NO Selective Sensing Elements for Combustion Exhausts

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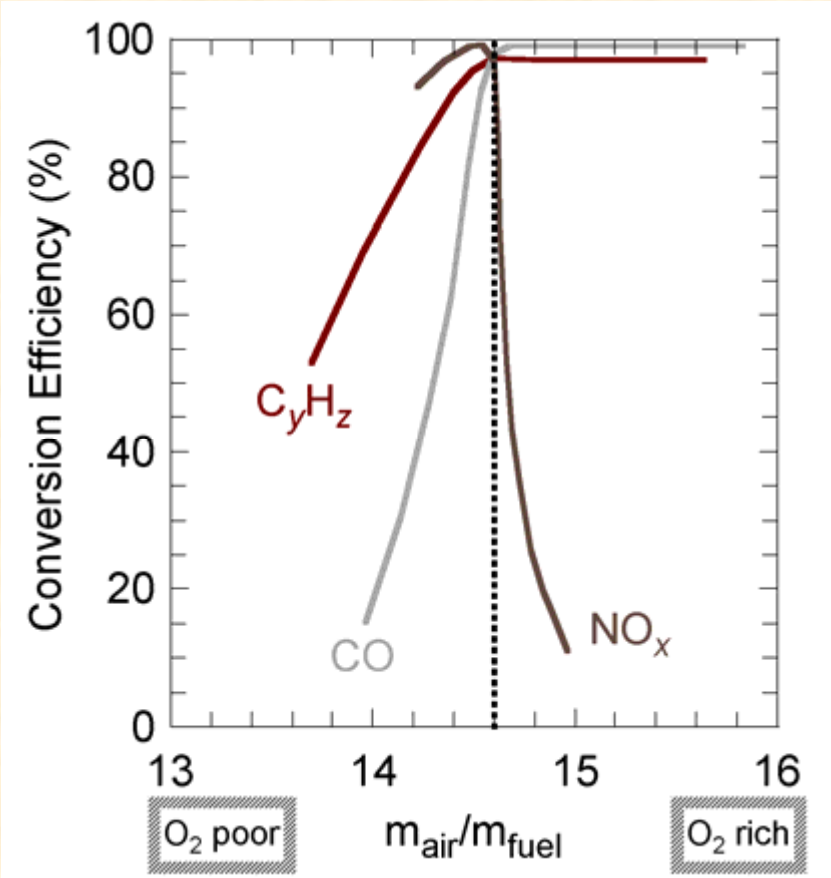
Background and motivation

Three-way catalyst (TWC) efficiency†



⇒ Currently, TWC unable to remove NO_x from O_2-rich (e.g., diesel, lean-burn) exhausts.

⇒ These exhausts will require NO_x remediation with NO_x traps or reagent injection.

⇒ Both technologies will need NO_x sensors for control and diagnostics.

⇒ Sensor operating conditions: T ~600°C, ~10–1000 ppm_V NO_x, varying $[O_2]$.‡

⇒ Above ~500 °C NO is dominant equilibrium NO_x species. (NO_2 dominates below ~500 °C.)

†Woestman and Logothetis, *The Industrial Physicist* , **1**, (1995).

‡Menil, Coillard, and Lucat, *Sensors and Actuators B*, **67**, (2000).

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Goals and methodology

⇒ Goals

- 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.
  - ⇒ Vary electrode materials, look for commonalities.
  - ⇒ Vary electrode geometry and T, study effect(s) on response magnitude and speed.

⇒ Methodology

- Substrates fabricated by tape casting and lamination, electrodes by screen printing.
- Tube furnace used to simulate elevated temperature service.
- Test parameter boundaries:
  - ⇒ $500\ ^{o}C \leq T \leq 700\ ^{o}C$.
  - ⇒ $20\ ppm_V \leq [NO_x] \leq 1500\ ppm_V$, $[O_2] = 7$ vol%, N_2 balance.

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†Miura *et al.*, *Solid State Ionics*, **65**, pp. 283-90 (1999);
Ho *et al.*, *Journ. Cer. Soc. Jpn.*, **104**, pp. 995-9 (1996);
Grilli *et al.*, *Journ. Electrochem. Soc.*, **148**, pp. H98-102 (2001);

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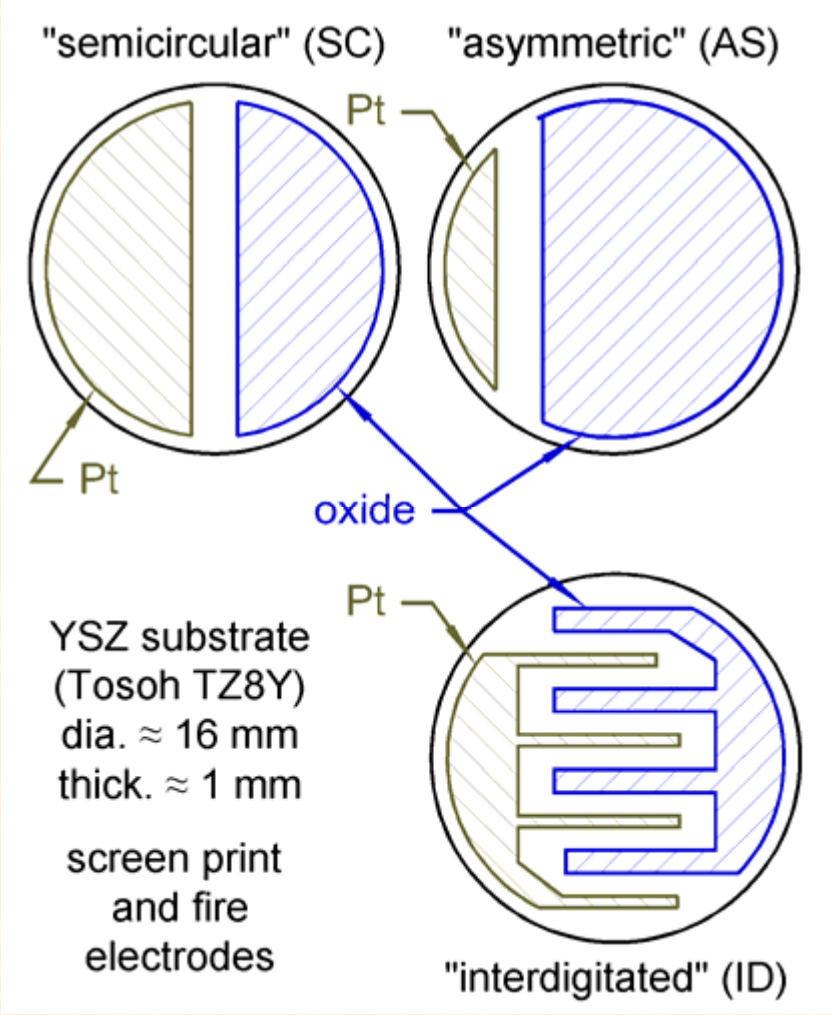
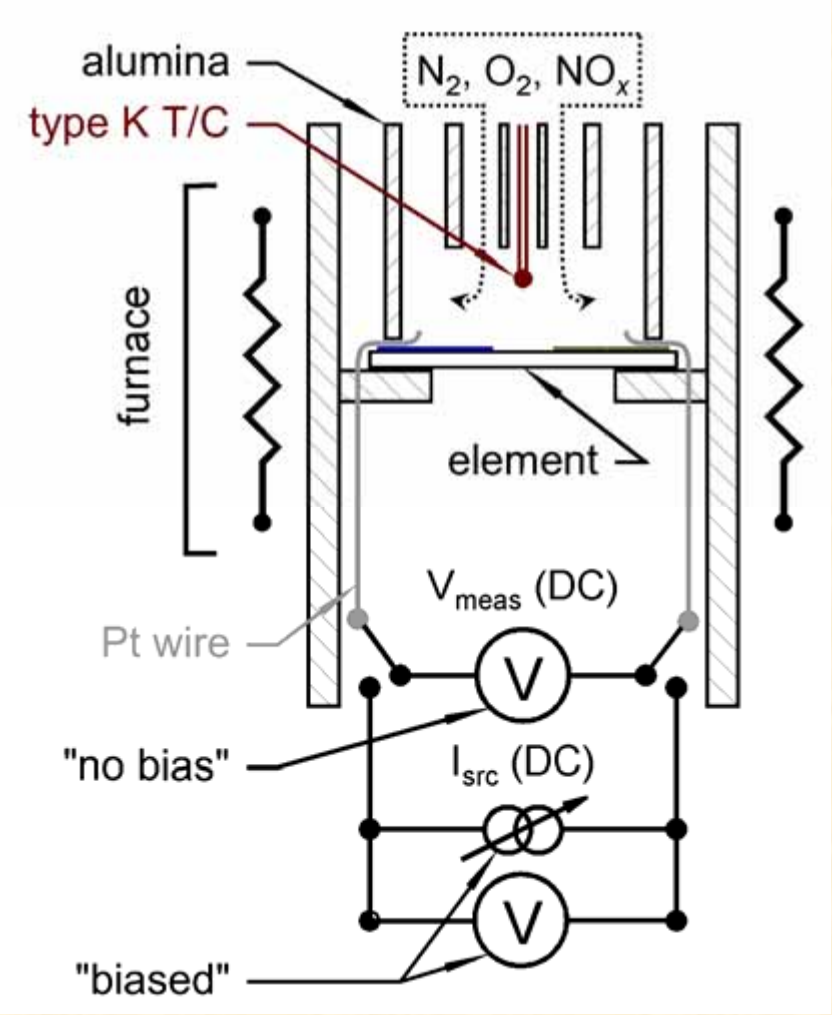
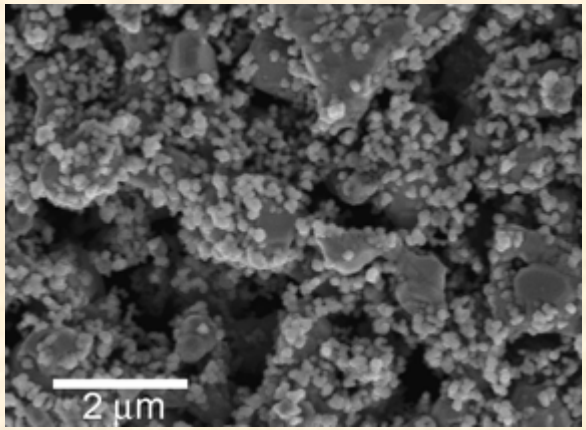
Sensing element geometries, test fixture schematic

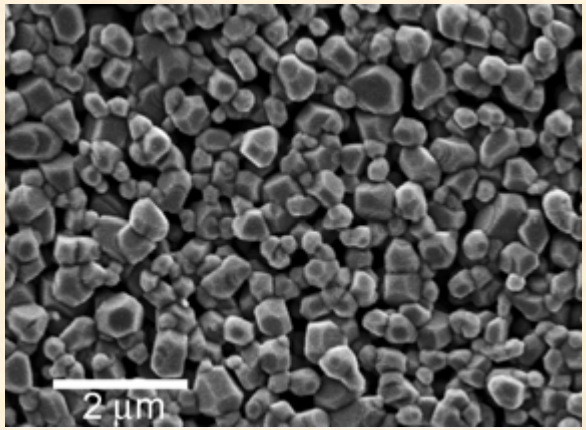




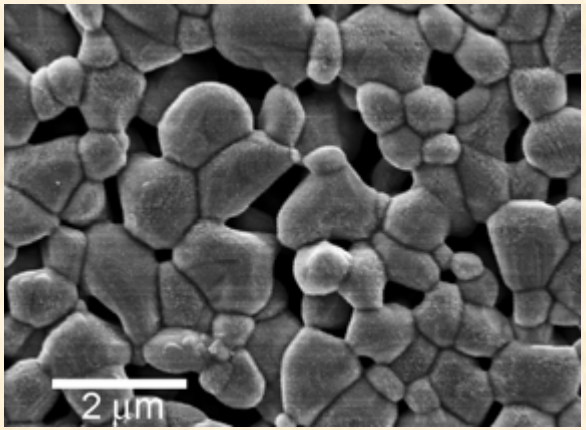
Electrode materials and microstructures



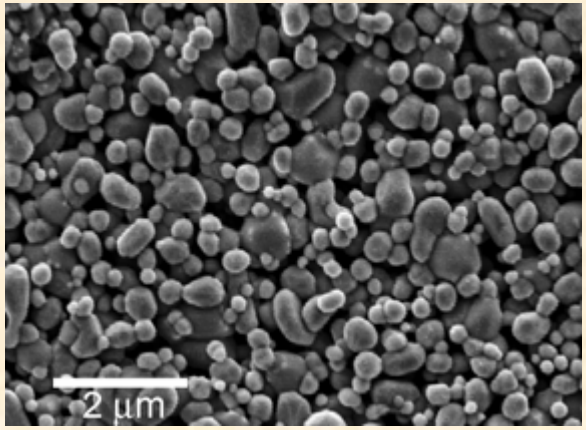
Pt
Electroscience



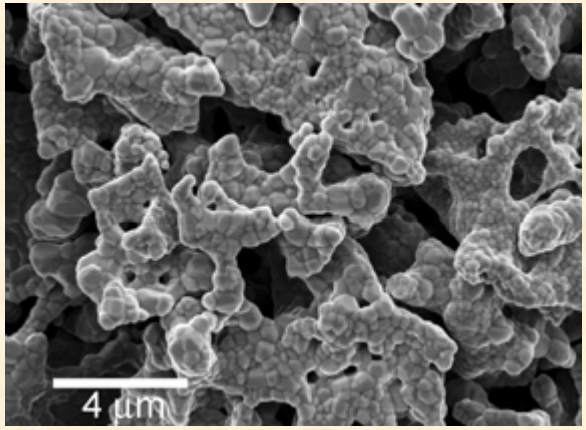
NiO
J.T. Baker



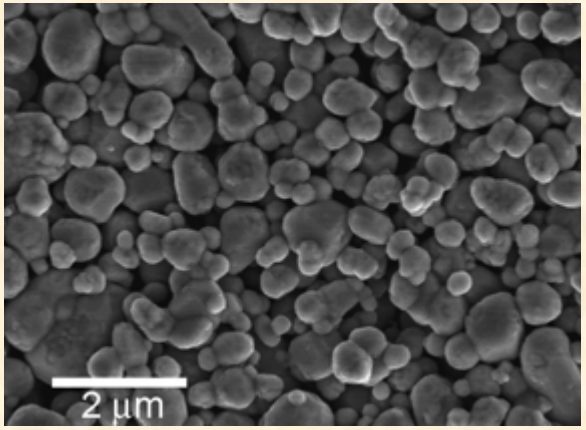
ZnO
Alfa Aesar



$La_{0.85}Ba_{0.15}CrO_3$ (LBC)
Praxair



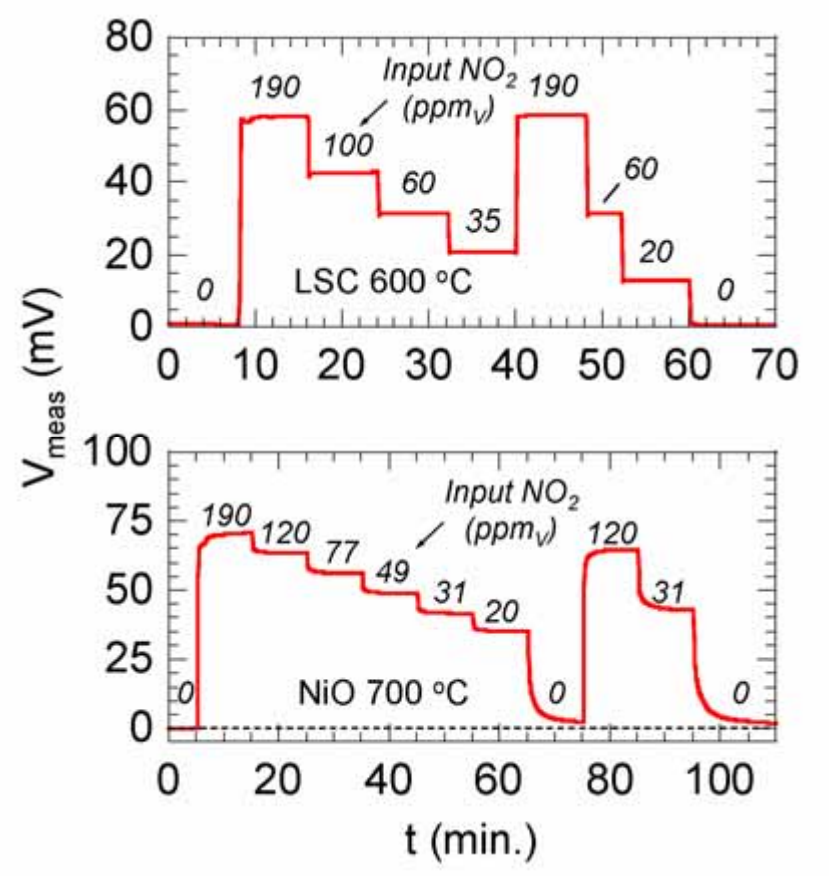
$La_{0.8}Sr_{0.2}FeO_{3-\delta}$ (LSF)
Praxair



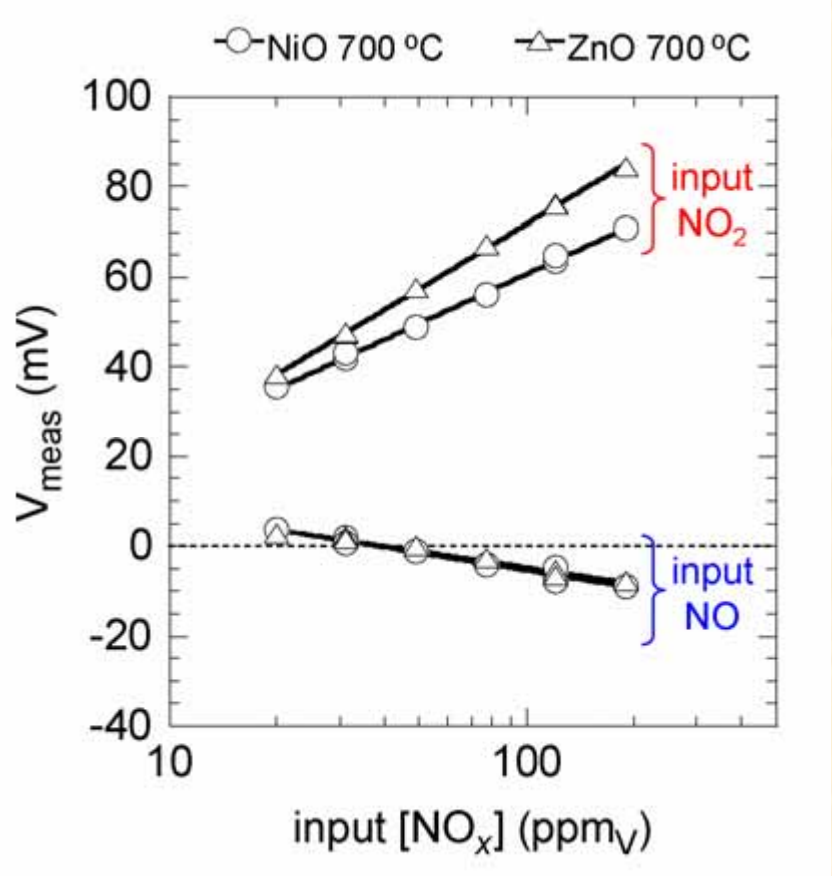
$La_{0.85}Sr_{0.15}CrO_3$ (LSC)
Praxair

No bias: Strong NO_2 response, NO weak

$V_{meas} = f(t)$



$V_{meas} = f([NO_x])$



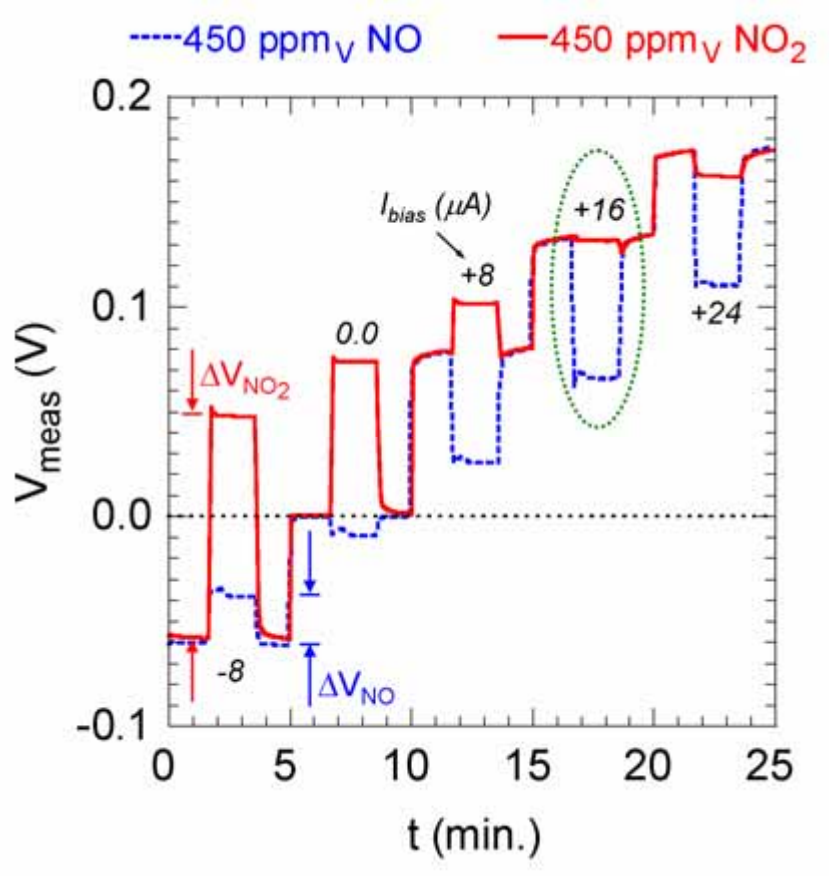
⇒ Semicircular (SC) geometries.

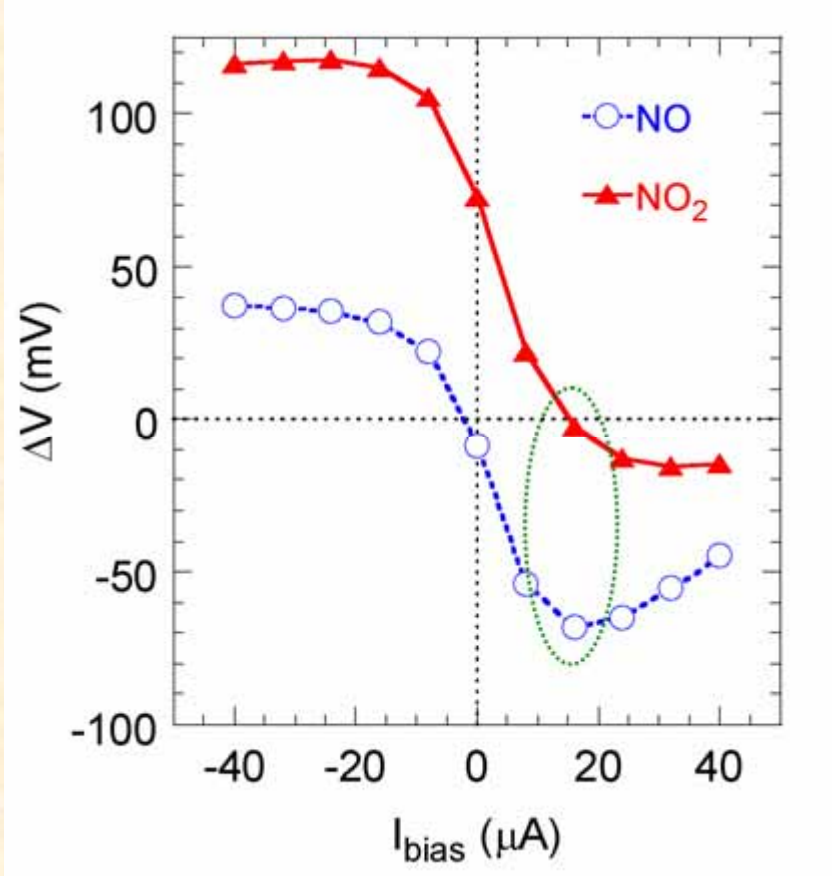
⇒ Data collected in 7 vol% O_2.

Effect of varying I_{bias} on NO_x responses

Pulses of 450 ppm_V NO_x at varying I_{bias}

$\Delta V = f([I_{bias}])$



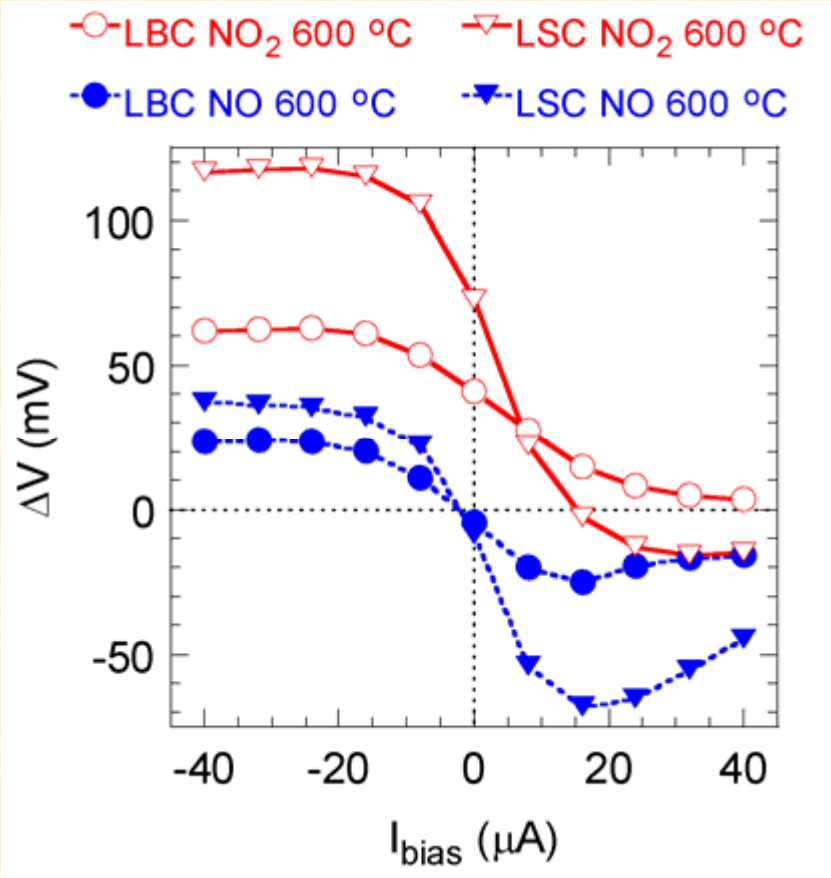


⇒ Data collected at 600 °C, 7 vol% O_2. LSC/Pt, semicircular (SC) geometry.

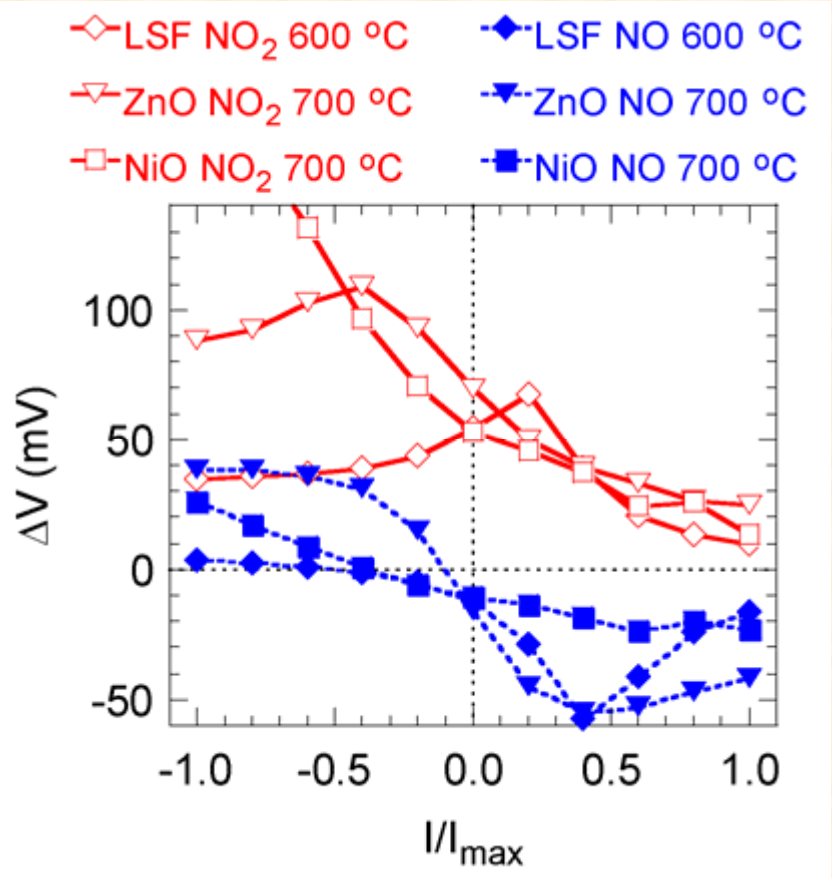
⇒ "Positive bias": Oxide electrode +, Pt electrode -.

Alkaline earth-doped chromites yield "NO-selectivity"

$La_{0.85}A_{0.15}CrO_3$ (A = Ba, Sr)



LSF, ZnO, NiO

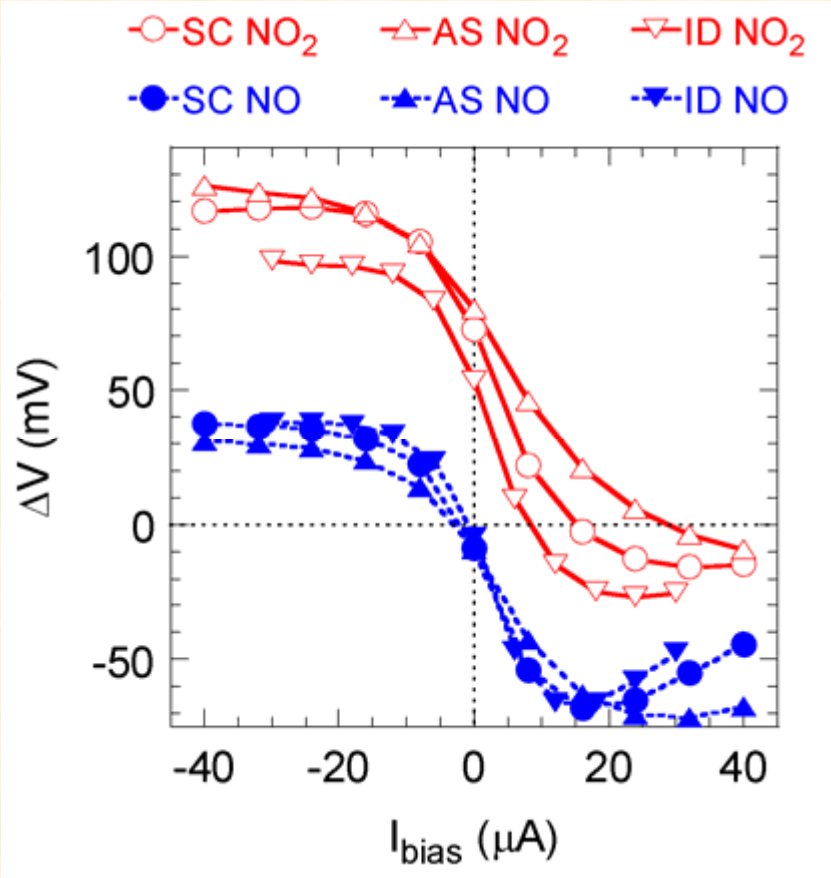


⇒ All data collected with SC geometry, 0/450 ppm_V NO_x in 7 vol% O_2.

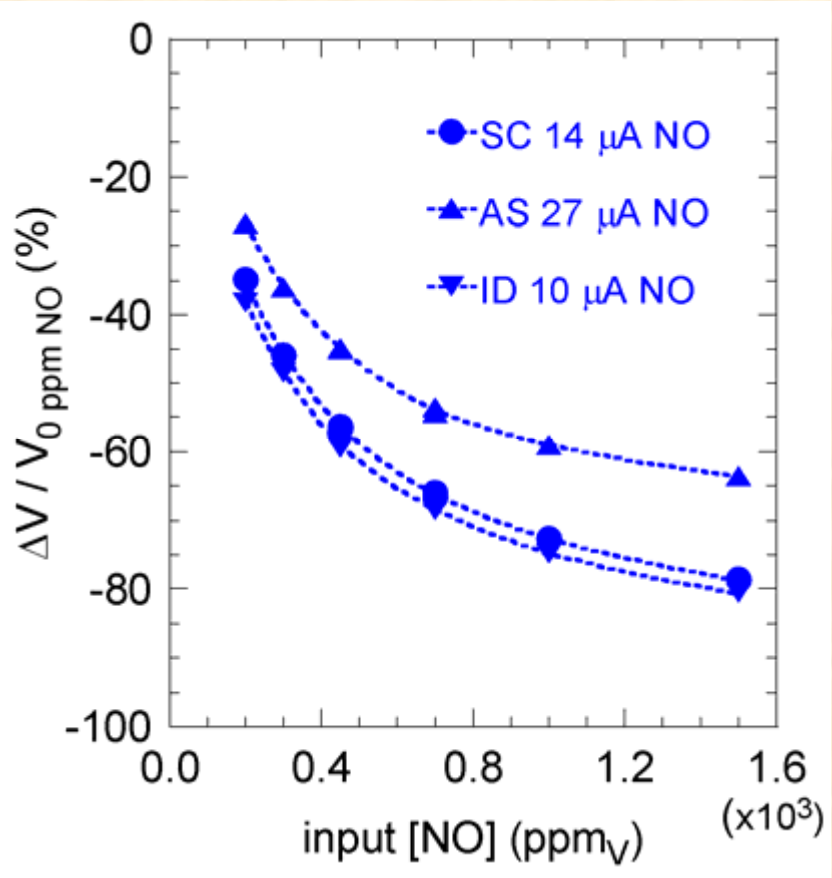
⇒ Focus further study on LSC.

Little geometry influence on NO response magnitude

$\Delta V = f([I_{bias}])$



$\Delta V = f([NO])$

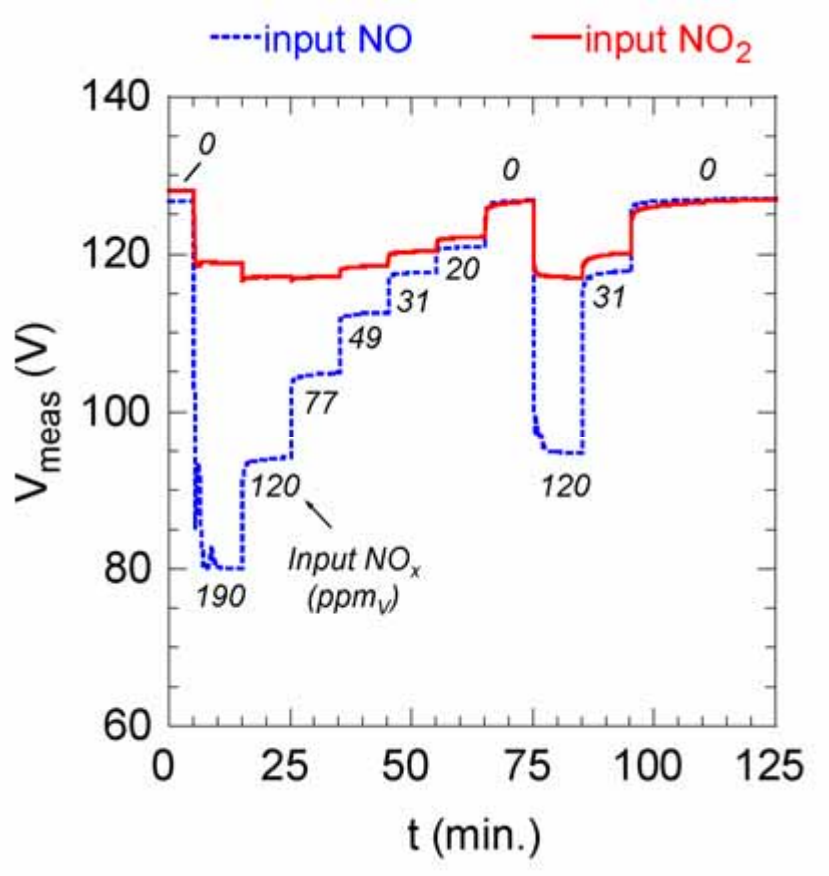


⇒ All elements constructed with LSC/Pt.

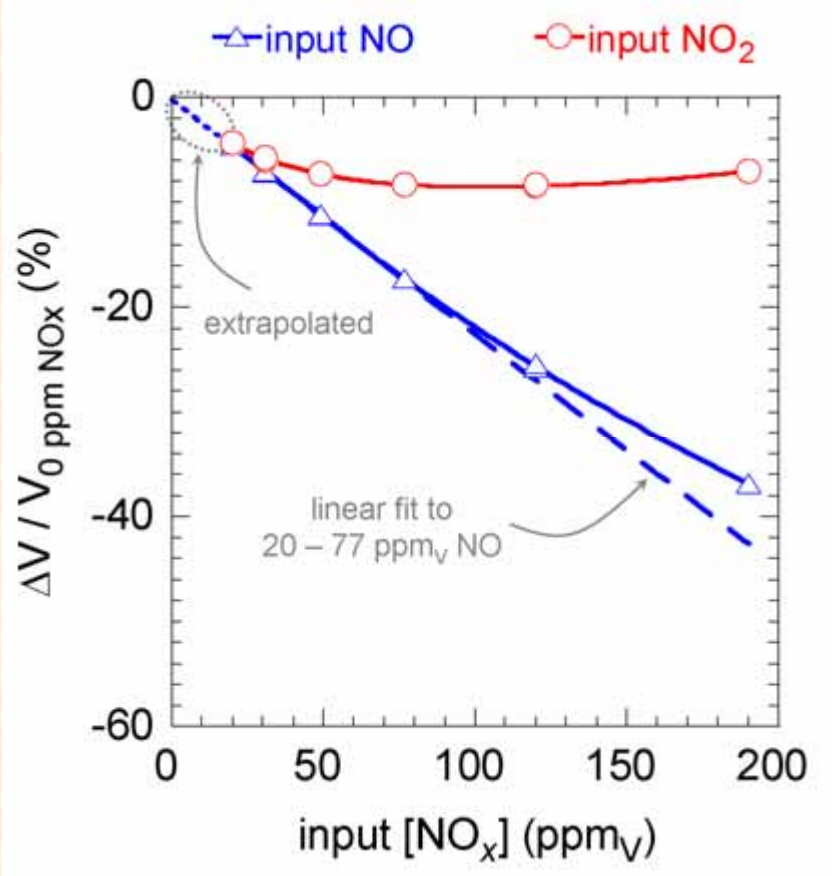
⇒ Data collected at 600 °C, 7 vol% O_2.

Sensing performance with "low" input [NO_x]

V_{meas} = f(t) (10 μA bias)



$\Delta V = f([NO_x])$

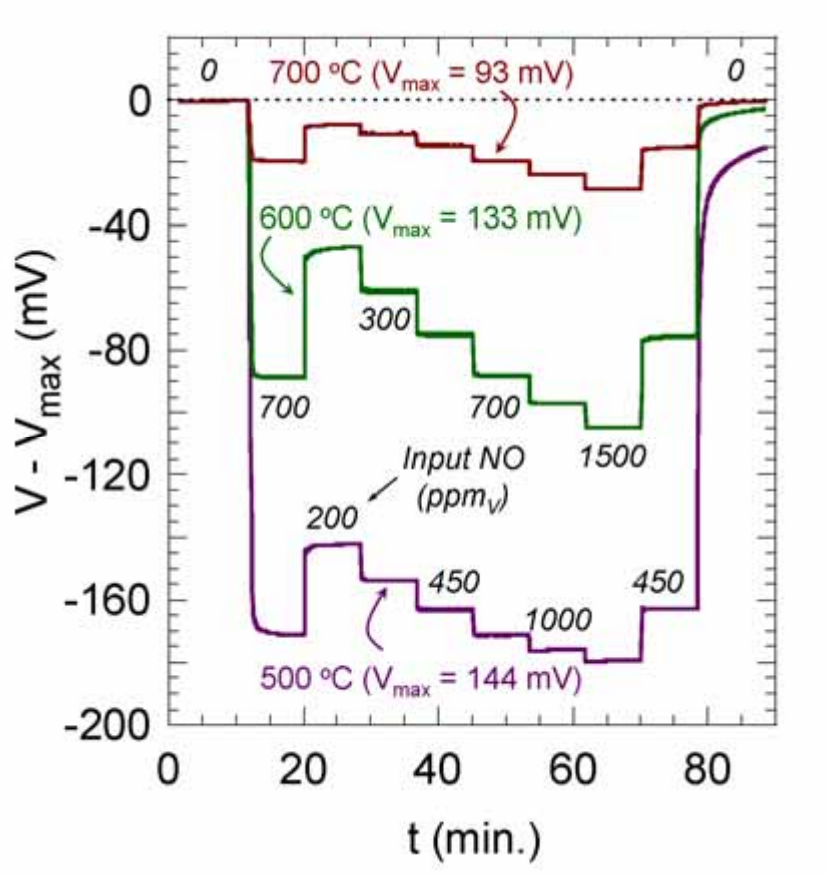


⇒ SC element geometry (LSC/Pt).

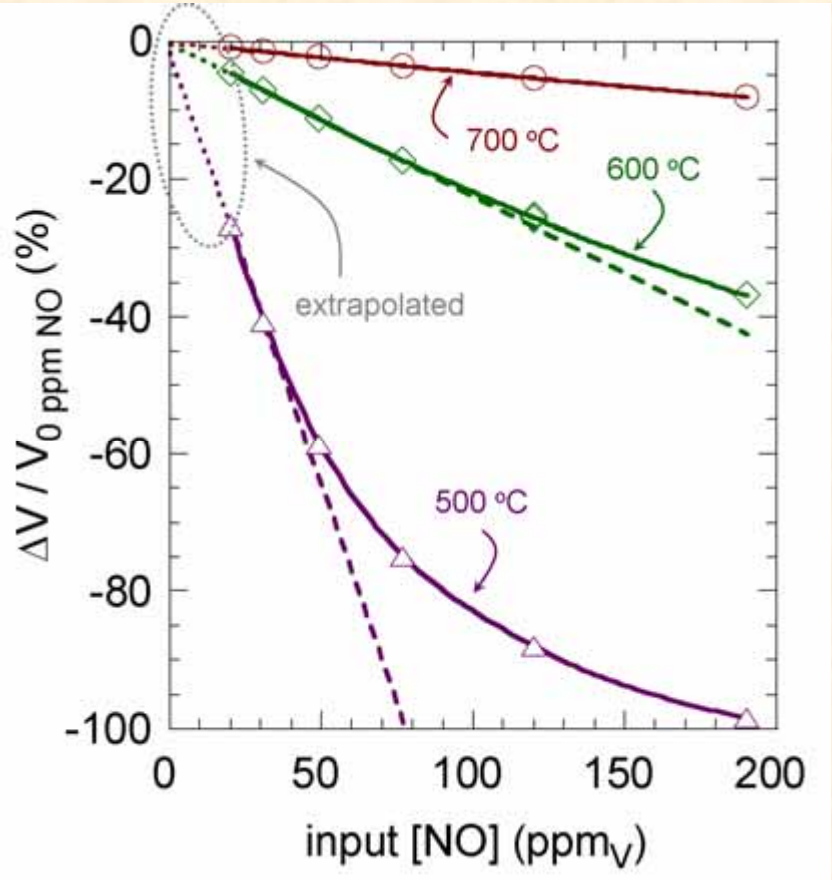
⇒ Data collected at 600 °C, 7 vol% O_2.

Increasing T decreases NO response magnitude

"high" input [NO]



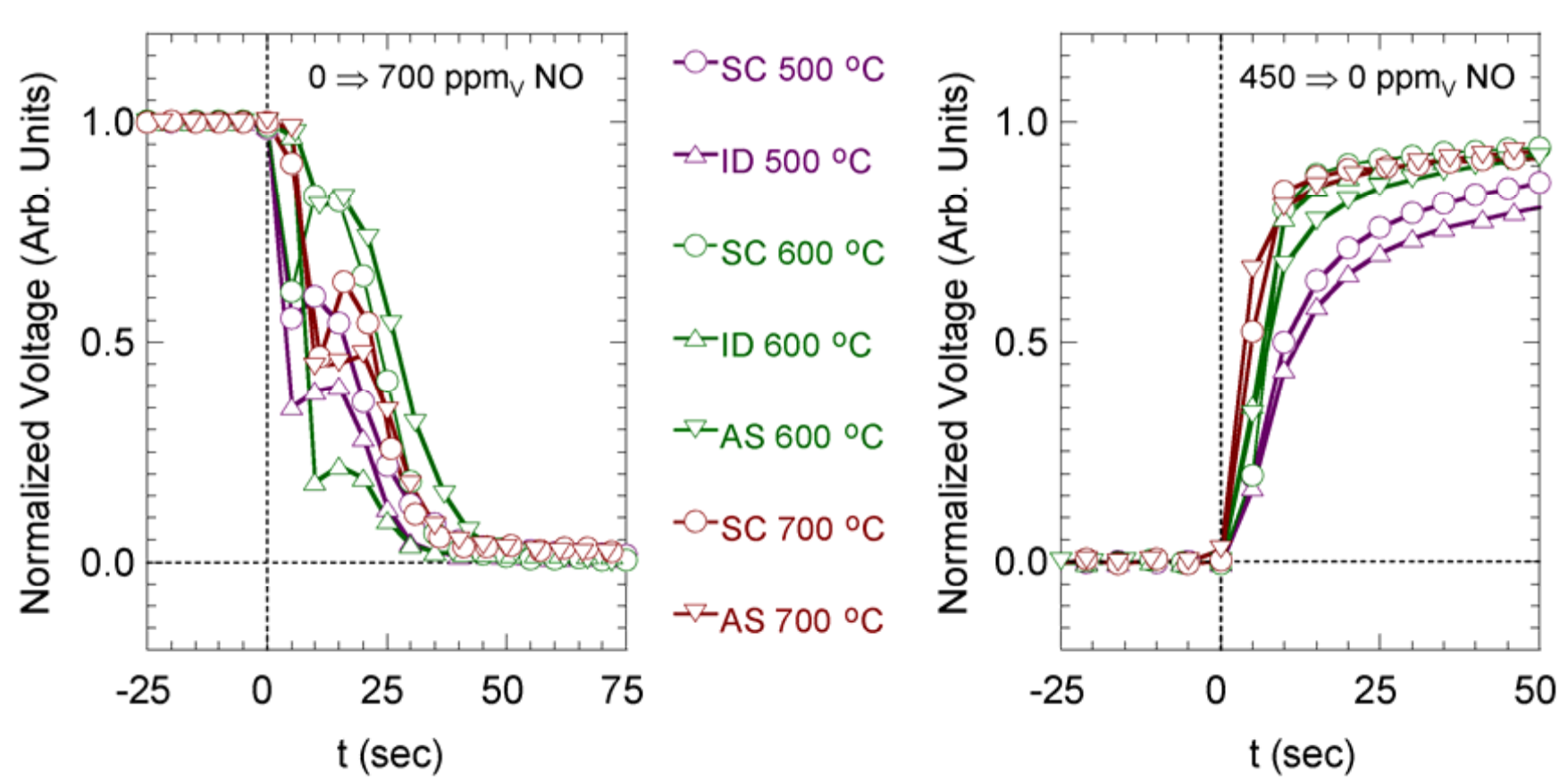
"low" input [NO]



⇒ SC element geometry with LSC.

⇒ Data collected in 7 vol% O_2.

Decreasing T mainly affects recovery time



⇒ All data collected in 7 vol% O_2.

Summary and future work

⇒ Experimental approach

- ♦ DC-electrically biased sensing elements on YSZ substrates.
- ♦ Co-planar electrodes (one oxide, one Pt).

⇒ Results

- ♦ Enhanced NO response (relative to NO_2 response) for elements with LSC and LBC as the oxide. Effect not seen with all oxides.
- ♦ Linear [NO] dependence with low input NO, extent of linear regime decreased with decreasing T.
- ♦ NO response magnitude strong function of T, weak function of electrode geometry. Step recovery time mainly controlled by T.

⇒ Future work

- ♦ Study/elimination of step response transient & background drift.
- ♦ Characterize cross-sensitivity (CO, H_2O, etc.).
- ♦ Explore DC voltage and low-frequency AC biasing.
- ♦ Extend work to other Cr-containing oxides.

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⇒ B. L. Armstrong and C. A. Walls (ORNL).

- YSZ substrate fabrication.
- Screen printing ink formulation and production.

⇒ L. C. Maxey and B. E. Evans (ORNL).

- Electronics and automation.

⇒ D. Kubinski, R. Soltis, and J. Visser (Ford SRL).

- Consultation in mobile power sensing requirements and technologies.

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