NO_x Sensors for Heavy Vehicle Applications

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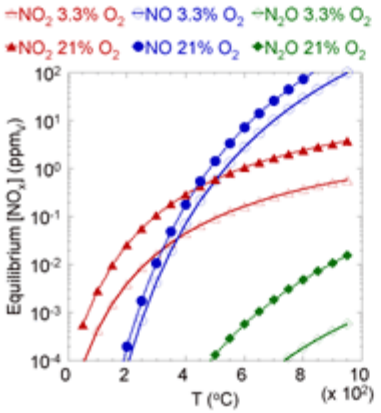
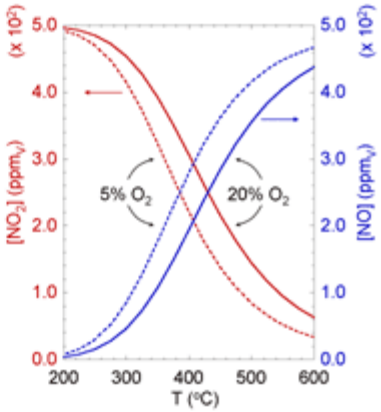
Introduction:

NOx sensors are an enabling technology which will promote the advancement of diesel engines by permitting improved engine control along with mandated on-board diagnostics. In addition, NOx sensors are required for new NOx remediation technologies such as selective catalytic reduction (SCR) utilizing hydrocarbon (HC) and urea injection. These sensors should be operative at T ~600 oC (thus avoiding the prospect of the sensor being a "cold finger" in the exhaust stream), able to measure [NOx] in the range ~1 ppmV to ~1500 ppmV, and be relatively insensitive to varying O2 concentrations in the exhaust stream. "NOx" refers to mixtures of nitrogen monoxide (NO) and nitrogen dioxide (NO2). NO2 dominates at lower temperatures and higher O2 concentrations but NO is the dominant species at higher temperatures and in O2-poor environments. Due to this equilibrium between the mono- and dioxides of nitrogen, complete [NOx] characterization of exhausts will require two of three concentrations to be accurately measured; [NO], [NO2], [NOx] (=[NO] + [NO2]).



Calculated equilibrium [NO_x] in mixtures of N_2 and O_2.



$NO(g) + \frac{1}{2}O_2(g) = NO_2(g)$.

Objective:

This project seeks to develop NOx sensing elements able to operate at ~600 oC. The initial focus has been on planar sensing elements that do not require a reference electrode. An immediate goal is to develop sensing electrode materials sensitive to NO and/or "total NOx" [NOx] with minimal [O2] sensitivity.

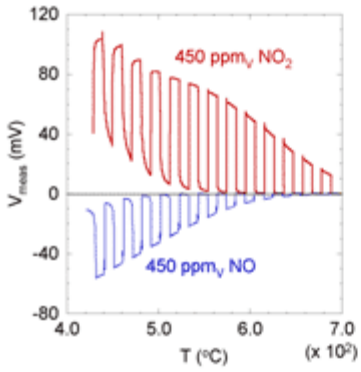
Approach:

Both "mixed-potential" and "biased" approaches are being evaluated. For both approaches,

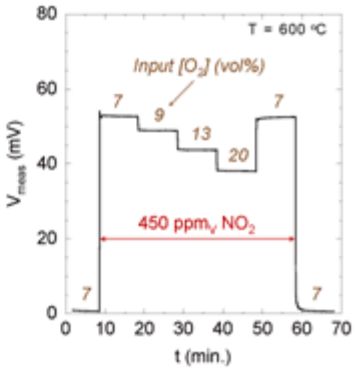
the sensing elements consist of screen-printed co-planar electrodes on an oxygen-ion conducting (YSZ) substrate.
Sensing element characterization is carried out with an automated test stand capable of operation up to 800 oC. Gas concentrations are usually 7 vol% = [O2] = 20 vol% and 20 ppmV = [NOx] = 1500 ppmV, with the balance being N2. The ability to test cross-sensitivity to interfering gas species (e.g., CO, CxHy) is available.

Results:

Evaluation of "mixed-potential" sensing elements typically indicates that the response to NO is weaker and opposite in sign to that for NO2. Strong oxygen dependence of the NO2 response is also often observed.

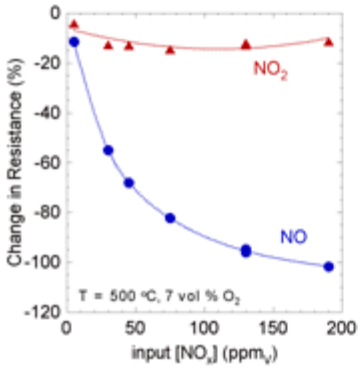


● Response to NO_x pulses in 7 vol% O_2 (dT/dt =2 °C·min^{-1}).

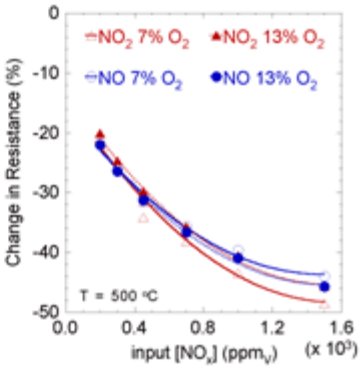


● [O_2] dependence of the 450 ppm$_V$ NO_2 response.

"Biasing" enables adjustment of the sign and magnitude of the NOx responses.

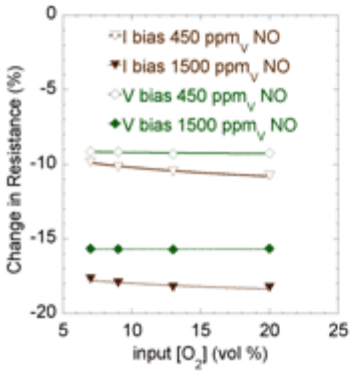


● Element current-biased to a "NO-selective" condition.

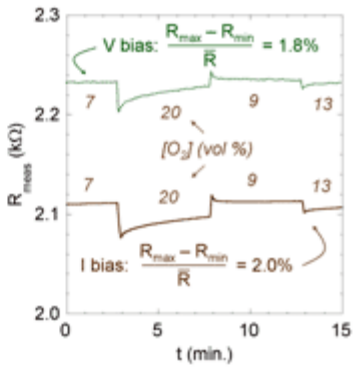


● Element current-biased to a "total NO_x" condition.

Minimal [O2] sensitivity at 600 oC achieved with both voltage (V) and current (I) biasing.



● [O_2] dependence of the NO response.



● [O_2] dependence with input [NO_x] = 0.

Summary:

Prototype NOx sensing elements have been fabricated and characterized. Investigations indicate that "biasing" is a promising technique for both "NO selective" and "total NOx" sensing. Future work will be targeted towards minimizing response and recovery times, decreasing the O2 sensitivity, characterization of selectivity and cross-sensitivity, and determination of long-term sensing element stability. Avenues for exploration include electrode composition and processing as well as sensing element geometry.
