removed by running sensor at higher T. Optimize before next campaign using data [NO_x] data.
- Confirmed data presented last year (diesel) that NO_x sensor output good fit to NO_2 in exhaust gas stream.
- HC sensor worked well but not much to show: HC concentrations did not change appreciably (pre-TWC) during these experiments.
- Monitoring of YSZ HFR show good T stability during dyno runs (extra HC sensor pre-TWC). Continue with adequate T control using R_H.
- Porous overcoat did not affect sensor response aside from T.

Future Work

- Locate "sensor rack" in unoccupied area of dyno cell and leave sensors in a more robust, permanent arrangement.
  - Continue to test multiple sensors simultaneously, piggy-backed to NRTC testing schedule.
  - Use switches to isolate sensors from analytical instrumentation to maintain small impact factor to NRTC testing schedule.
  - Opportunity to collect durability data.
- Test a sensor in direct contact with exhaust gas to avoid slipstream testing – test new *in situ* probe packaging.
- Focus on diesel testing and lean burn conditions testing – technology more mature for this application than stoichiometric operation.
  - Response from sensors during rich burn operation more complicated to explain.
- Move to exclusive testing of prototype sensors from ESL that have the protective ceramic overcoat applied.
- Path forward to partner with commercial Tier 1 supplier on track (resulting from LANL hosted Jan. '15 Webinar).

Acknowledgements

- The authors wish to thank Roland Gravel of the DOE Office of Vehicle Technologies for providing the funds to enable prototyping of LANL mixed potential sensors to move forward.

- Dr. Fernando H. Garzon, University of New Mexico, Sandia National Laboratories

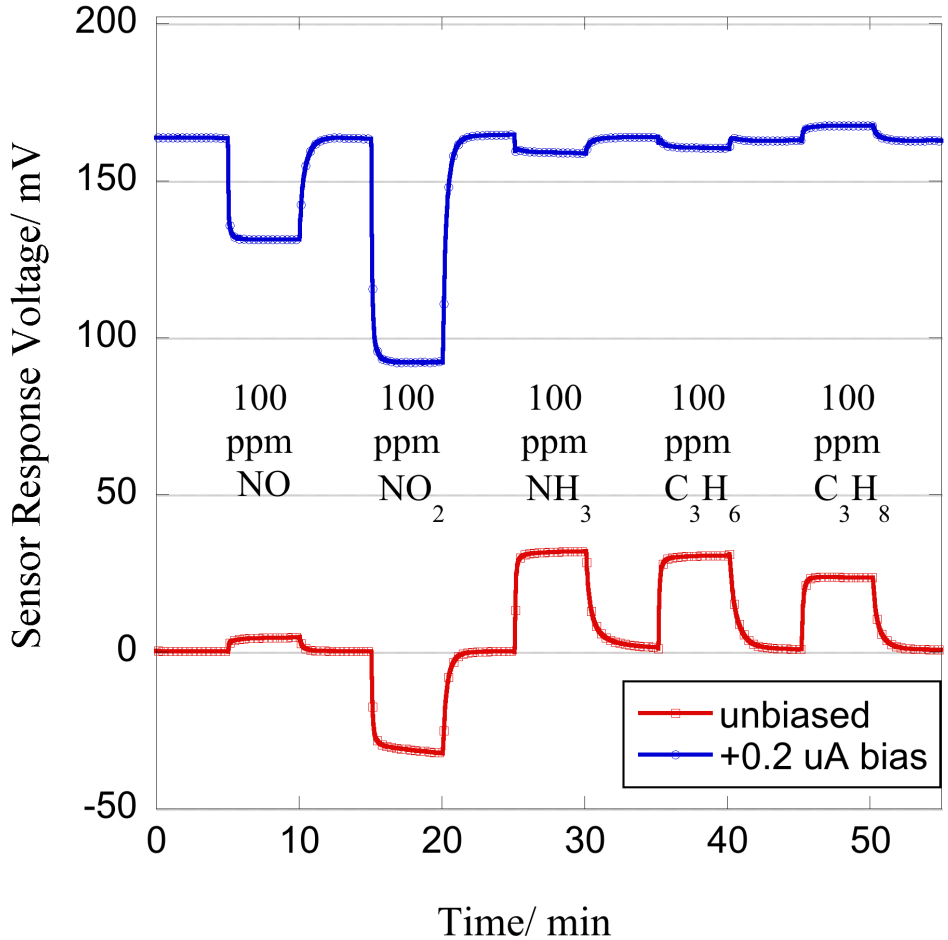
- Dr. Wenxia Li, Dr. Ponnusamy Palanisamy, and ESL ElectroScience.

- LANL also wishes to recognize sources of sensor R&D funding over past decade:
  - USCAR, Freedom Car and Vehicle Technologies, Advanced Reciprocating Engine Systems, LANL - Technology Maturation Fund, LANL - Royalty Income
  - Also, we wish to thank the Technology Transfer Division at the Los Alamos National Laboratory for providing the Strategic Innovation Investment fund to pursue this research and matching funds provided by the MPA division at LANL.

- William Penrose, Custom Sensor Solutions, Inc.

2nd generation NO_x / HC sensor: CLEERS '14 Talk

Sensor response to application of current bias



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