ASME Internal Combustion Engine Division
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High-T NO_x Sensing Elements using Conductive Oxides and Pt

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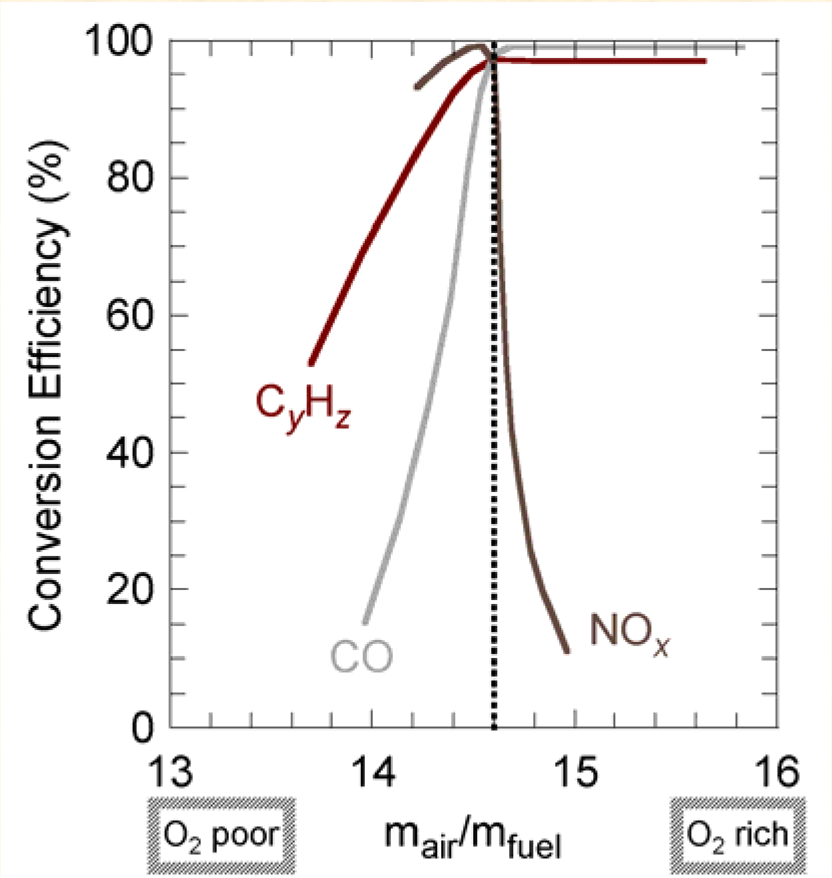
Background I – need for NO_x sensors

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 (LNT) or reagent injection (SCR).

⇒ Both technologies will require compact and robust NO_x sensors.

⇒ Sensor controls trap regeneration for LNT, reagent injection for SCR.

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

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†Woestman and Logothetis, *The Industrial Physicist* , **1**, (1995).
‡Menil, Coillard, and Lucat, *Sensors and Actuators B*, **67**, (2000).

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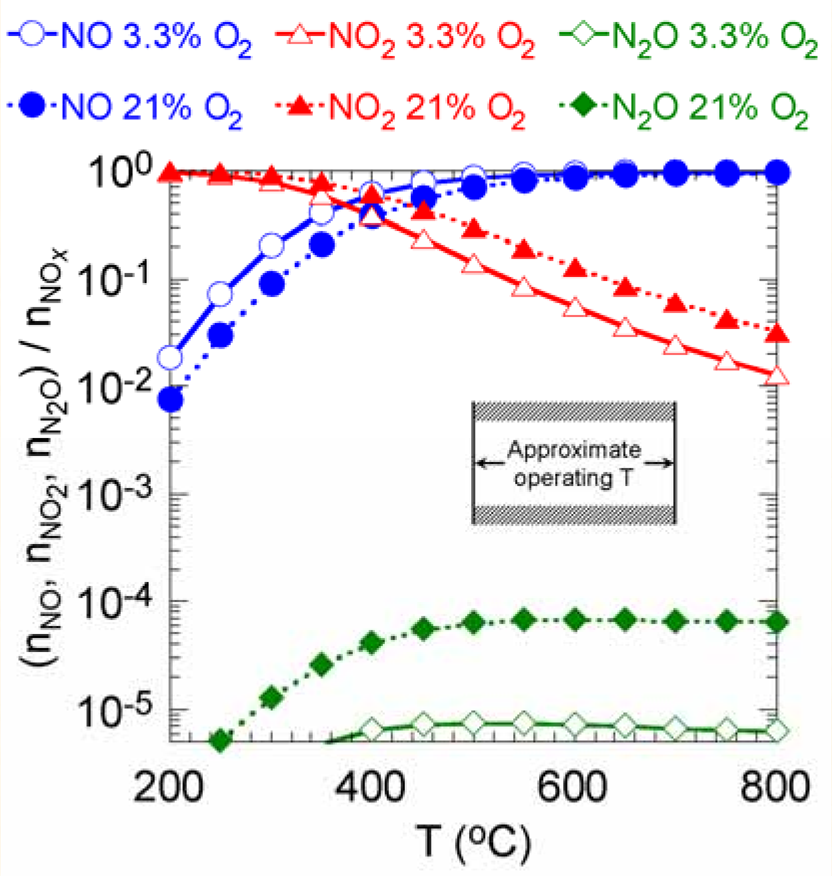
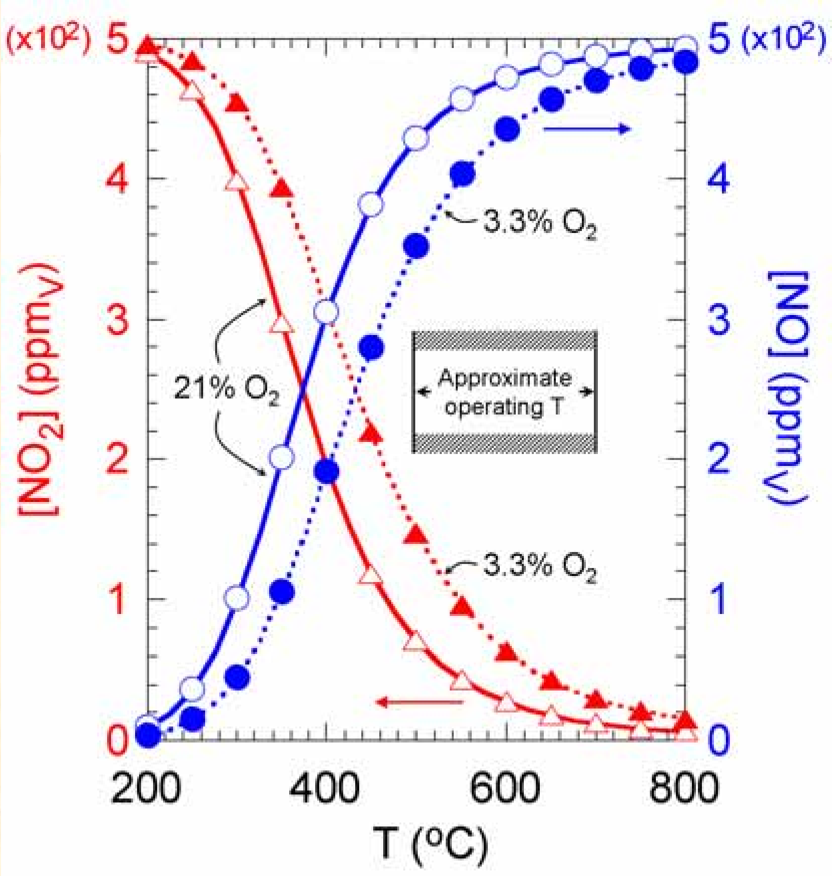
Background II: NO_x species

Equilibrium NO_x abundances†



$NO_2 = NO + ½O_2$†



⇒ NO is dominant equilibrium NO_x species above 500 °C.

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†In mixtures of N_2 and O_2, FactSage (Thermfact Ltd., Quebec) used for calculations.

Experimental approach and methodology

⇒ Experimental approach

- High-T NO_x sensing elements based on YSZ.
  - ⇒ Co-planar sensing elements (conductive oxide / Pt).
- Vary conductive oxide and element geometry.
- Study effects of DC constant current "bias".†

⇒ Methodology

- Electrodes applied by screen printing and thermal treatment.
- Tube furnace used to simulate elevated temperature service.
- Test parameter boundaries:
  - ⇒ 500 ^{o}C ≤ T ≤ 700 ^{o}C.
  - ⇒ 20 ppm_V ≤ [NO_x] ≤ 1500 ppm_V, [O_2] = 7–20 vol%, bal. = N_2.

⇒ Performance metrics

- NO_2 and NO response magnitude, effect of varying [O_2].
- Response/recovery time.

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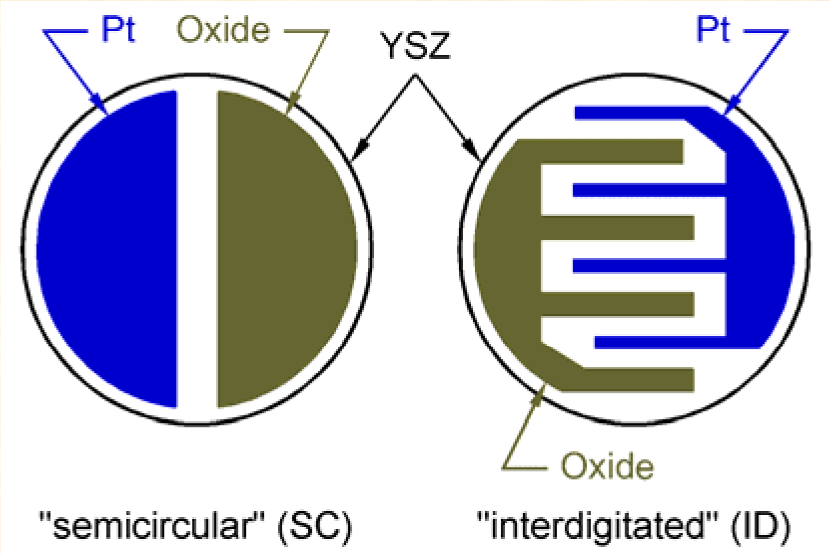
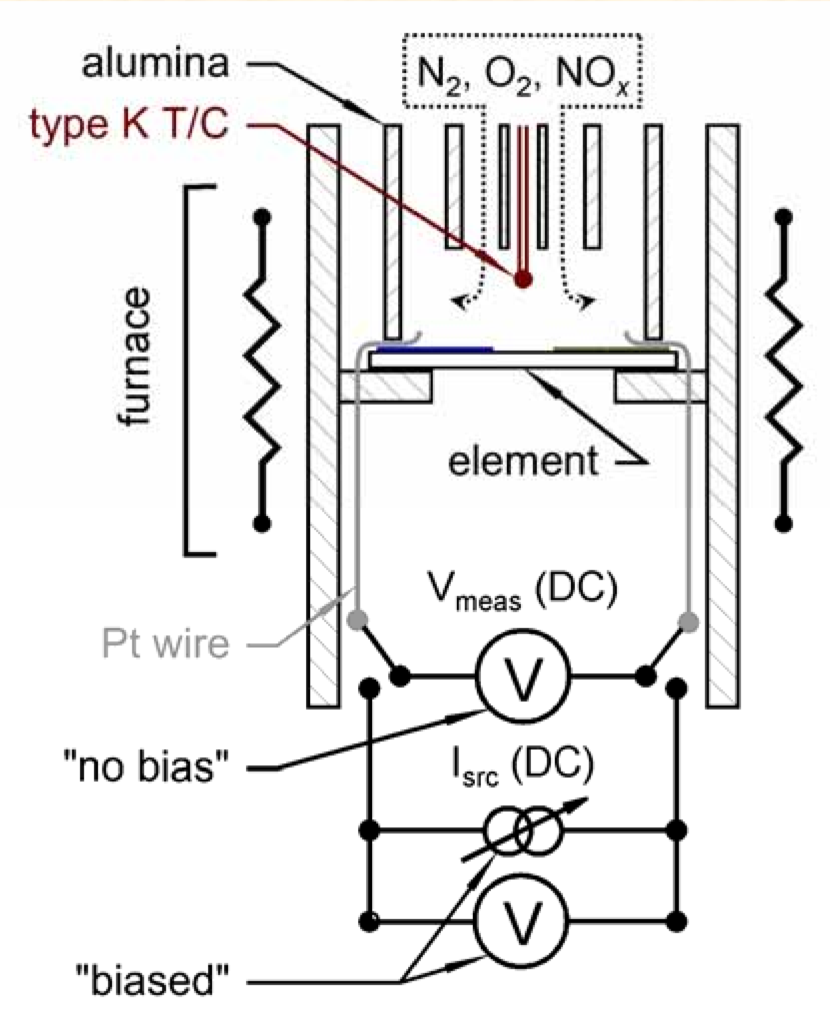
†Miura *et al.*, *Solid State Ionics*, **65**, pp. 283-90 (1999);
Ho *et al.*, *Journ. Cer. Soc. Jpn.*, **104**, pp. 995-9 (1996);
Grilli *et al.*, *Journ. Electrochem. Soc.*, **148**, pp. H98-102 (2001);

Sensing element geometries, test fixture schematic





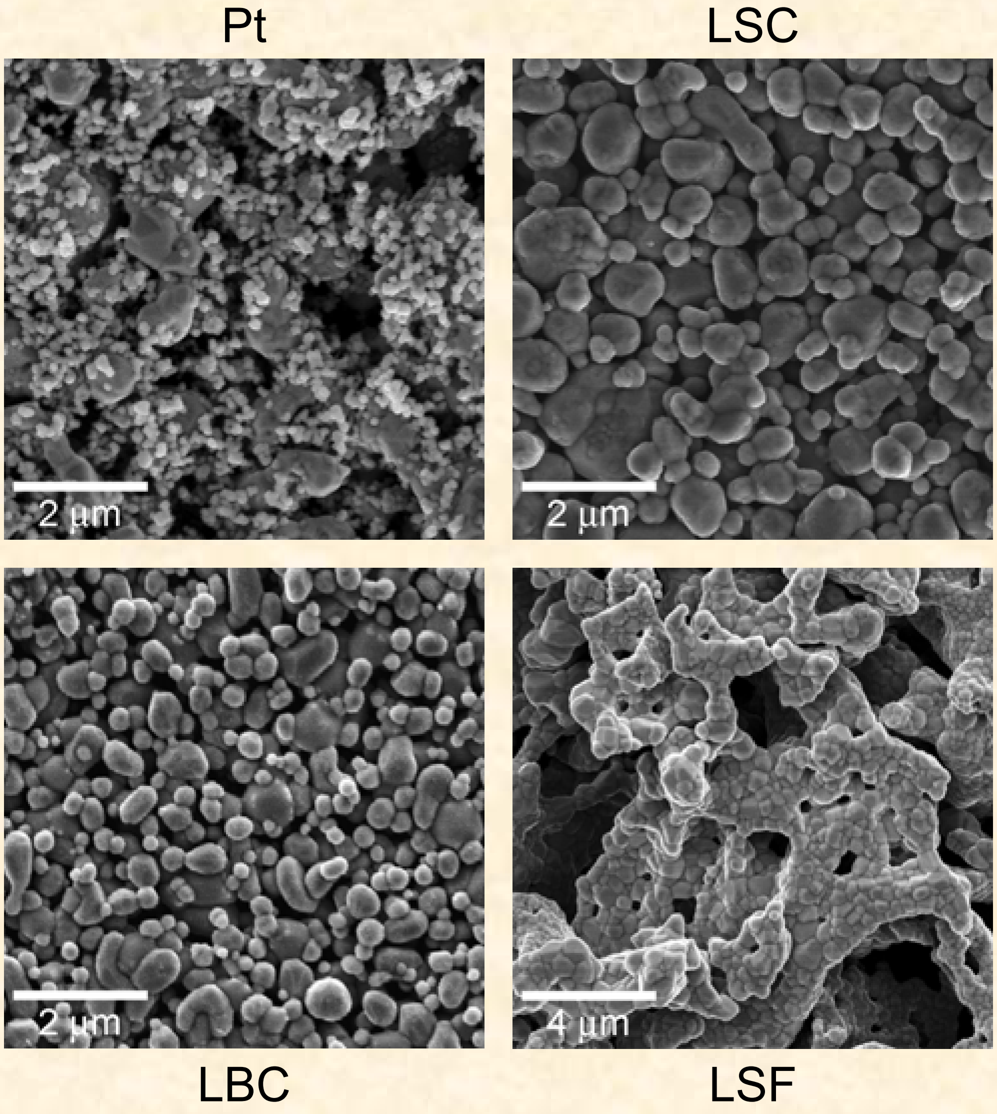
⇒ YSZ (Tosoh TZ8YS) substrate.

- dia. ~16 mm, thickness ~1 mm.

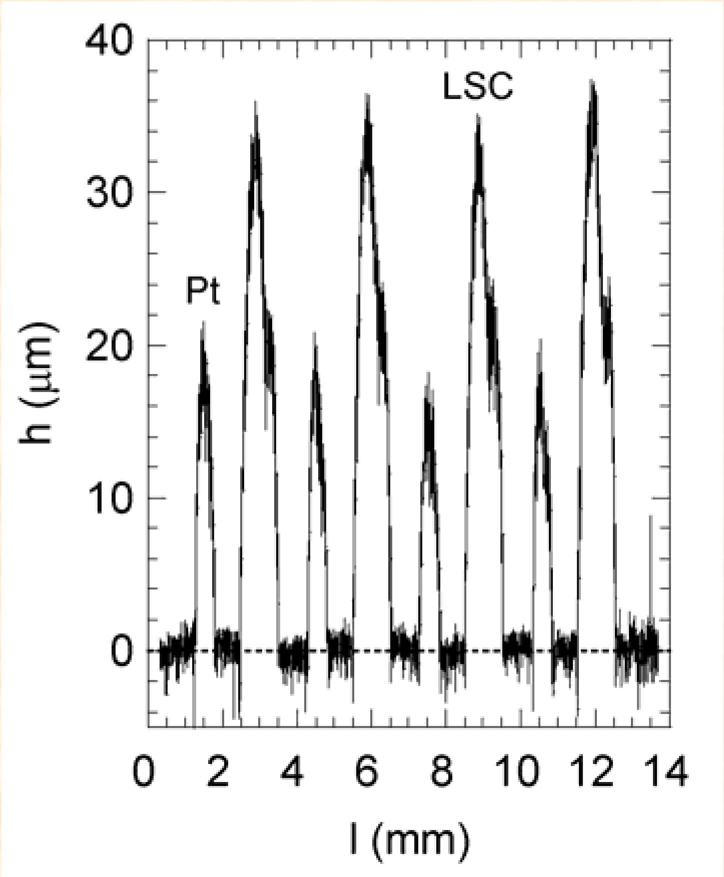
⇒ Screen printed electrodes.

- T_{fire} (^{o}C) = 1100 (Pt), 900 (oxide).
- Oxides: $La_{0.85}Sr_{0.15}CrO_3$ (LSC), $La_{0.85}Ba_{0.15}CrO_3$ (LBC), $La_{0.80}Sr_{0.20}FeO_3$ (LSF).

Electrode microstructures and thickness

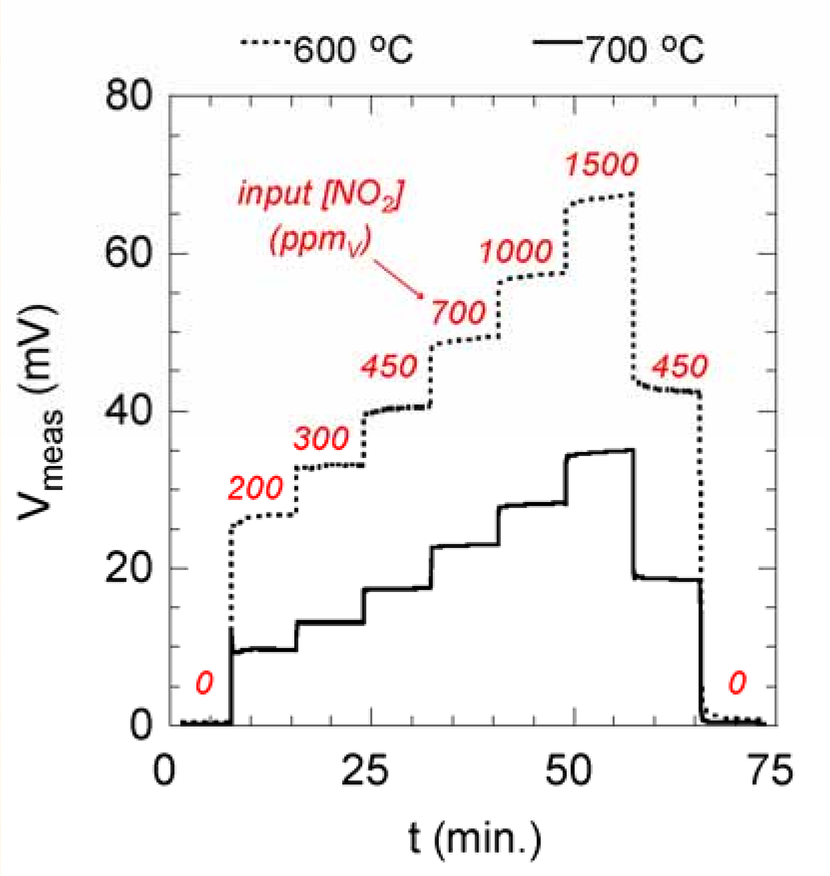


LSC/Pt interdigitated

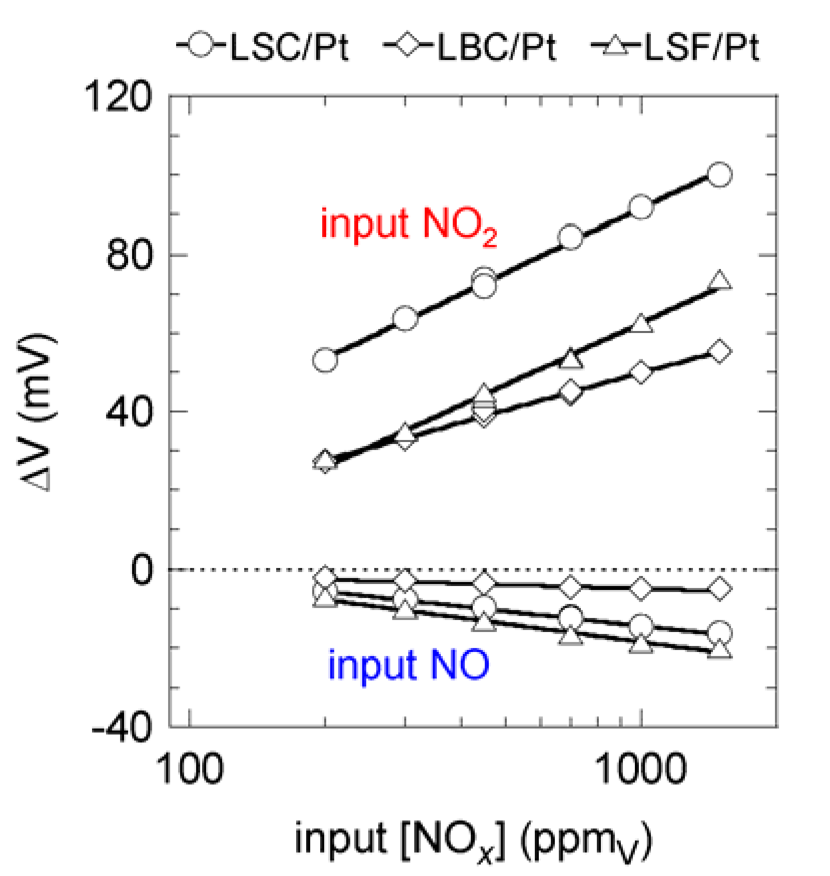


No bias: Strong NO_2 response

V_{meas} = f(t) (LSF/Pt, 13 vol% O_2)



V_{meas} = f([NO_x]) (600 °C, 7 vol% O_2)



⇒ Semicircular (SC) geometries.

⇒ Mechanism for *in situ* $NO_x \rightarrow NO_2$† required, focus on NO_2 response.

†Szabo and Dutta, *Sens. Actuators B; Chem.*, **88**, pp. 168-77 (2002);
Kunimoto *et al.*, *SAE Tech. Pap. Ser. 1999-01-1280* (1999)

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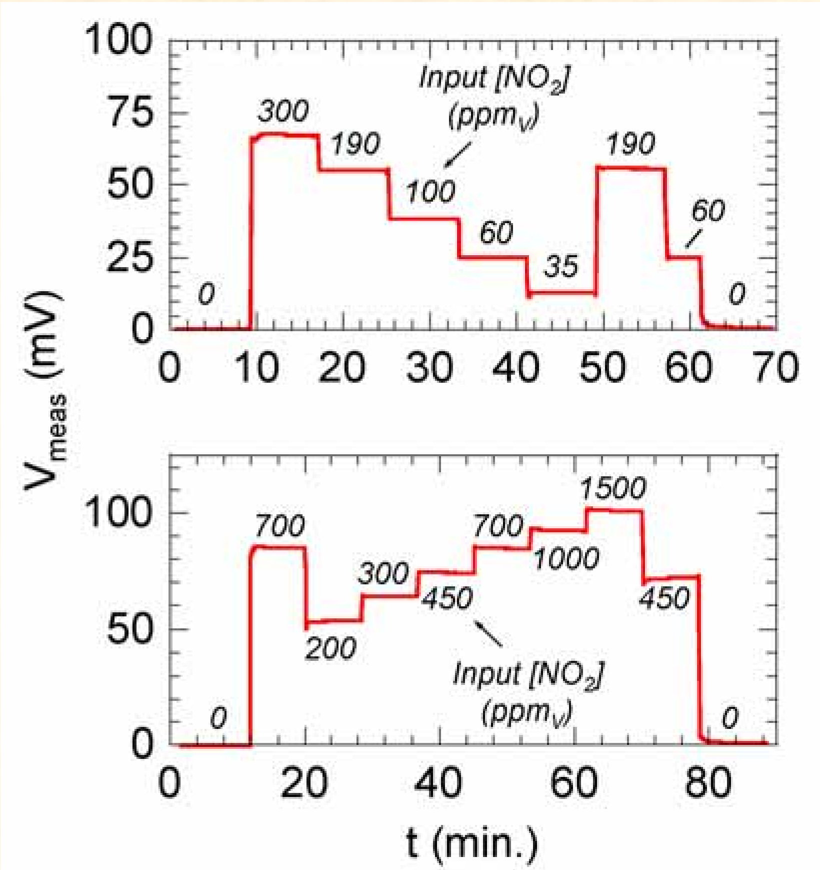
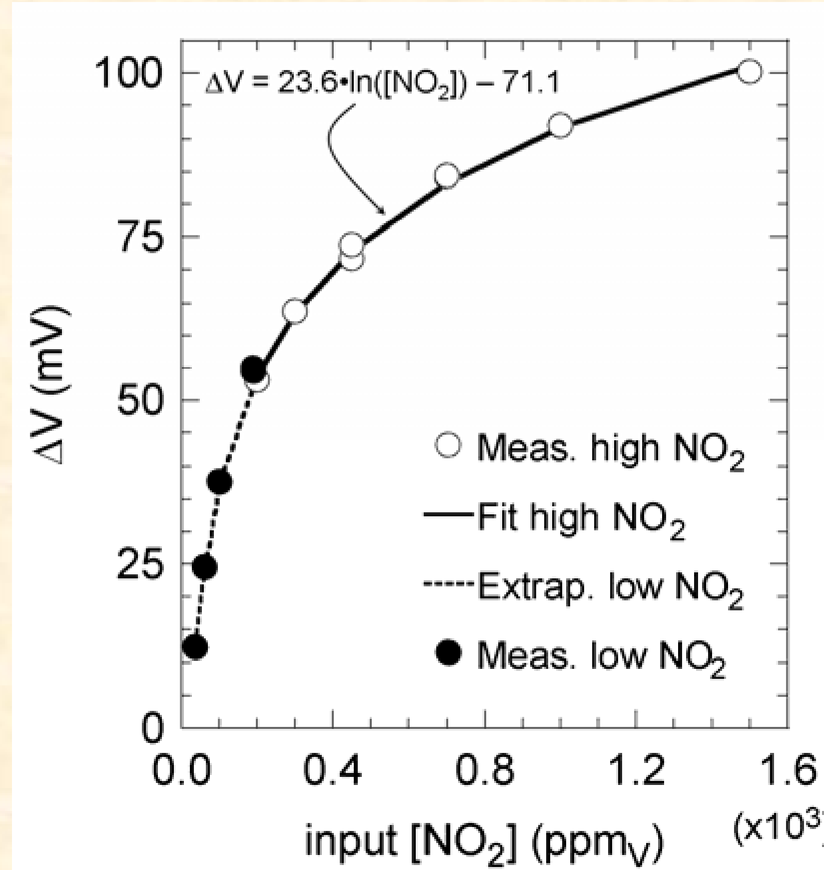
No bias: Logarithmic signal over a wide $[NO_2]$

$V_{meas} = f(t)$ $\Delta V = f([NO_2])$



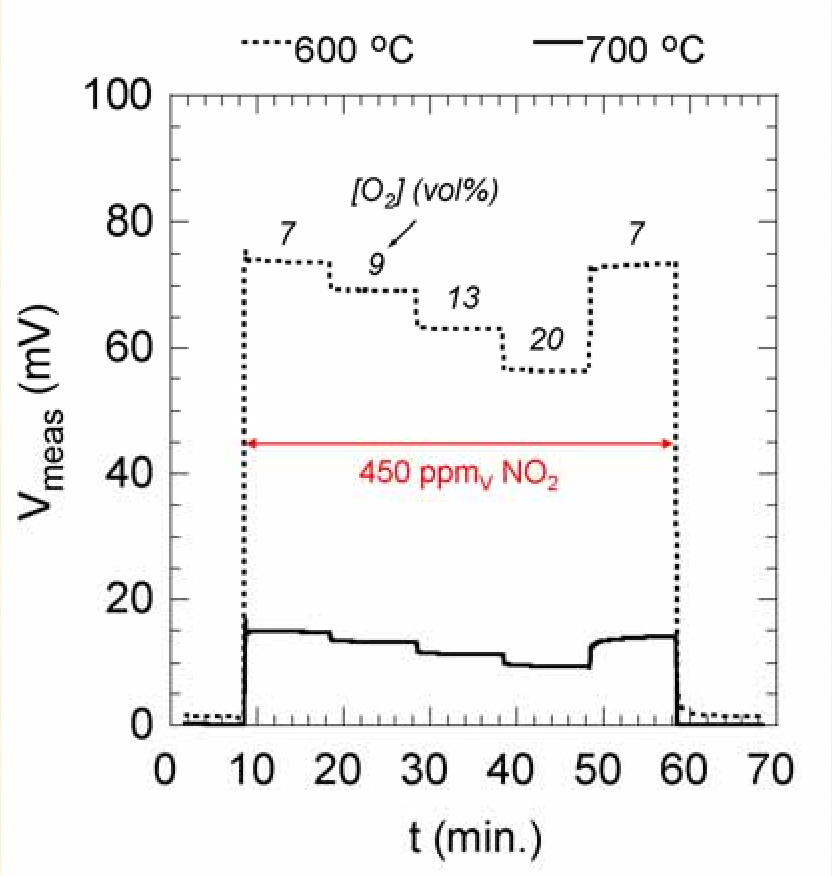


⇒ Data collected at 600 °C, 7 vol% O_2.

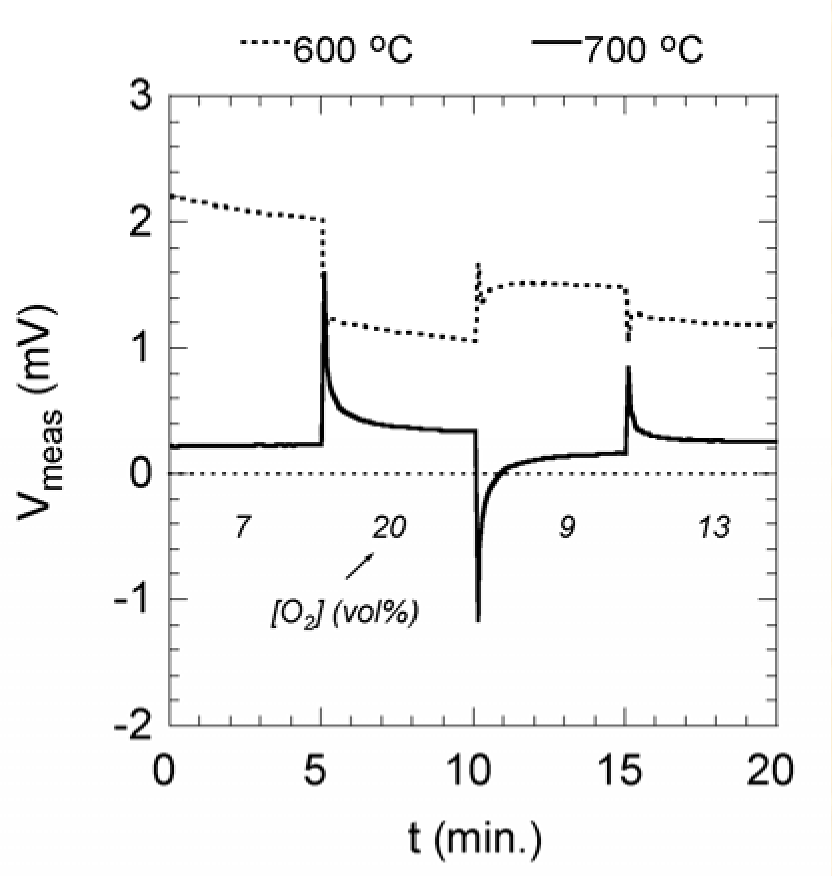
⇒ LSC/Pt sensing element, semicircular (SC) geometry.

[O_2] affects response to NO_2

Varying [O_2] with 450 ppm_V NO_2



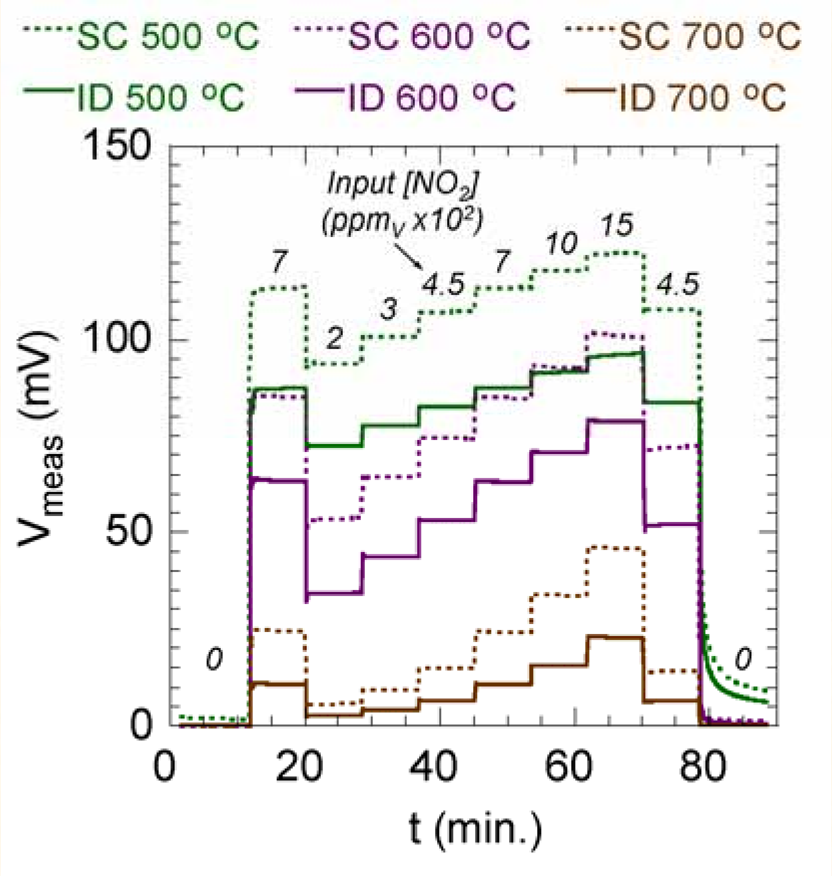
Varying [O_2] with 0 ppm_V NO_2



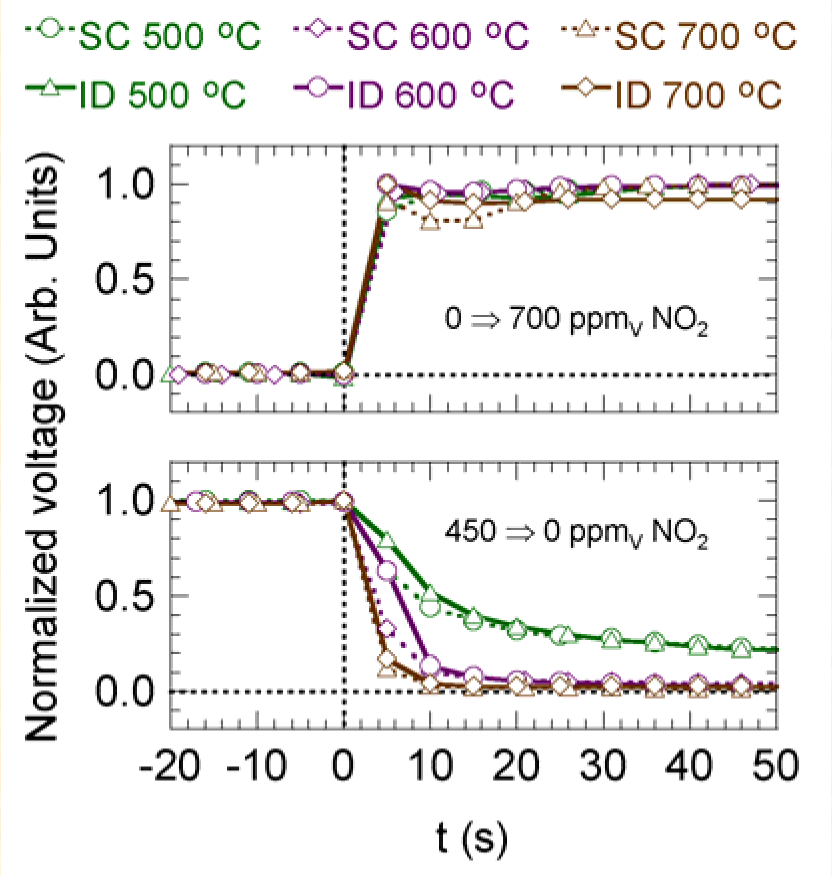
⇒ LSC/Pt sensing element, semicircular (SC) geometry.

T controls signal magnitude, recovery time

Varying $[NO_2]$



Step response / recovery

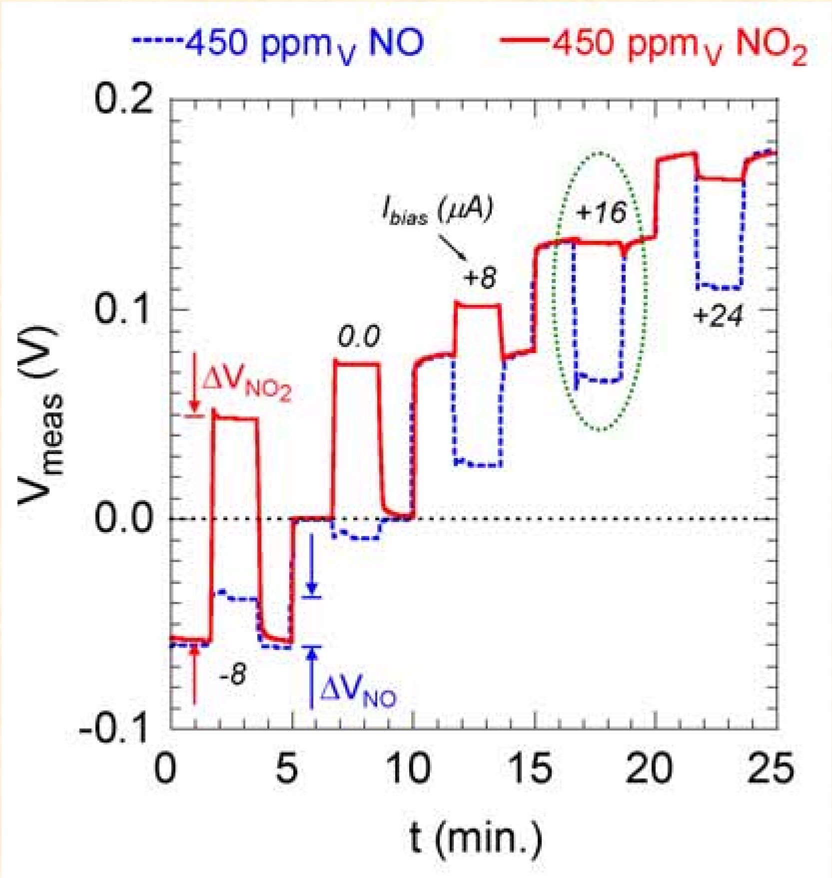


⇒ SC = "semicircular", ID = "interdigitated".

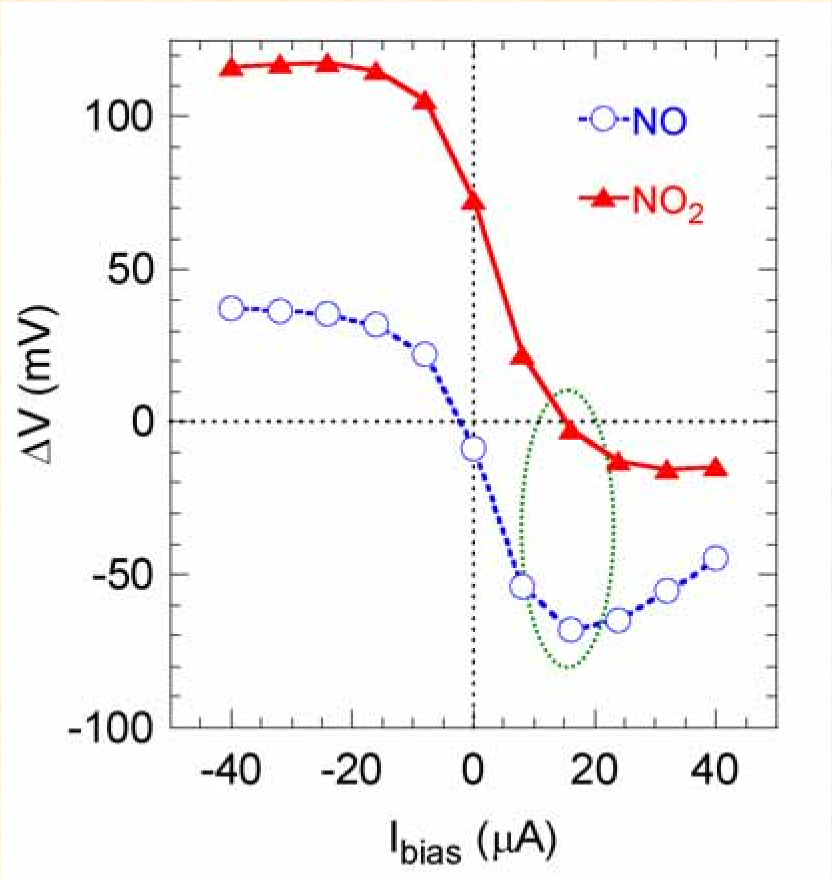
⇒ LSC / Pt sense elements, data collected in 7 vol% O_2.

Effect of varying I_{bias} on NO_x responses

Pulses of 450 ppm_V NO_x at varying I_{bias}



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

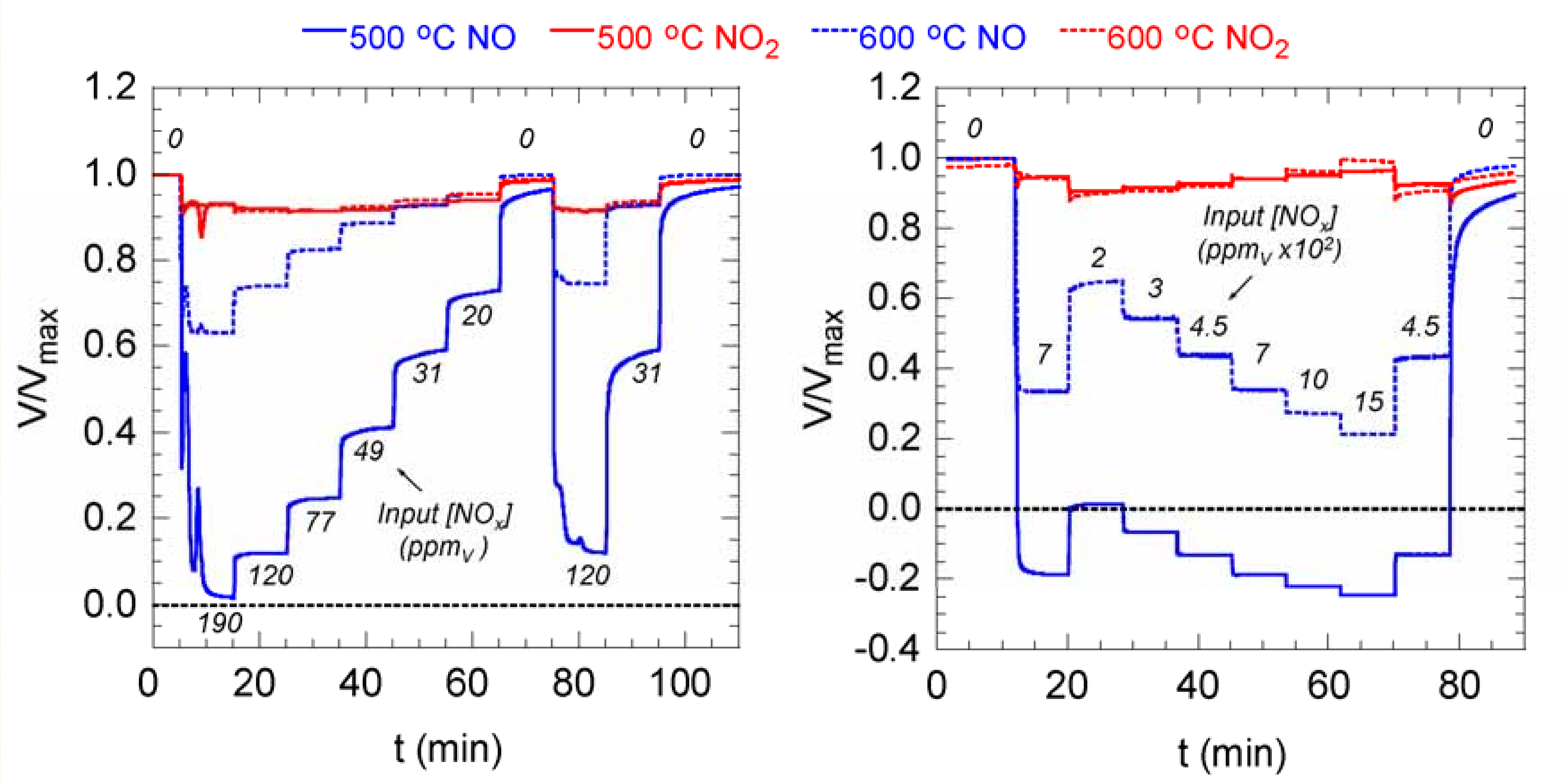


⇒ Data collected at 600 °C, 7 vol% O_2. LSC/Pt, semicircular (SC) geometry.

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

Asymmetry in biased response over wide $[NO_x]$

$V_{meas} = f(t)$ (LSC/Pt SC sensing element, 7 vol% O_2)

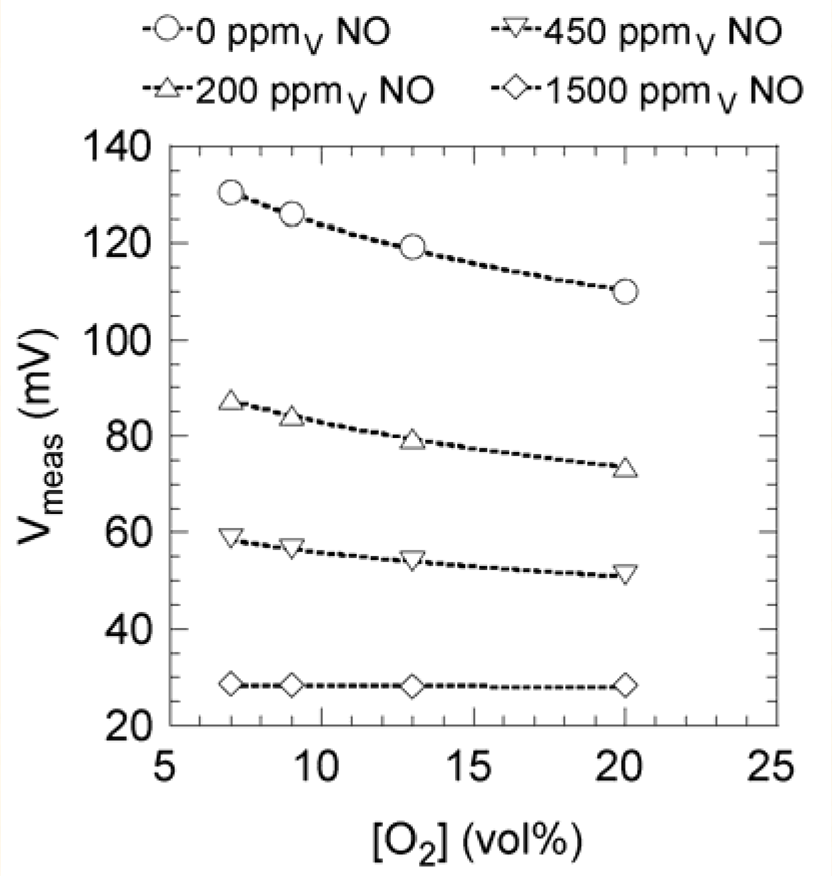


⇒ +1.5 (500 °C) and +14 (600 °C) μA biases.

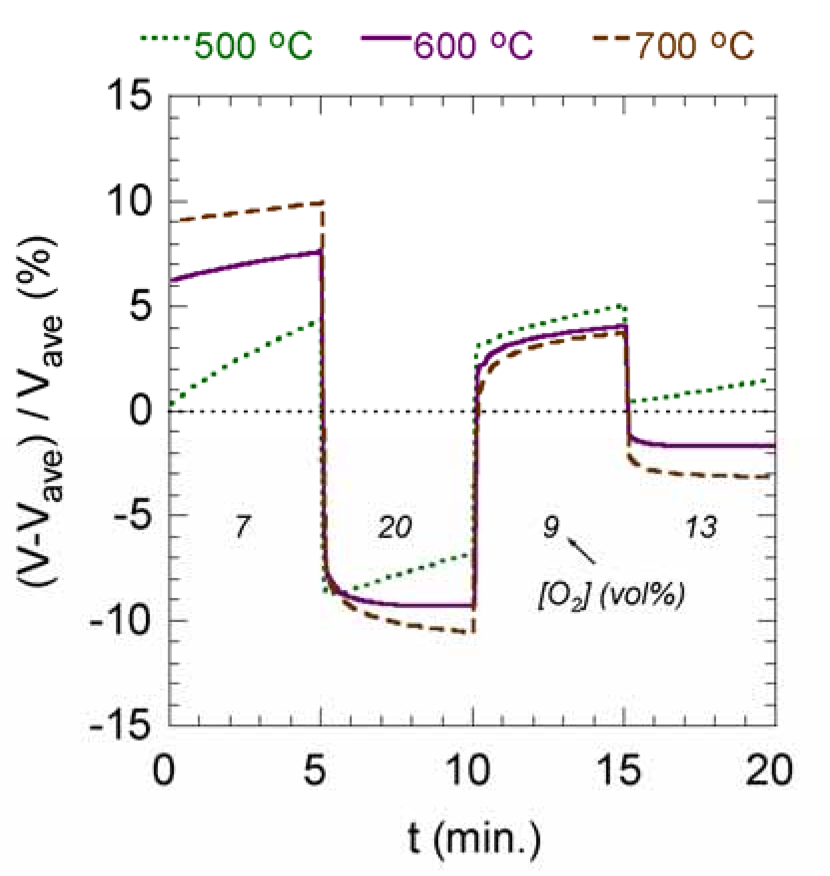
⇒ Focus on NO response with biased elements.

Biased: $[O_2]$ dependence a decreasing function of [NO]

Varying $[O_2]$ at 600 °C



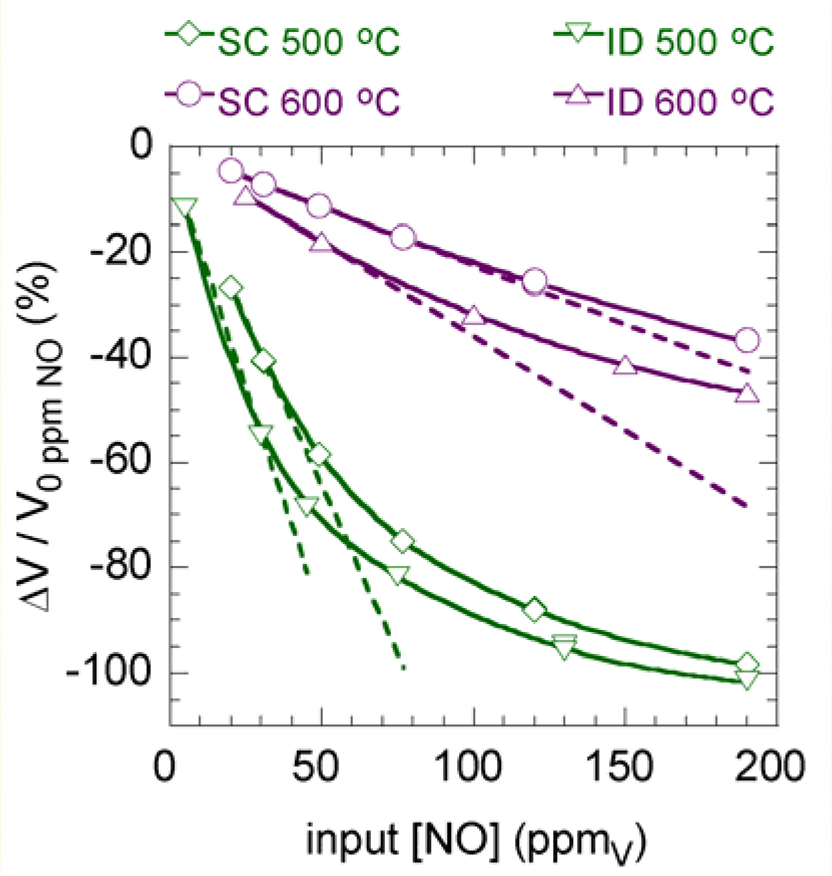
V = f(t) with 0 [NO]



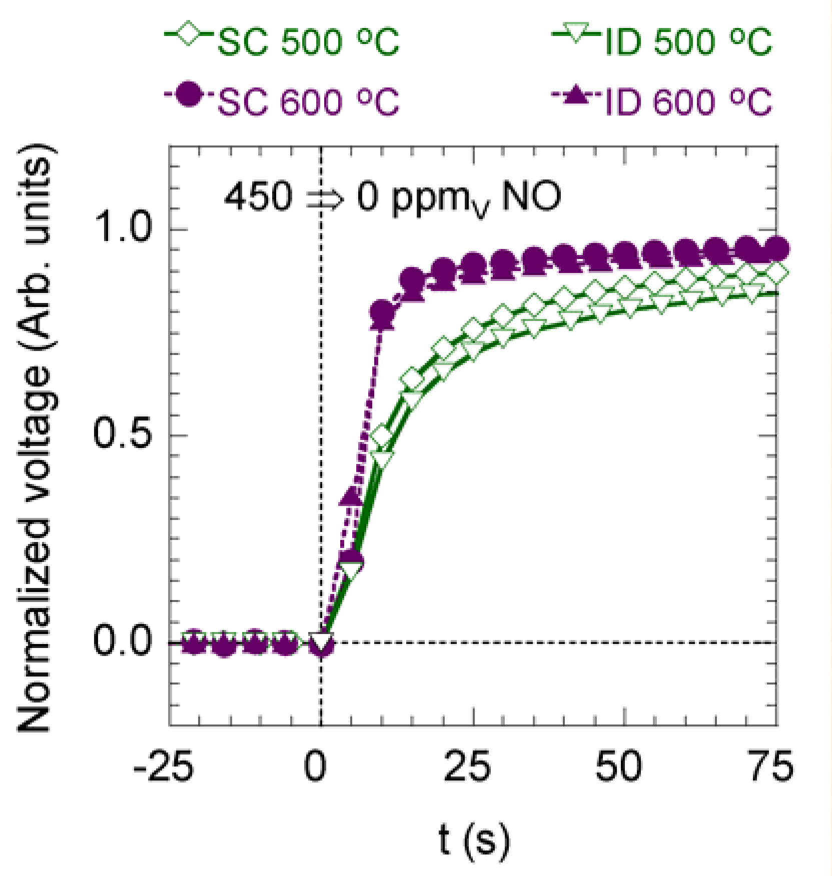
⇒ LSC /Pt semicircular (SC) sensing element. 700 °C bias = 60 μA.

T still controls response magnitude, recovery time

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



Recovery from 450 ppm_V NO

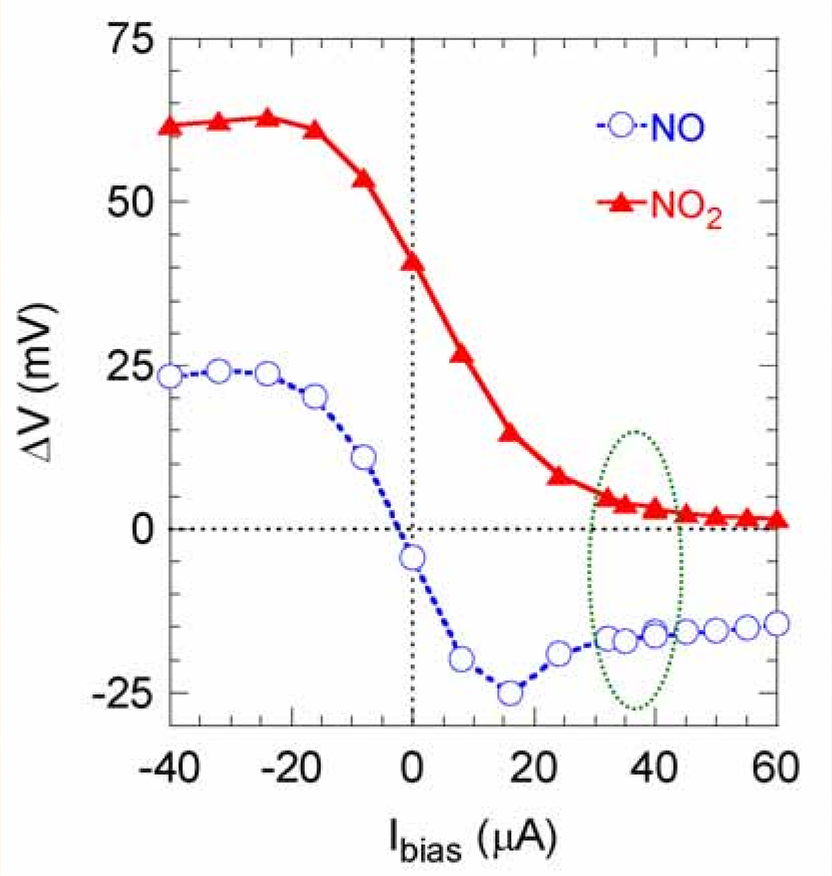


⇒ LSC /Pt sensing elements.

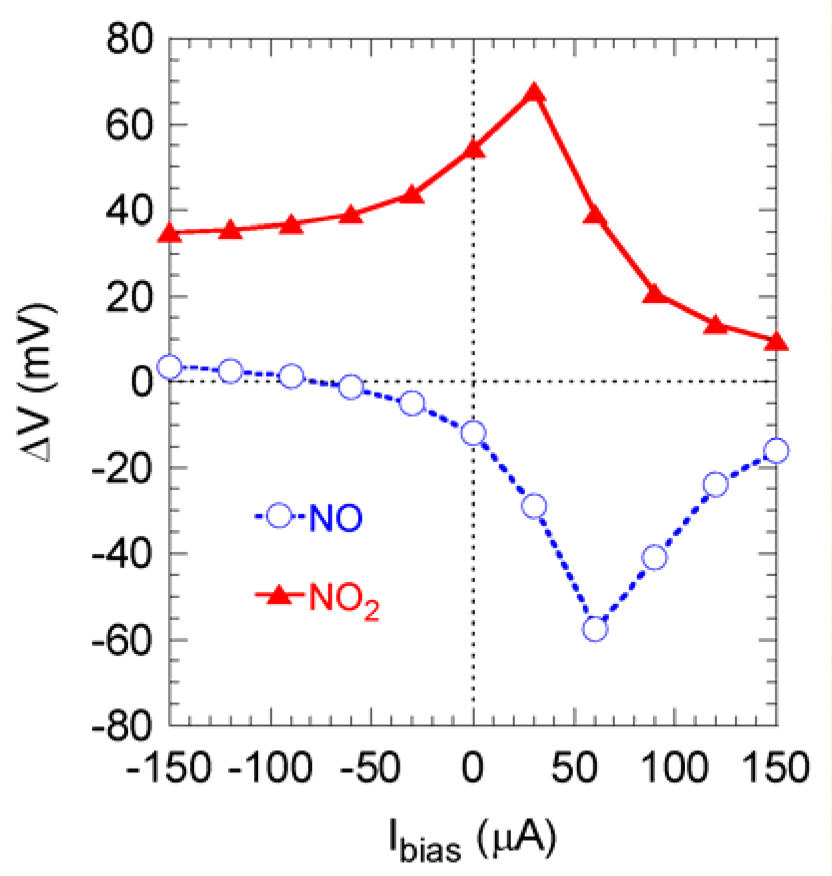
⇒ Biased to "NO-selective" condition.

Ferrite behaved differently than chromites with bias

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



$La_{0.8}Sr_{0.2}FeO_3$ (LSF)



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

⇒ LSC /Pt semicircular (SC) sensing elements.

Summary and conclusions

⇒ Experimental approach

- ♦ Sensing elements with co-planar electrodes (oxide /Pt).

⇒ Observations

- ♦ Strong NO_2 response without bias.
  - ⇒Response logarithmic 20 – 1500 ppm [NO_2].
  - ⇒Function of [O_2] only in presence of [NO_2].
  - ⇒Magnitude, recovery time decrease with T.
- ♦ Enhanced NO response possible with DC biasing.
  - ⇒Response linear at low [NO].
  - ⇒[O_2] sensitivity inversely proportional to [NO].
  - ⇒Magnitude, recovery time decrease with T.
  - ⇒Not all oxides behave similarly.

⇒ Conclusion and future outlook

- ♦ Use of biasing enables sensing of NO as opposed to NO_2.
- ♦ Characterization of stability and selectivity still required.

Acknowledgements

⇒ 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).

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

- Consultation in mobile power sensing requirements and technologies.

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Thank you for your attention!