207TH MEETING OF THE
ELECTROCHEMICAL SOCIETY

All-Oxide "Total NO_x" Sensing Elements

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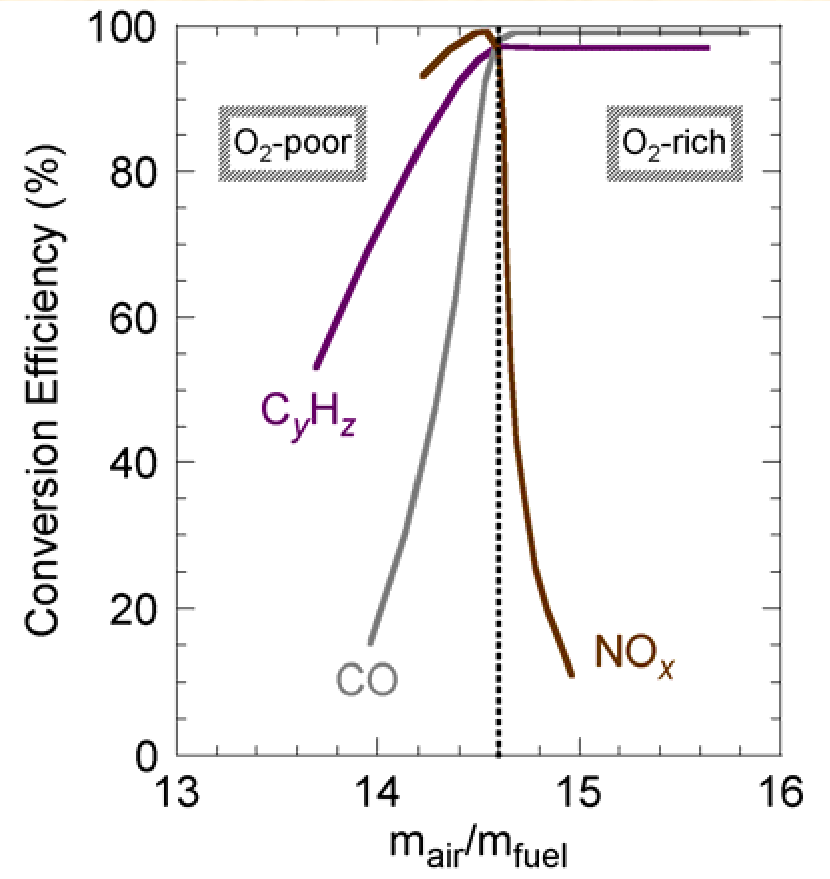
Motivation for NO_x sensor development

Three-way catalyst (TWC) efficiency†



- Diesel and lean-burn exhausts are O_2-rich, TWC cannot remove NO_x.
- Proposed remediation approaches: Lean NO_x traps (LNT) and selective catalytic reduction (SCR).
- Both will require NO_x sensors.
- Operating conditions ("rough"): T ~600°C, ~10–1000 ppm_V NO_x, varying $[O_2]$.‡
- "NO_x" is a mixture of NO and NO_2 (primarily NO), but usually cannot assume $[NO]/[NO_2]$.
- May need NO or NO_2-selective, and/or "total NO_x" sensors for $[NO_x]$ characterization.

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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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Experimental approach and methodology

- General approach
  - Sensing elements using YSZ substrates.
    - Co-planar interdigitated oxide electrodes.
    - Electrodes identical in composition.
  - Use applied DC electrical signal ("bias").[†]
- Methodology
  - Electrodes applied by screen printing and thermal treatment.
  - Tube furnace used to simulate elevated temperature service.
  - Typical operating conditions:
    - $550\ ^{o}C \leq T \leq 650\ ^{o}C$.
    - Mixtures of NO or NO_2, O_2 (7–20 vol%), and N_2.
- Performance metrics
  - NO_x responses.
  - Effect of varying $[O_2]$ & T.

[†]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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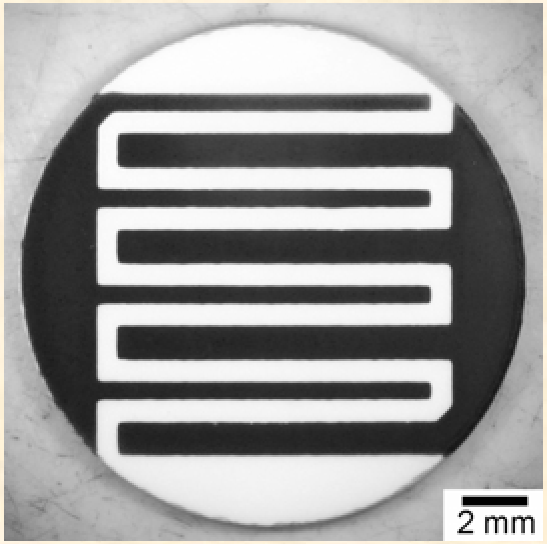
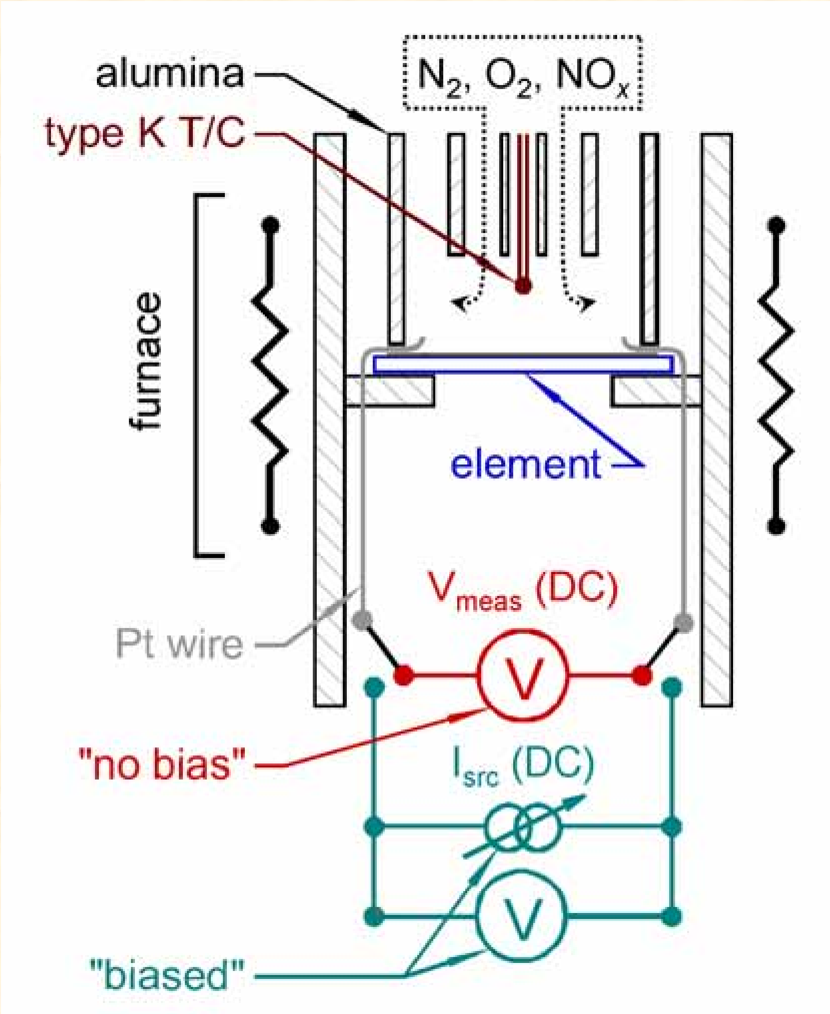
Sensing element geometry, test fixture schematic

Element geometry



Schematic of test fixture

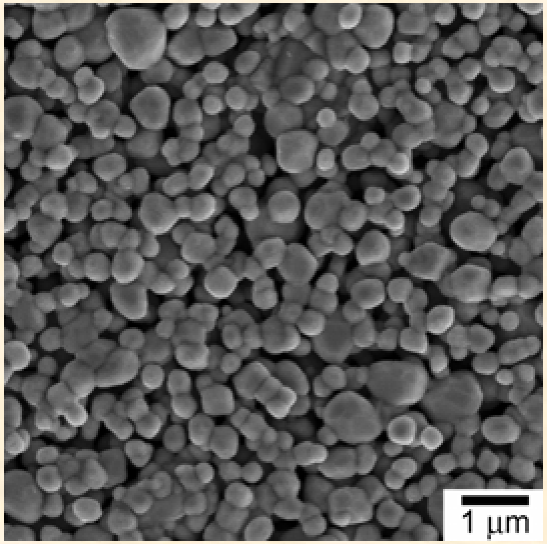


- YSZ (Tosoh TZ8YS) substrate
  - Tape cast and laminated
  - T_{sinter} = 1400 °C
  - d ~16 mm, t ~1 mm
- Screen-printed oxide electrodes
  - Usually $La_{0.85}Sr_{0.15}CrO_3$ (LSC)†
  - T_{fire} = 1200 °C

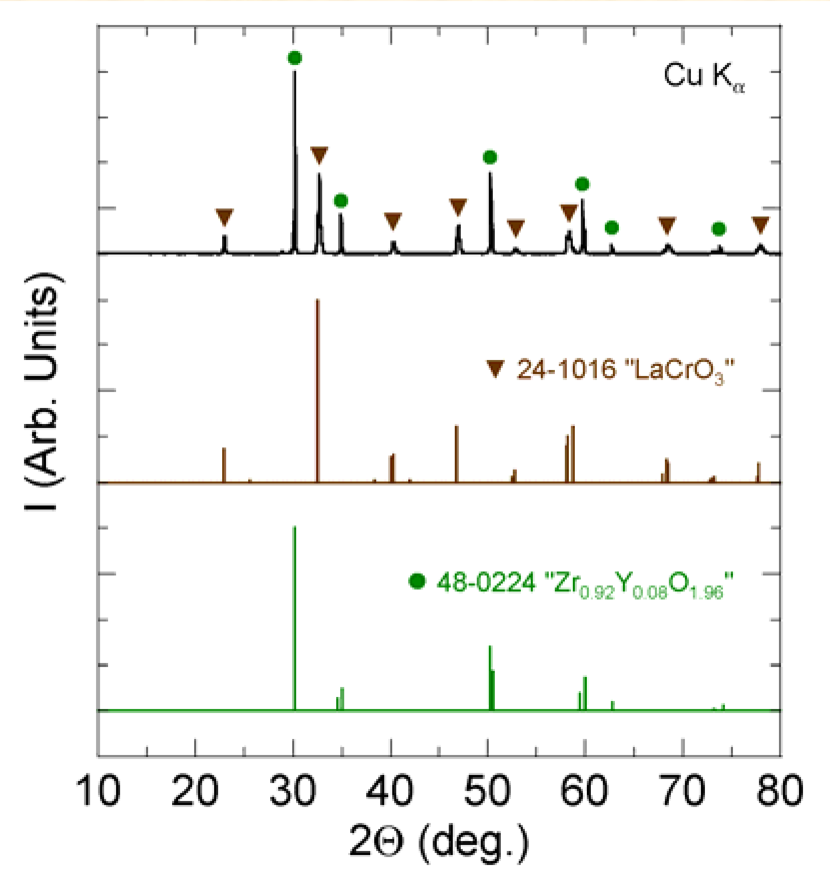
†Praxair Specialty Ceramics. Woodinville, WA

Microstructure, thickness, phases present

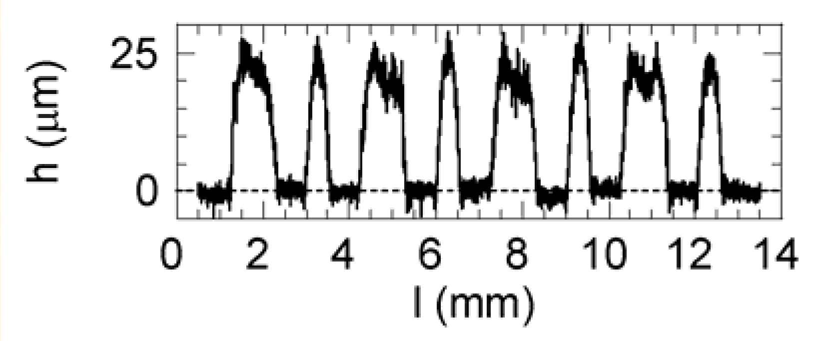
Electrode surface



XRD of electroded surface



Profilometer trace



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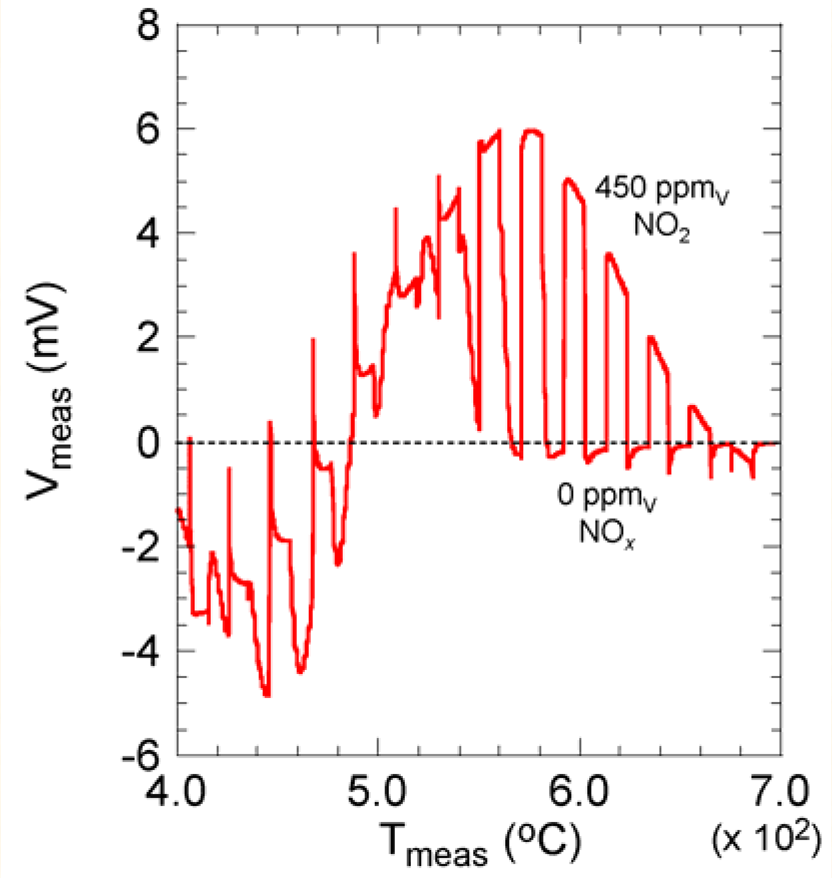
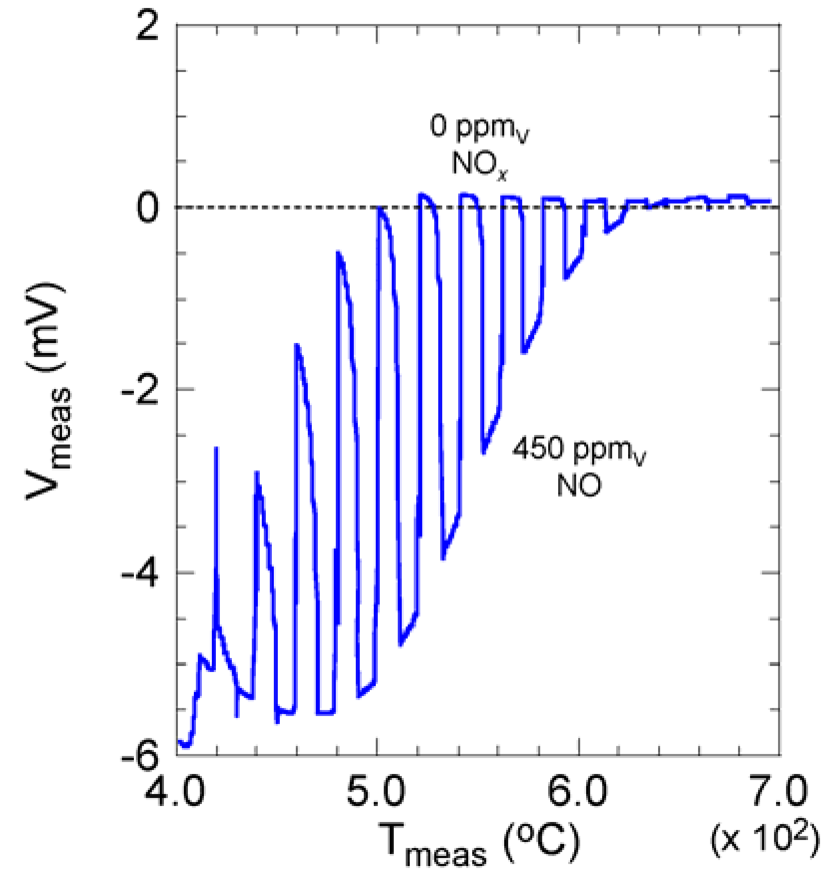
Only small voltages in "mixed-potential" mode

input NO_2



input NO

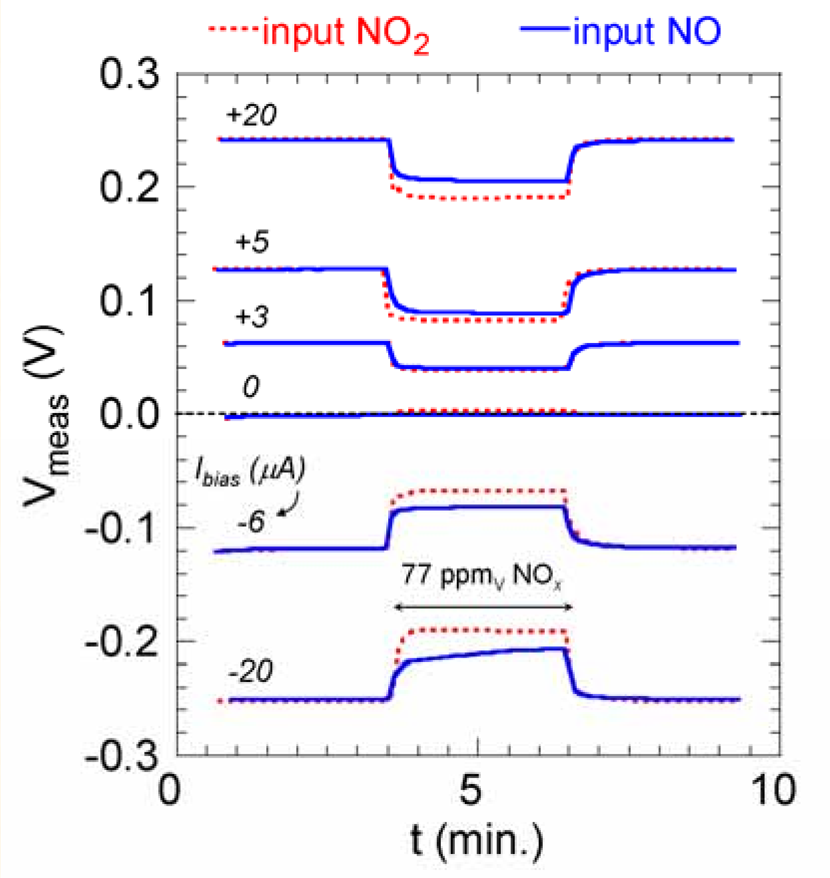


⇒ 5 min. NO_x pulses (7 vol% O_2) while ramping T at 2 deg./min.

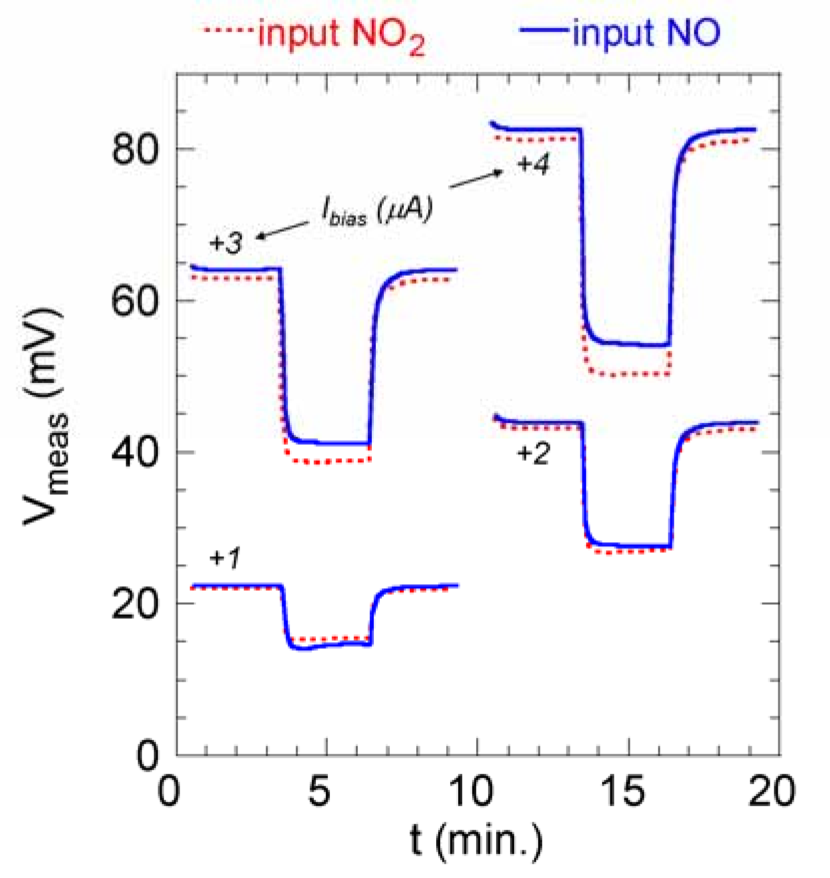
⇒ Behavior with input NO and NO_2 distinctly different.

Applied current influences NO_x responses

$-20\ \mu A \le I_{app} \le +20\ \mu A$



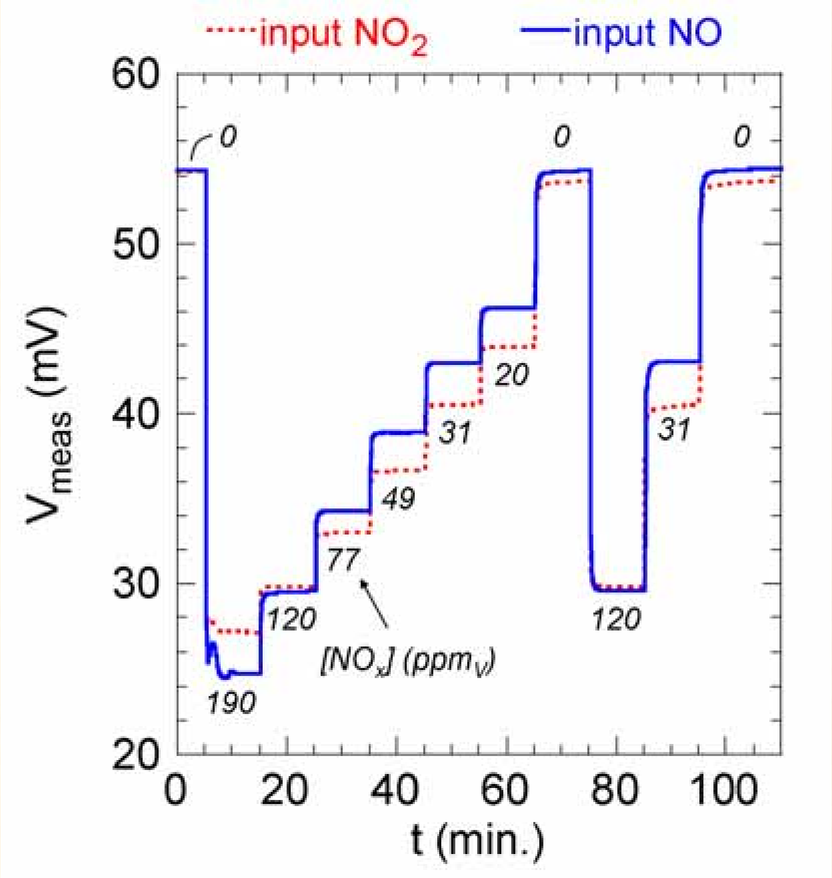
$+1\ \mu A \le I_{app} \le +4\ \mu A$



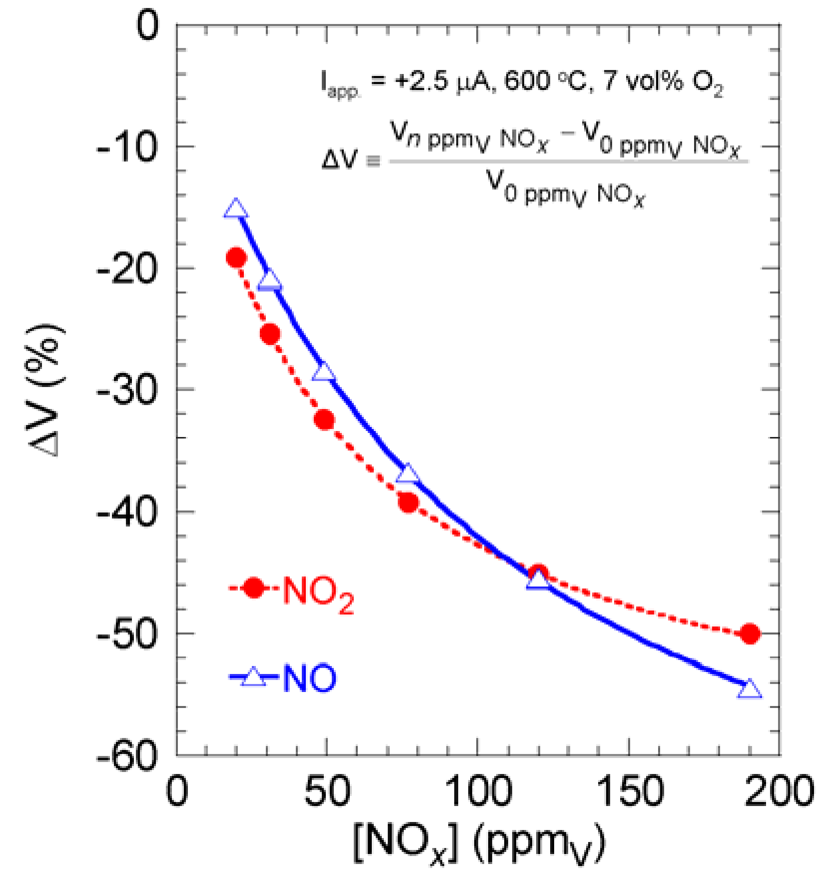
⇒ T = 600 ^oC, 7 vol% O_2.

Symmetric response 20 $ppm_V \leq [NO_x] \leq 200\ ppm_V$

$V_{meas} = f(t)$



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

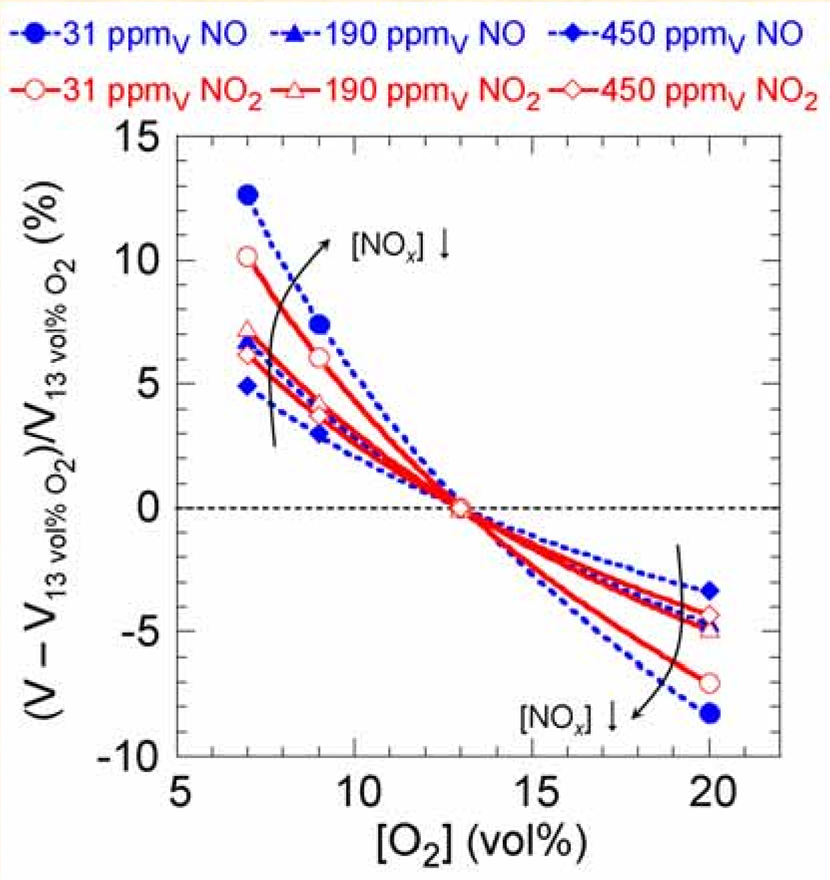


⇒ 0.8 ppm_V: $\Delta V_{NO} = -0.5\%$, $\Delta V_{NO2} = -0.7\%$.

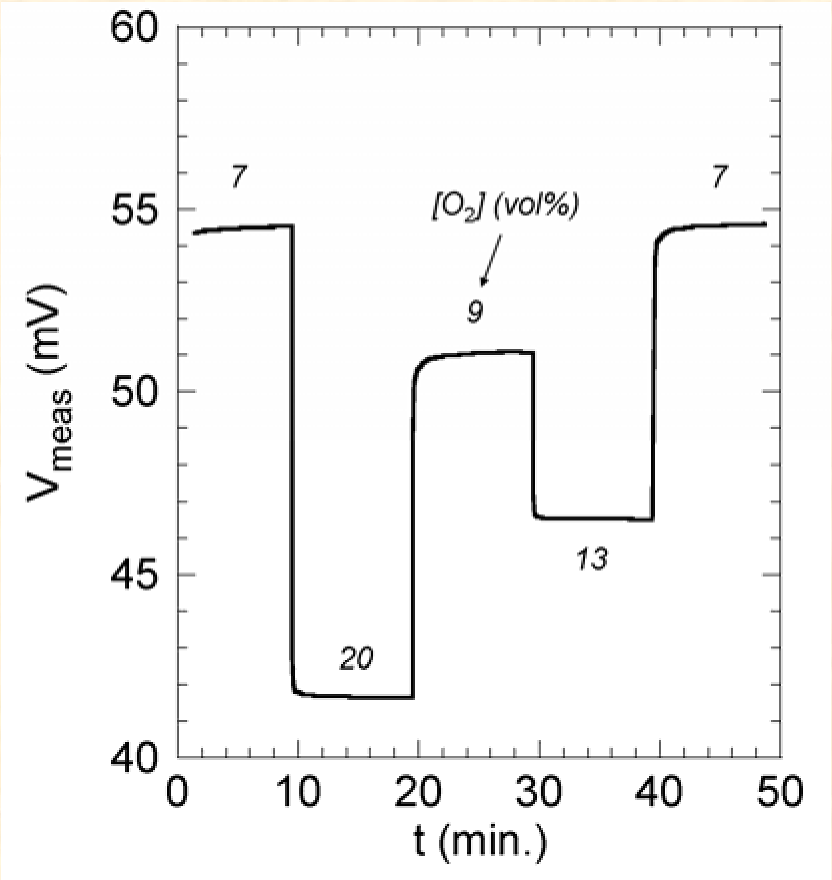
⇒ 1500 ppm_V: $\Delta V_{NO} = -80\%$, $\Delta V_{NO2} = -68\%$.

$[O_2]$ dependence a decreasing function of $[NO_x]$

$V_{meas} = f([O_2])$



$V_{meas} = f(t)$ (0 ppm_V NO_x)

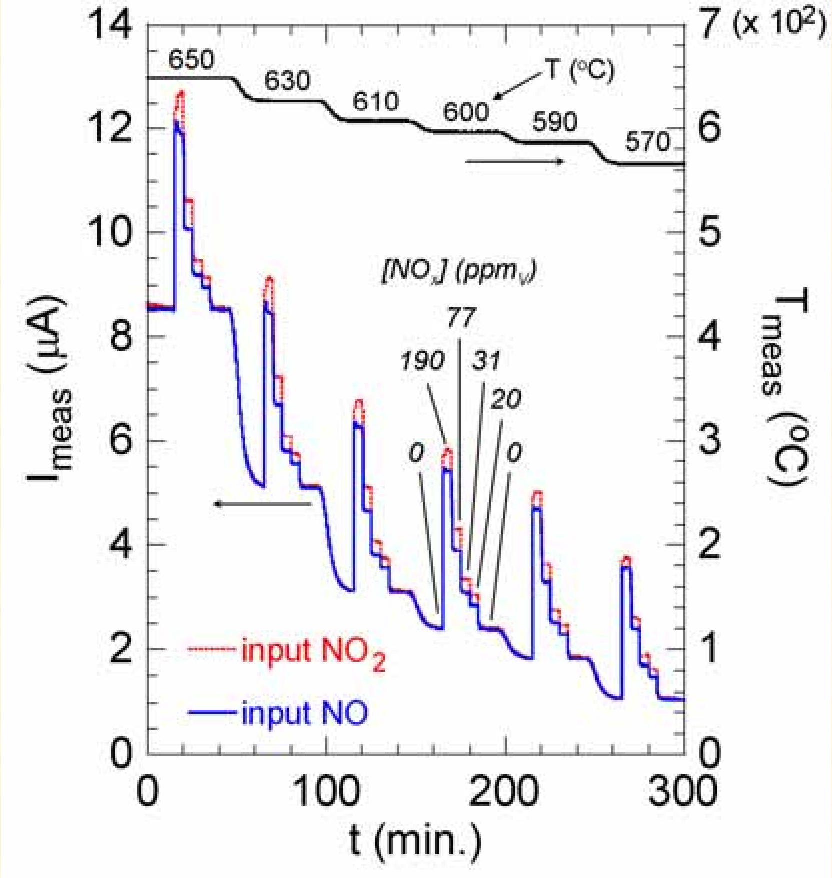


⇒ I_{app} = +2.5 μA, T = 600 °C.

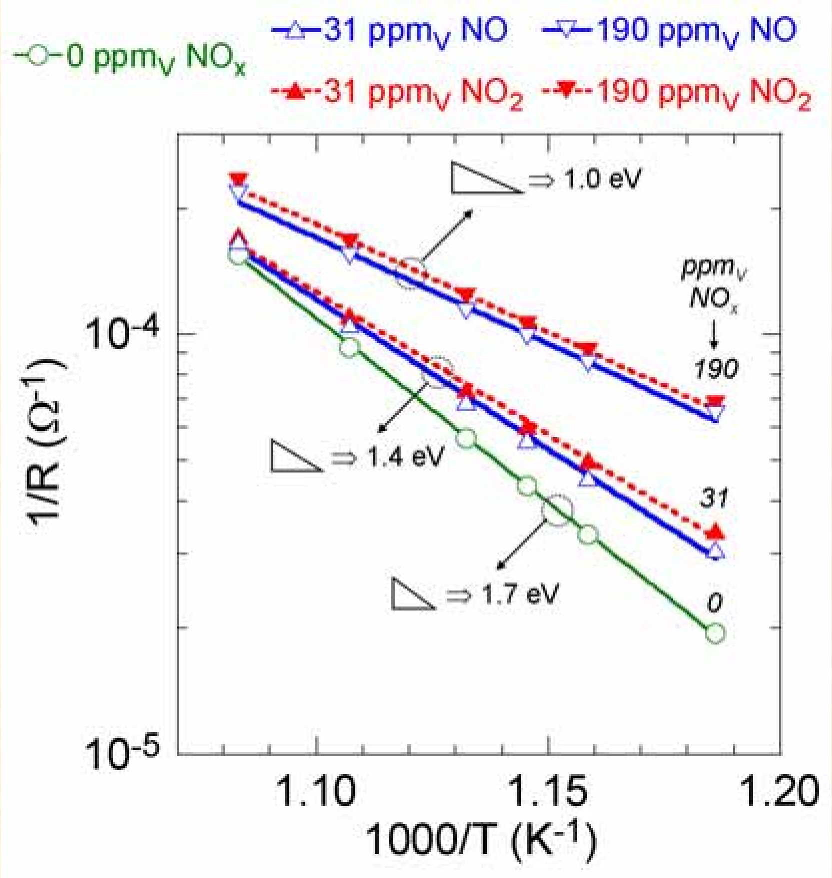
⇒ Fits to $V_{meas} = f([O_2])$ logarithmic.

Element resistance varies exponentially with T

I_{meas}, T_{meas} = f(t)



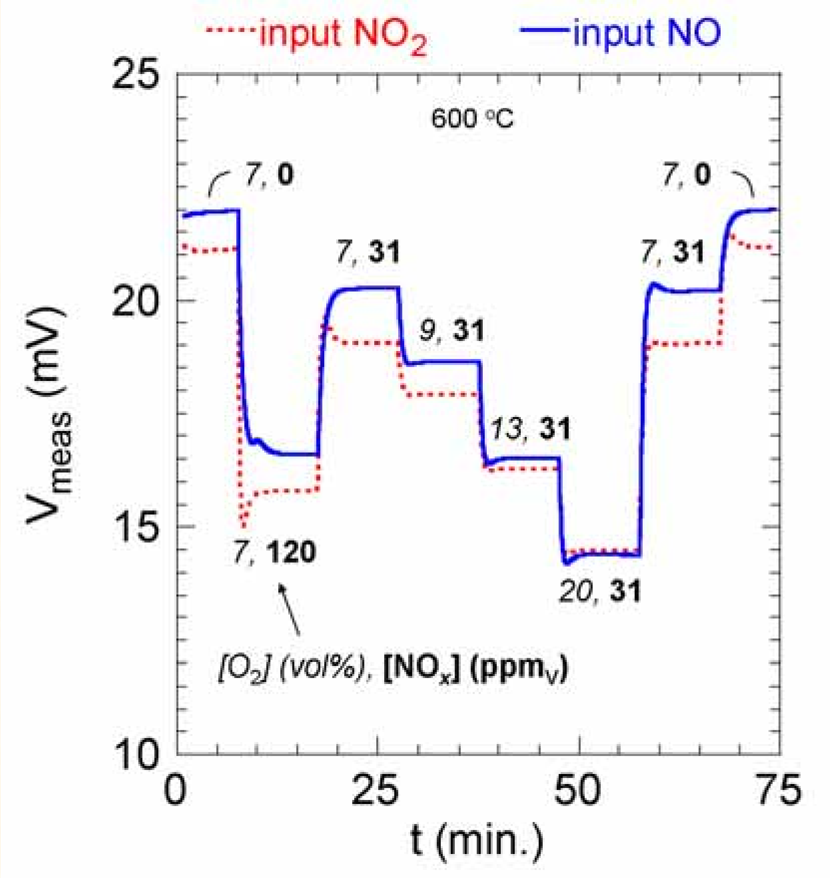
"Arrhenius" plot ln(G) = f(1/T)



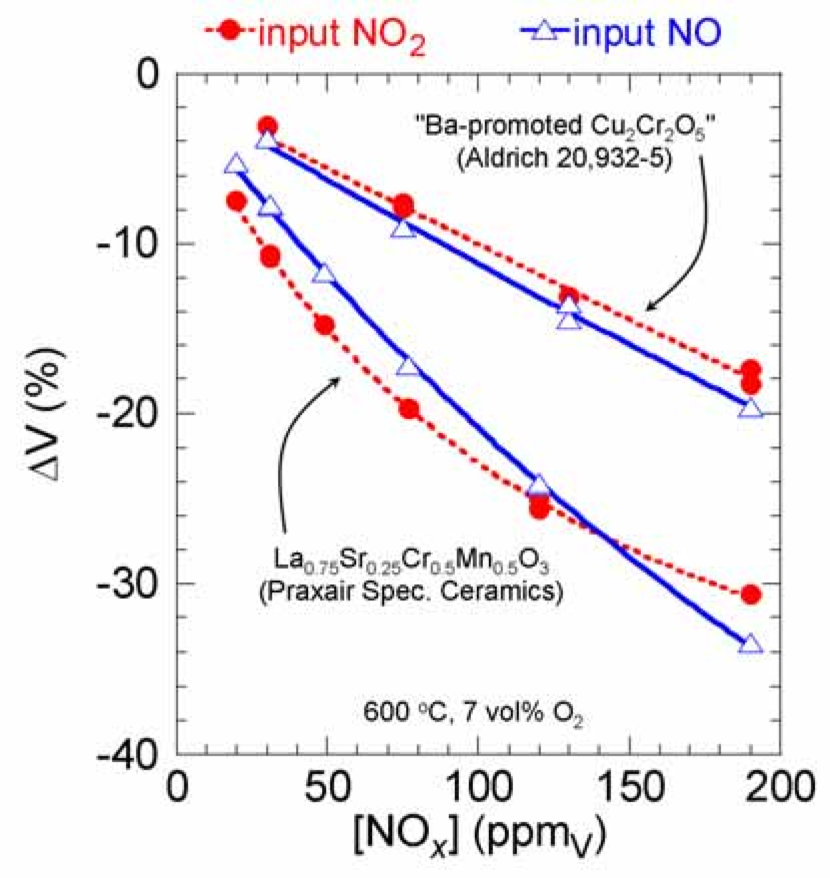
⇒ +55 mV applied voltage, 7 vol% O_2.

Oxides other than LSC can yield "total NO_x"

$La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$



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



⇒ $La_{0.85}Ba_{0.15}CrO_3$ and $La_{0.8}Sr_{0.2}FeO_3$ could not yield "total NO_x".

Summary and conclusions

- Focus of investigation
  - Sensing elements with compositionally identical oxide electrodes.
- Observations (550 ^{o}C ≤ T ≤ 650 ^{o}C, 7% ≤ [O_2] ≤ 20%)
  - Use of applied electrical stimulus (bias) yields:
    - Equal response to NO and NO_2 in fairly narrow bias range.
    - Symmetry of response 20-200 ppm_V.
    - [O_2] sensitivity that is a decreasing function of [NO_x].
    - Signal *levels* exponential function of T, *changes* due to NO_x decrease with T.
    - Several different oxides have shown "total NO_x" behavior.
- Conclusion and future outlook
  - Elements may be useful in "total NO_x" sensor.
  - Areas for further investigation:
    - Selectivity.
    - Stability of response and electrode materials in exhaust environment.

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