ORNL NO_x Sensor Program

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Introduction / outline

Overall objective

♦ Aid in development of NO_x sensor for on-board exhaust remediation and monitoring.

Desired sensor specifications

♦ Working range 2-1500 ppm total NO_x.

♦ Resolution ± 1 ppm (low end), ± 10 ppm (high end).

♦ Accuracy ± 1 ppm.

♦ Response time 0.5 s (remediation), ~3 s (monitoring).

♦ Light-off: 30 s.

Outline

♦ Background.

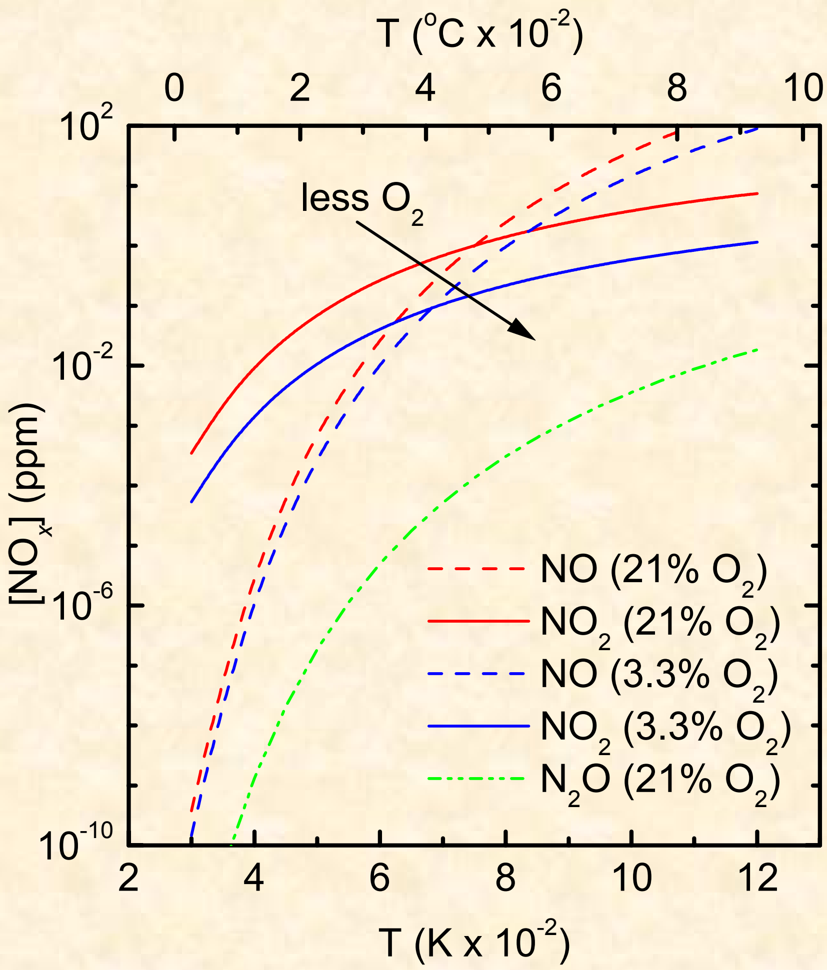
♦ Methodology / apparatus for evaluating electrode materials.

♦ Results and discussion.

♦ Future directions.

Primary NO_x species of interest are NO and NO_2

Relative abundances change with temperature



"Thermal NO_x"‡

$$N_2 + O_2 \Leftrightarrow 2NO$$

$$\Delta G^{298} \cong 173.1, \ \Delta H \cong 180.4 \text{ (kJ/mol)}^{\%}$$

$$NO + \frac{1}{2}O_2 \Leftrightarrow NO_2$$

$$\Delta G^{298} \cong -35.24, \ \Delta H \cong -57.07 \text{ (kJ/mol)}^{\%}$$

$$N_2 + \frac{1}{2}O_2 \Leftrightarrow N_2O$$

$$\Delta G^{298} \cong 104.2, \ \Delta H \cong 82.05 \text{ (kJ/mol)}^{\%}$$

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‡Schnelle and Browne, *Air Pollution Control Technology Handbook.*

%Atkins, *Physical Chemistry.*

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General sensor characteristics

Translations to the customer's objectives

⇒ Sensitivity

- Required to operate over ~3-4 orders of magnitude.
- Desired resolution ~1% of full scale.

⇒ Selectivity

- CO, H_2O, hydrocarbons present at varying levels.
- Varying O_2 concentration.

⇒ Stability

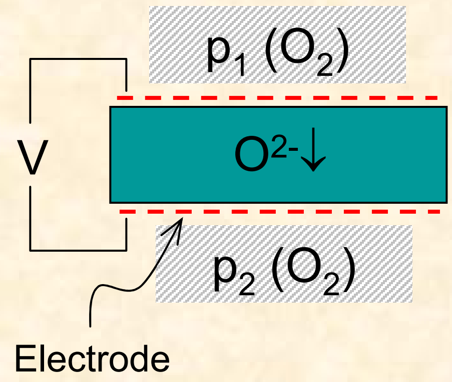
- Operating temperature ~700 ^{o}C.
- Possible presence of particulates and S.
- Desired operating lifetime ~5000 hr.

Types of electro-ceramic sensors I

(Typical $T_{oper.}$ ~ 400-800 °C, heating circuits omitted for clarity)

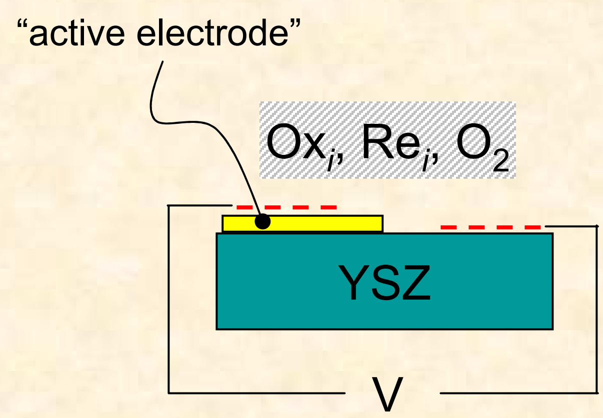
⇒ Potentiometric (e.g. λ sensor)[&]

- ♦ Voltage developed due to concentration (activity) differences.
- ♦ Physical barrier usually required between electrodes.
- ♦ Typically requires known concentration at one electrode.



⇒ Mixed-potential ("non-Nernstian")[†]

- ♦ Electrochemical activity of electrode material(s) alters reactivity.
- ♦ Both cathodic and anodic reactions at active electrode.
- ♦ Output (V) function of electrode materials and atmosphere.



[&] Azad et al., *J. Electrochem. Soc.*, **139**, pg. 3690. (1992).
[†] Garzon et al., *Solid State Ionics*, **136-7**, pg. 633. (2000).

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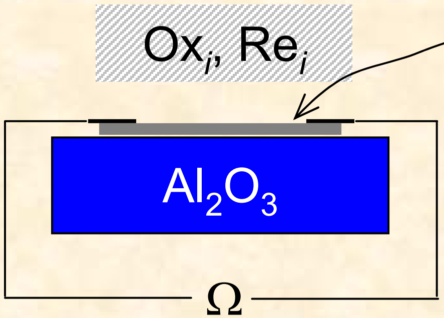
Types of electro-ceramic sensors II

(Typical $T_{oper.}$ ~ 400-800 °C, heating circuits omitted for clarity)

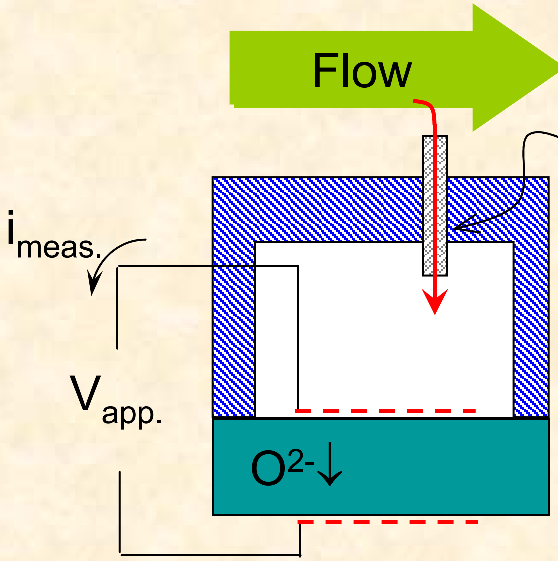
⇒ Conductimetric (e.g. SnO_2 sensor)[%]

- Absorption / interaction with surface alters resistivity.
- Can use multiple pads with pattern recognition (req. calibration).
- Typical operating T ≤ ~600 °C.



⇒ Amperometric ("limiting current")[$]

- $V_{app.}$ drives electrochemical reaction involving gas to be sensed.
- $i_{meas.} \propto$ concentration.
- $V_{app.}$, electrode materials can afford selectivity.



[%] Ihokura and Watson, *The Stannic Oxide Gas Sensor*. (1994).

[$] Gopel et al., *Solid State Ionics*, **136-7**, pg. 519. (2000).

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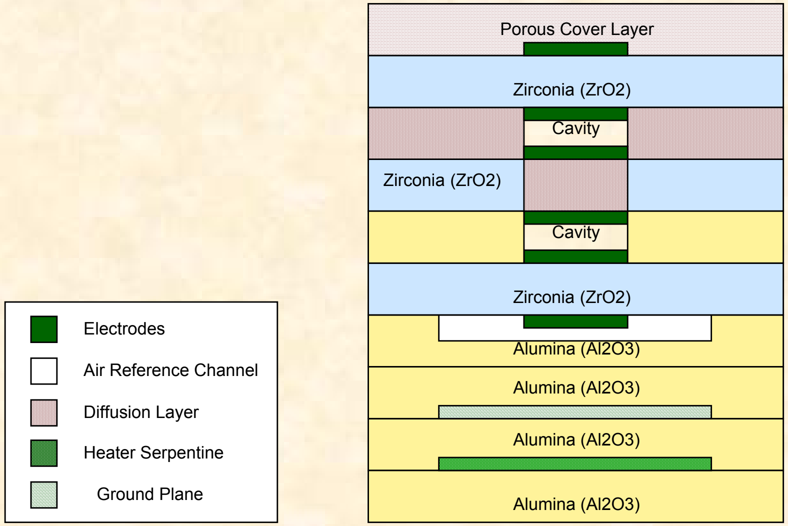
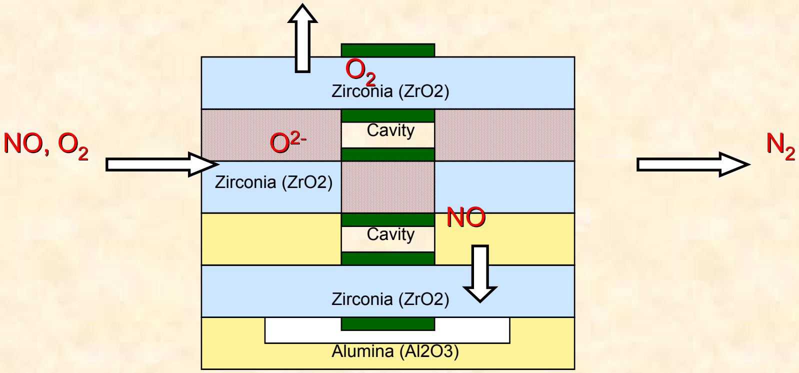
Background - Past ORNL NO_x Sensor Development





Sensor Type #1 (Gasoline lean burn engine)
Sensitivity: 100-200 ppm (potential lower detection limit for diagnostics)
Accuracy: +/- 20 ppm
Response Time: < 1 sec (0-90% full scale)
NO/NO_2: equally sensitive to NO and NO_2
Concerns: sulfur

Sensor Type #2 (Diesel application with urea)
Sensitivity: 20-300 ppm
Accuracy: +/- 20ppm
Response Time: < 1sec (0-90% full scale)
NO/NO_2: separately measure NO and NO_2
Concerns: soot, sulfur and urea(NH_3)

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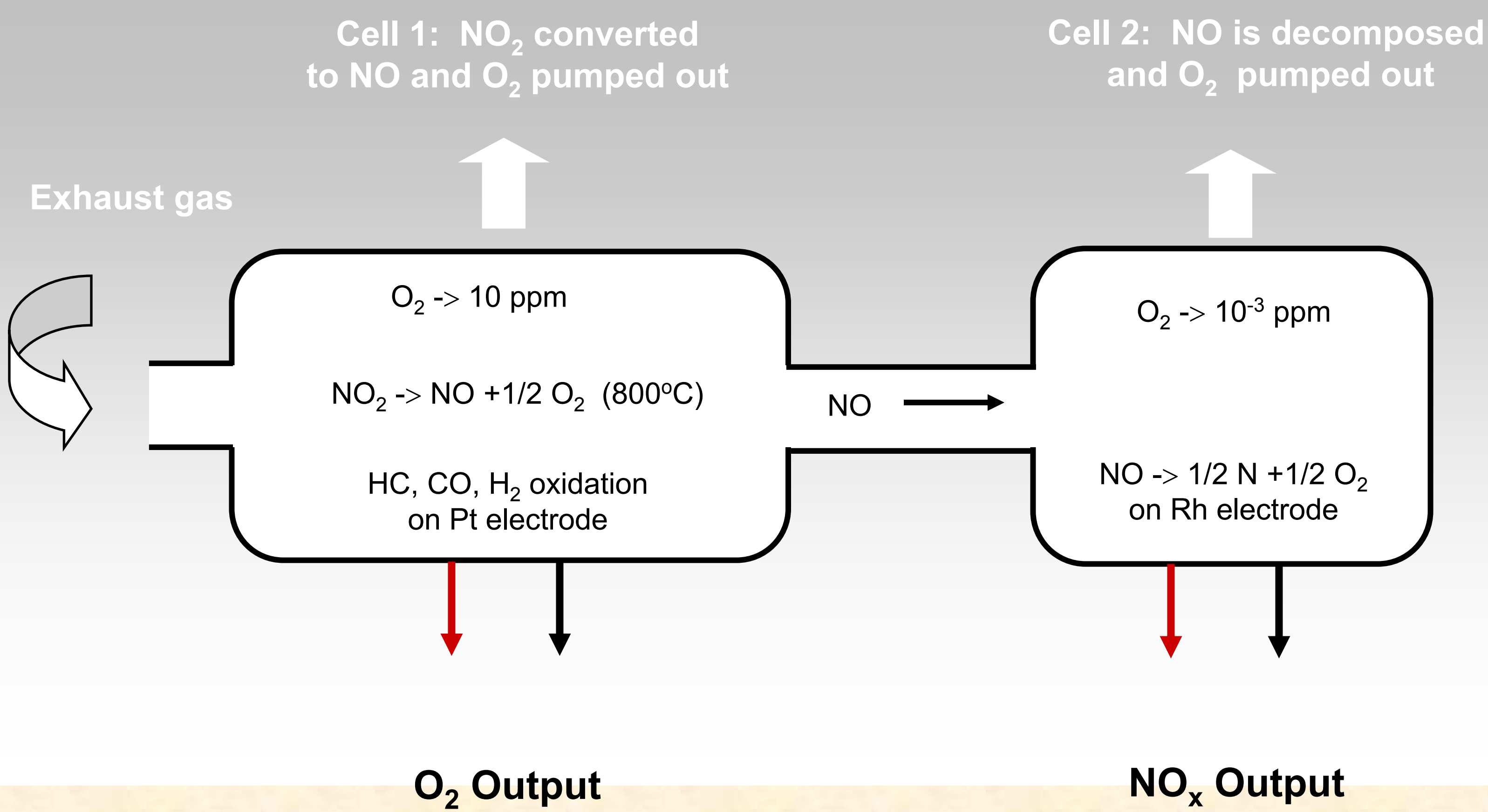
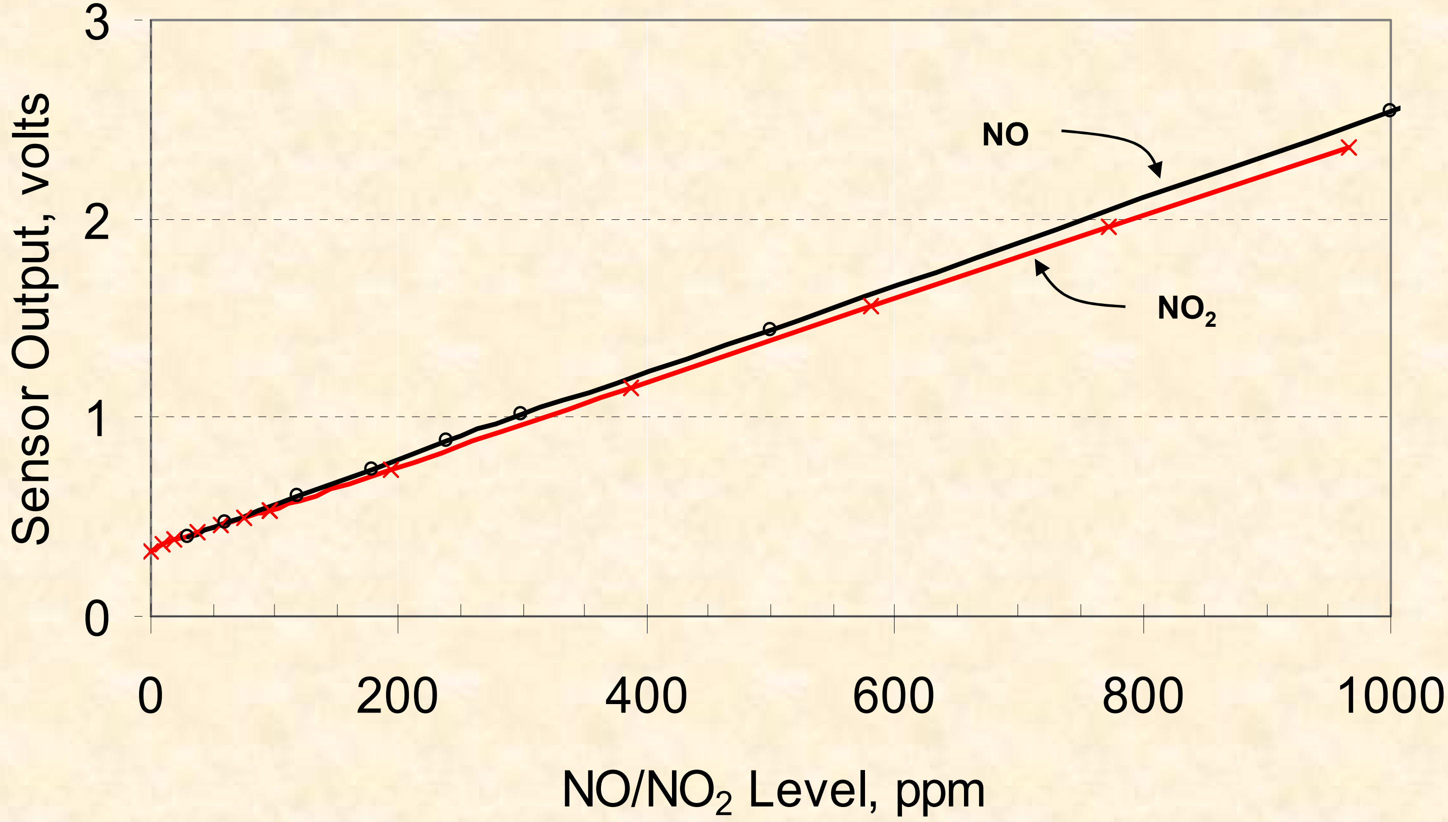
The NGK NOx sensor design consists of two cells with diffusion barriers

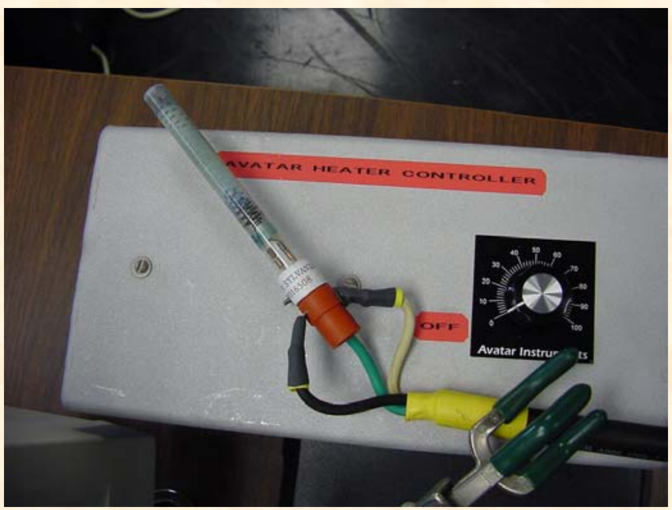


Steady-state measurements on the NGK sensor matched the results obtained by Ford researchers



The transient response of the NGK NOx sensors was sensitive to gas temperature

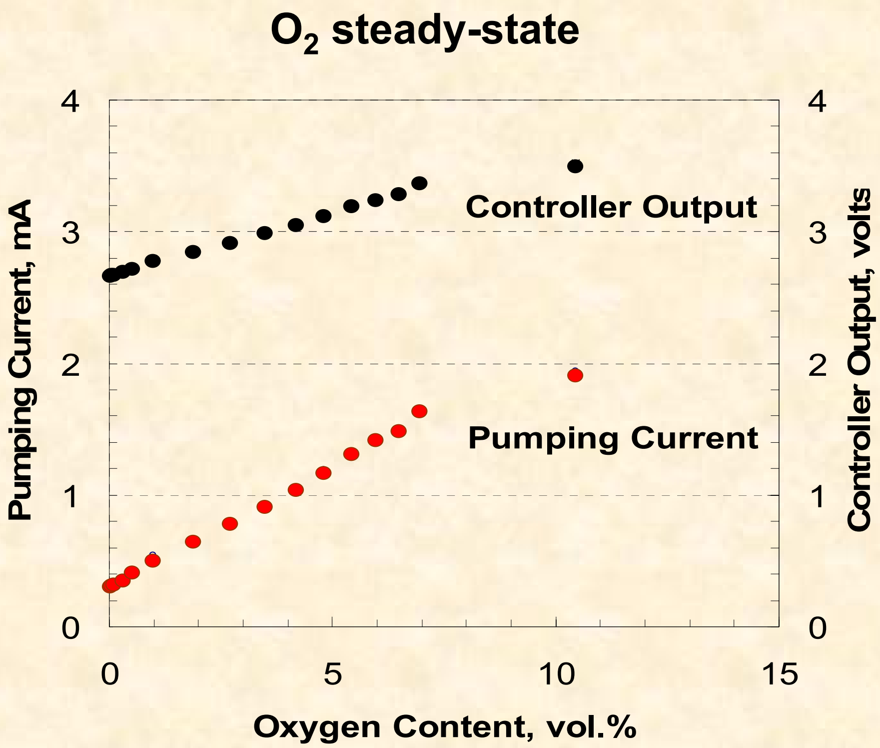
- **The time constants for the NOx output were noticeably longer (i.e. exhibited slower response) compared to measurements made during engine testing at Ford.**
- **An in-line gas heater was added to the test rig and the device was insulated to evaluate the influence of gas temperature on sensor response.**

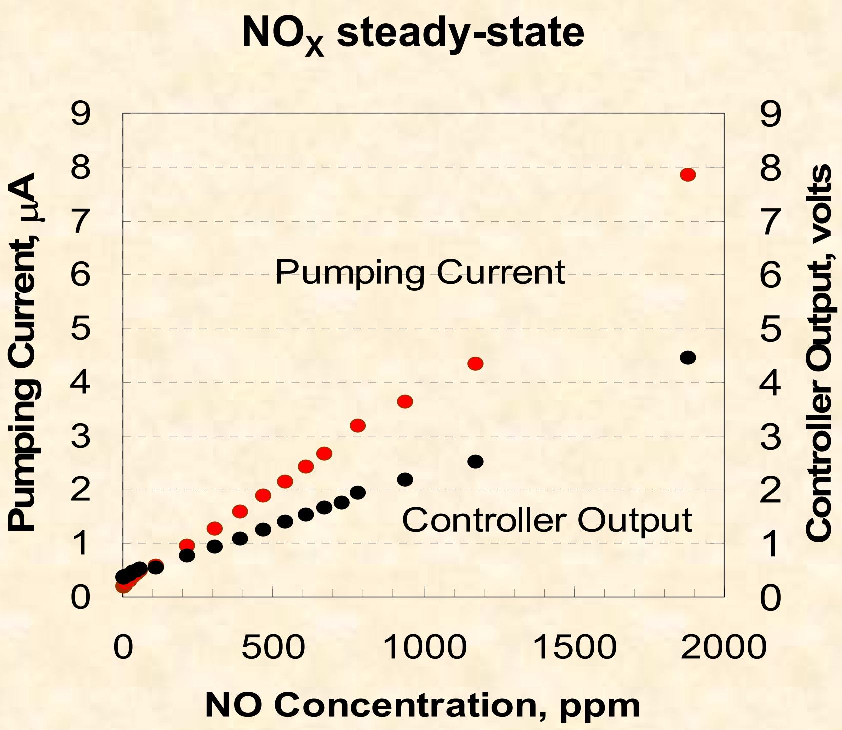


Sensor Output: NOx

Time Constant	Gas Temperature		
	27°C	188°C	350/400°C
RC	1.67s	1.18s	0.87s
t (10-90)	3.60s	2.60s	1.92s
t (33-66)	1.13s	0.80s	0.61s

The NOx pumping current was extremely low and required a quiet laboratory setting to properly measure





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ORNL Mixed Potential NOx Sensor Development Effort

Compact, high-T NO_x sensors: Selected previous work

Investigator(s)	Description	Comments
Miura *et al.*[1,2] (Kyushu Univ.)	Mixed potential, $CdMn_2O_4$ electrode. Mixed potential, $ZnFe_2O_4$ electrode.	$V \propto \ln[NO_x]$. Different response to NO and NO_2 (V changes sign).
" "	Amperometric[3], $CdCr_2O_4$ electrode.	Senses NO only.
Kato *et al.*[4-6] (NGK)	Amperometric, with additional cavity for oxygen pumping.	Relatively complex, multi-layered device.
Kunimoto *et al.*[7] (Riken)	Mixed potential, also has additional cavity.	" "
Lawless[8] (CeramPhysics)	Combined O_2 and NO_x sensor. NO_x sensed amperometrically.	" "
Gopel *et al.*[9,10] (Tübingen Univ.)	Amperometric, multi-electrode.	O_2, other gases removed by successive electrodes.

⇒ Mixed potential, amperometric approaches dominate prior art. ⇐

[1]*Solid State Ionics*, **86-8** pg. 1069, (1996). [2]*Sensors and Actuators* B, **83**, pg. 222, (2002). [3]*Solid State Ionics*, **117**, pg. 283, (1999). [4,5,6]SAE Technical Papers 960334, 970858, 980170. [7]SAE Technical Paper 1999-01-1280. [8]US Patent Application 20020046947 (2002). [9]*Solid State Ionics*, **136-7**, pg. 519 (2000). [10]*Sensors and Actuators B*, **35-6**, pg. 409 (1996).

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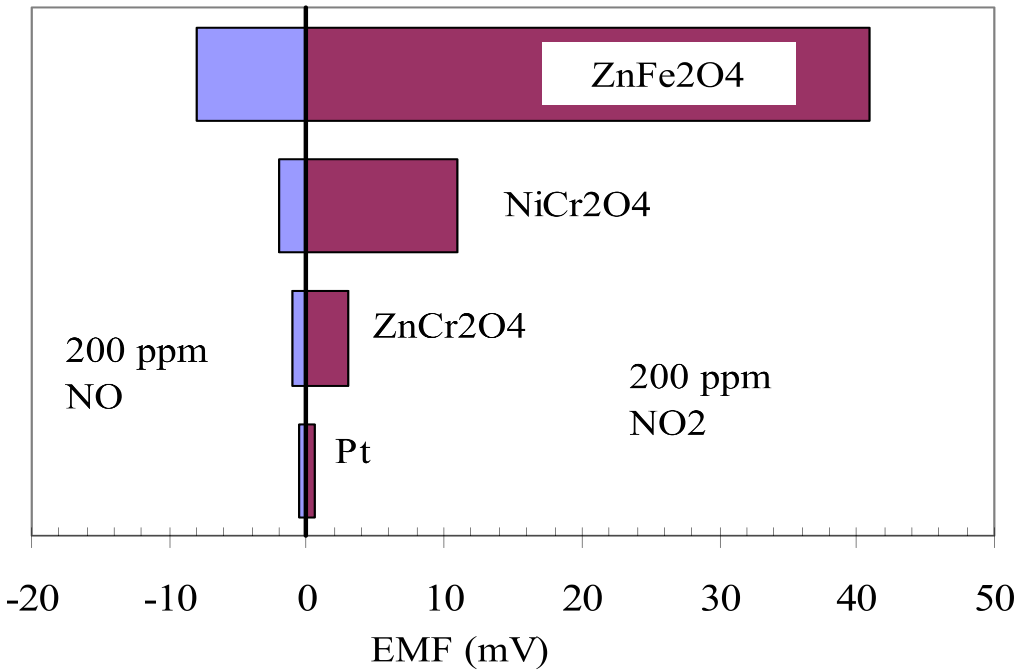
The chemistry of NO and NO_2 may affect sensor differently



N. Miura, et al., Sensors and Acatuators B 83 (2002)

- NO is reducing agent
- NO_2 is oxidizing agent
- Can result in opposing sensor signals
- Selectivity/sensitivity improved measuring single species

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Experimental Approach

Evaluation of materials as mixed potential sensing electrodes.

⇒ Determine specimen design/configuration.

- Prefer straightforward design, minimal process steps.
- Make use of literature available on previous designs and concepts.[#,$,%]
- Leverage pre-existing expertise in tape-casting and screen-printing.

⇒ Design and build test stand.

- Test fixture compatible with design selected above.
- Equipment for atmosphere generation.
- Furnace, electronics.

⇒ Benchmark test and evaluate progress.

[#] Lu *et al*., *Sensors and Actuators B*, **65**, pg. 125 (2000).
[$] Miura *et al*., *Sensors and Actuators B*, **47**, pg. 84. (1998).
[%] Brosha *et al*., *Solid State Ionics*, **148**, pg. 61. (2002).

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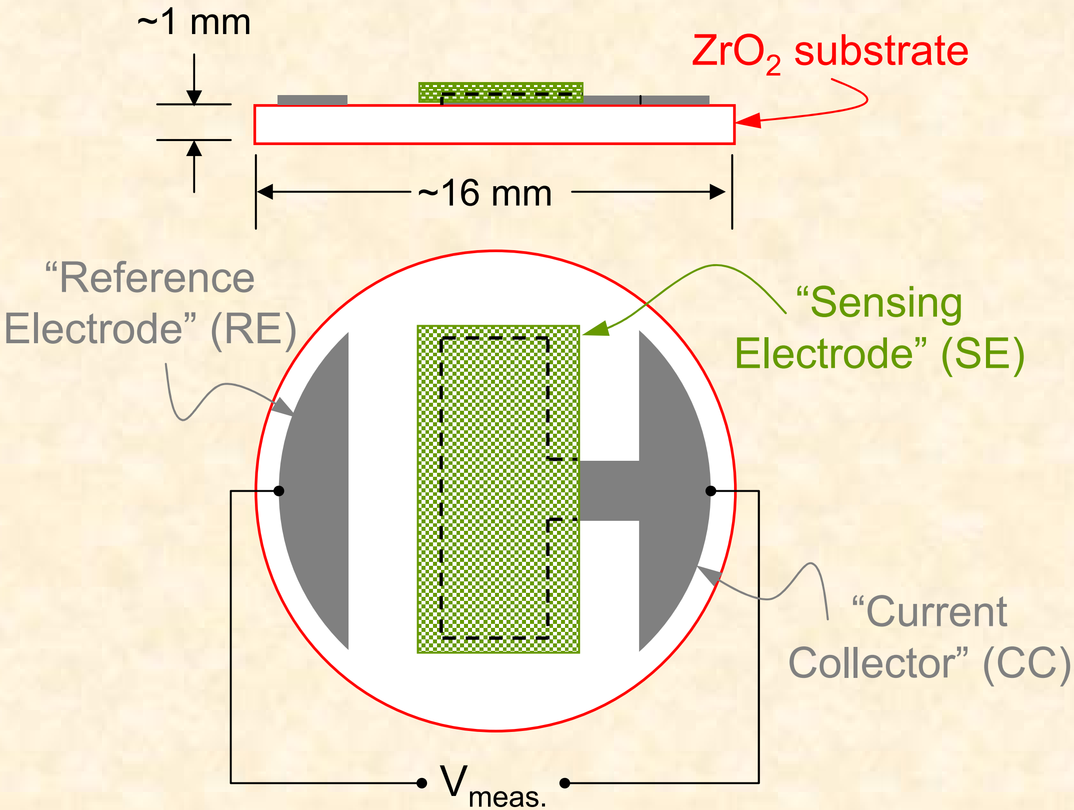
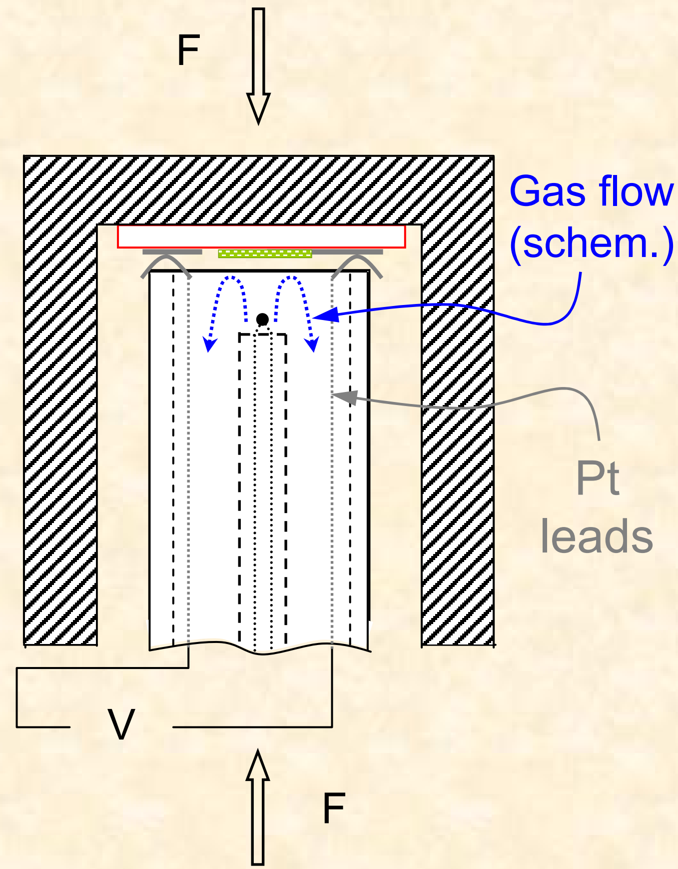
Specimen geometry and test fixture design



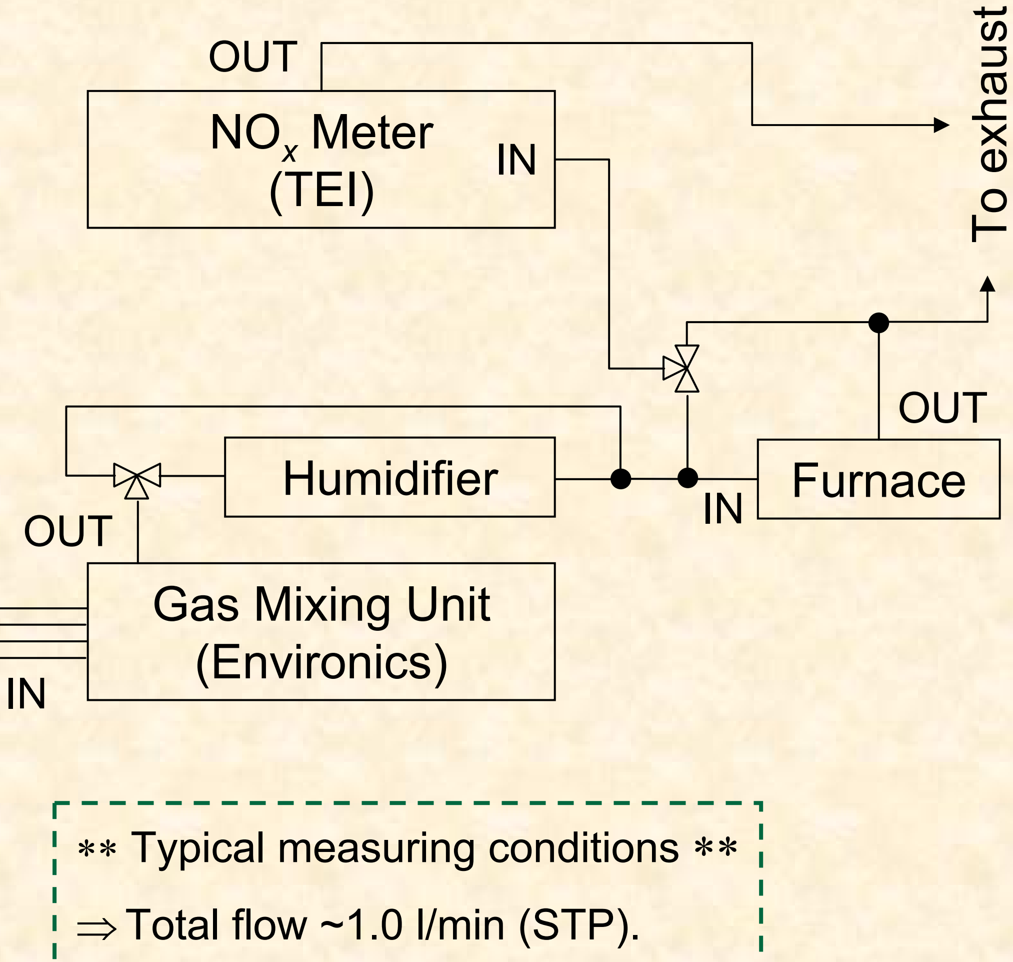


Test Fixture

- Substrate tape cast & laminated (Tosoh TZ-8Y ZrO_2).
- Pt, working electrode screen-printed. Dried & fired thickness ~30 μm (firing T ~1000 °C, air).

Equipment for gas handling

Environics 4-port mixer, TEI chemiluminescent NO_x monitor, etc.



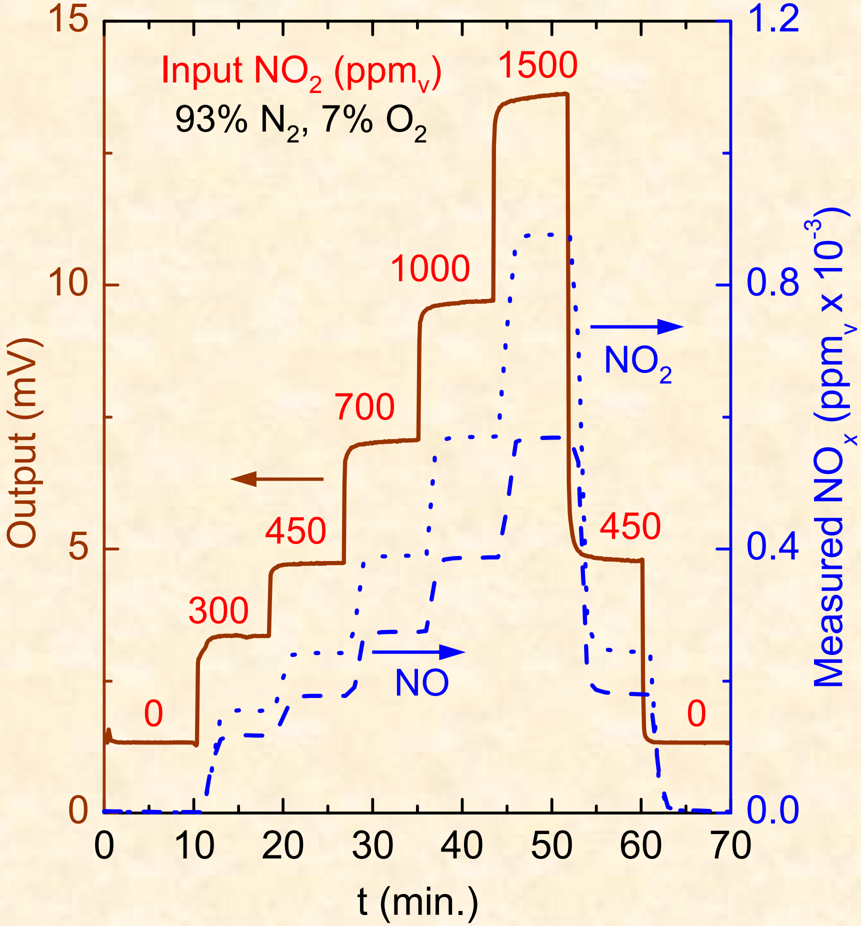
** Typical measuring conditions **

- ⇒ Total flow ~1.0 l/min (STP).
- ⇒ $5 \leq [O_2]$ (vol%) ≤ 20.
- ⇒ $300 \leq [NO_x]$ (ppm_v) ≤ 1500.

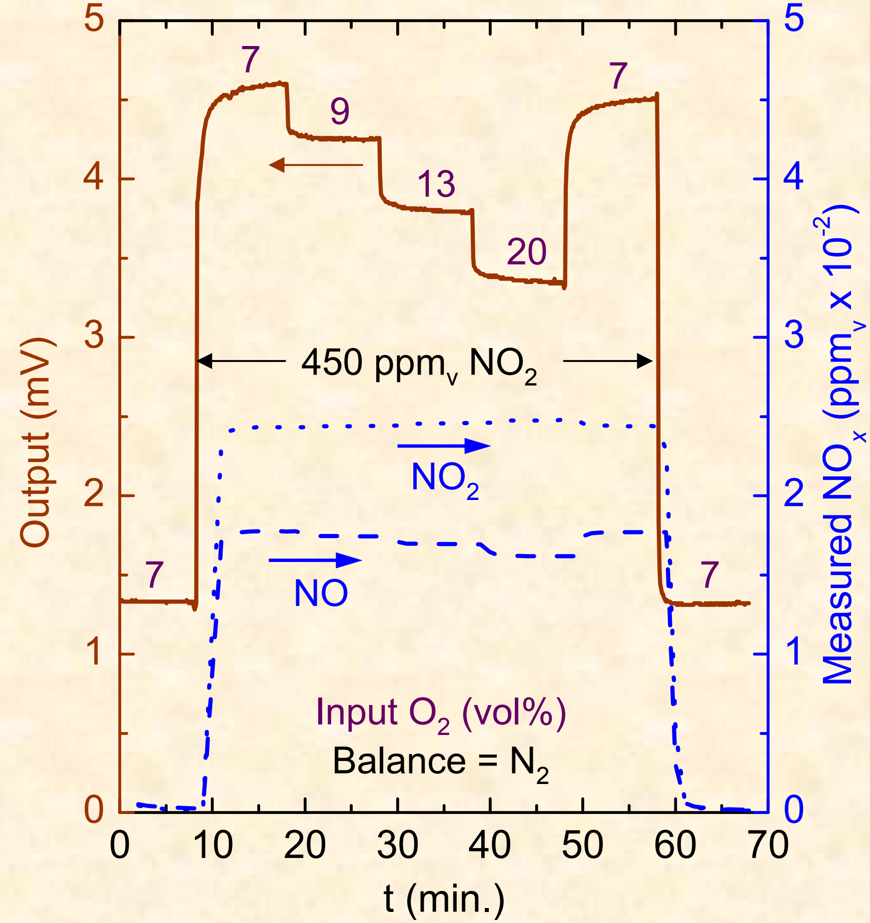
Sample response

$La_{0.85}Sr_{0.15}CrO_{3-\delta}$ SE, Pt RE/CC; input $NO_x = NO_2$

NO_2 variations, fixed (7 vol%) O_2



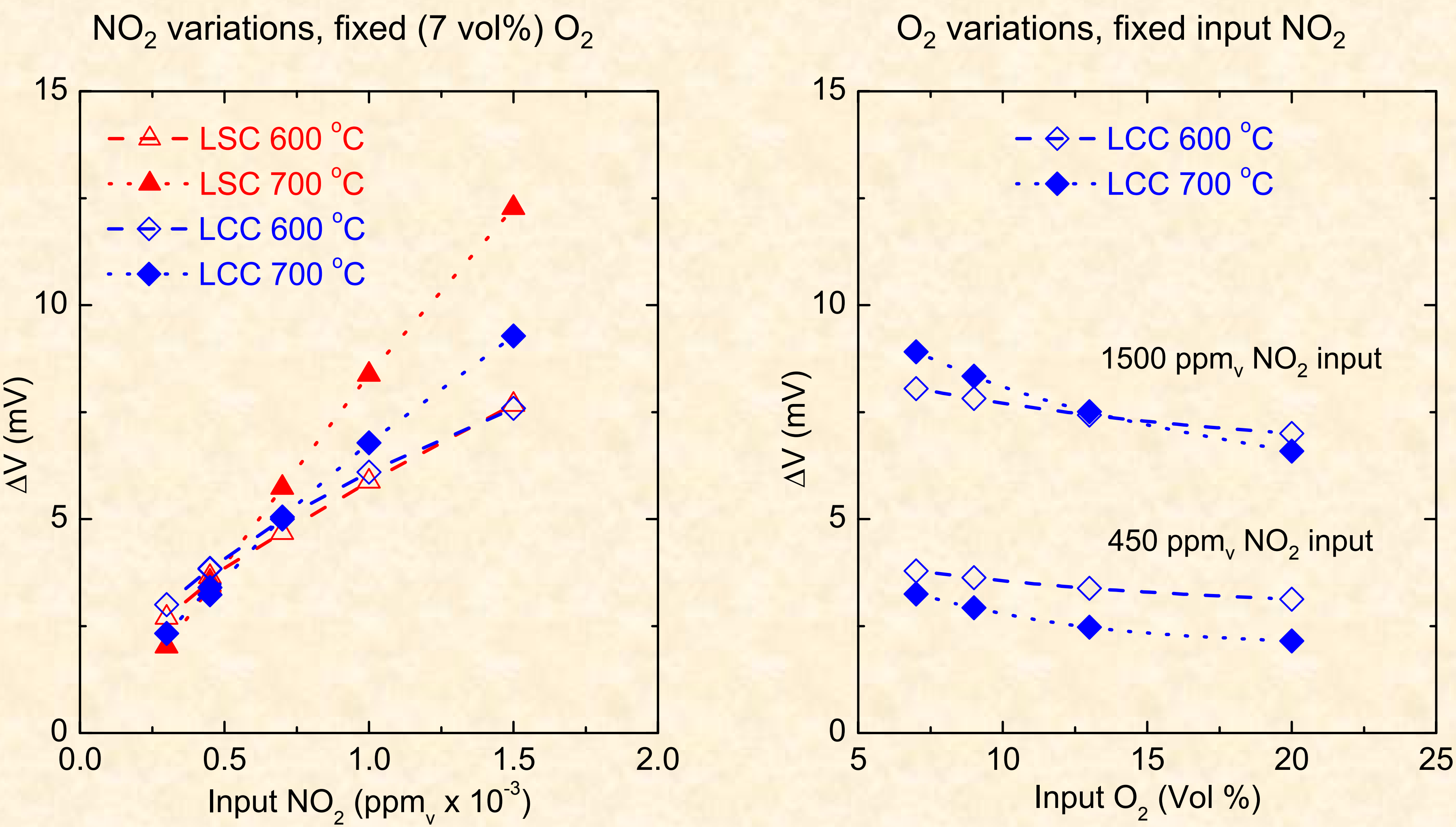
O_2 variations, fixed (450 ppm_v) NO_2



NO_x sampled from exit, at RT

Behavior in NO_2

$La_{0.85}Sr_{0.15}CrO_{3-\delta}$ (LSC), $La_{0.80}Ca_{0.21}CrO_{3-\delta}$ (LCC) SE, Pt RE/CC

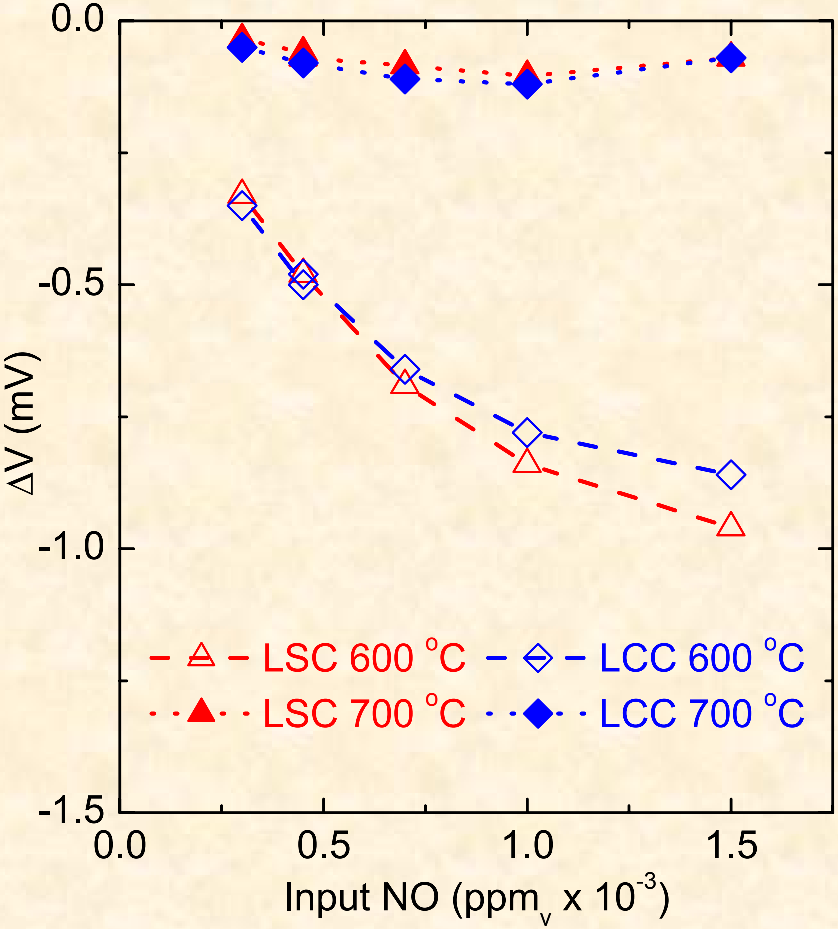


Balance gas = N_2

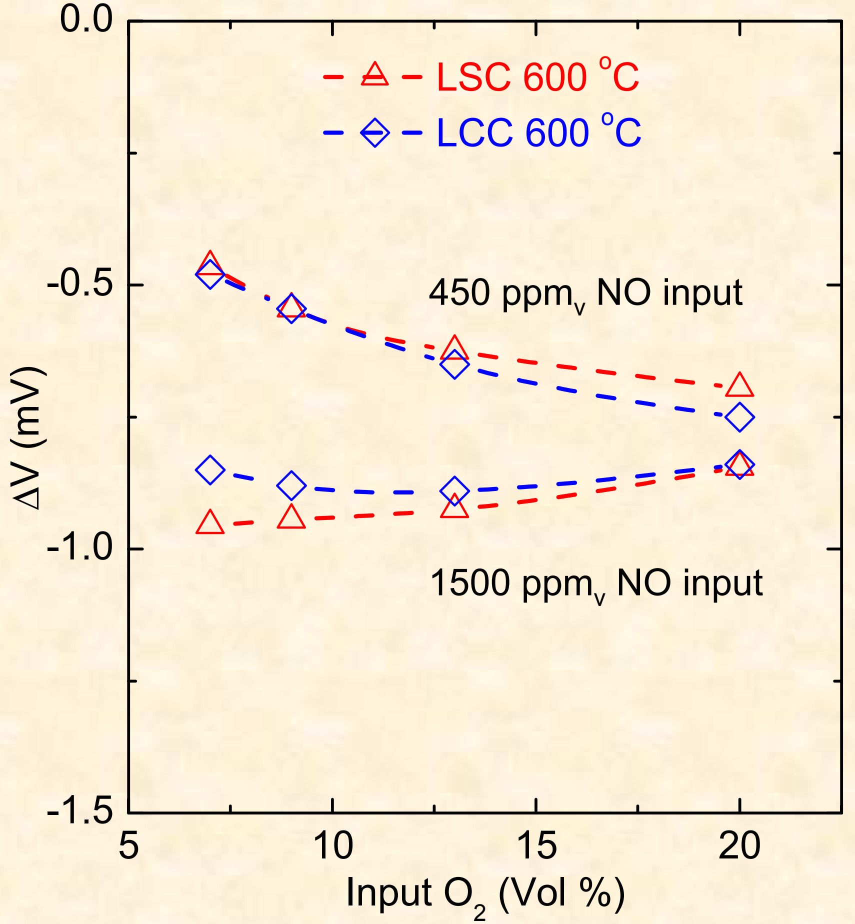
Behavior in NO

$La_{0.85}Sr_{0.15}CrO_{3-\delta}$ (LSC), $La_{0.80}Ca_{0.21}CrO_{3-\delta}$ (LCC) SE, Pt RE/CC

NO variations, fixed (7 vol%) O_2

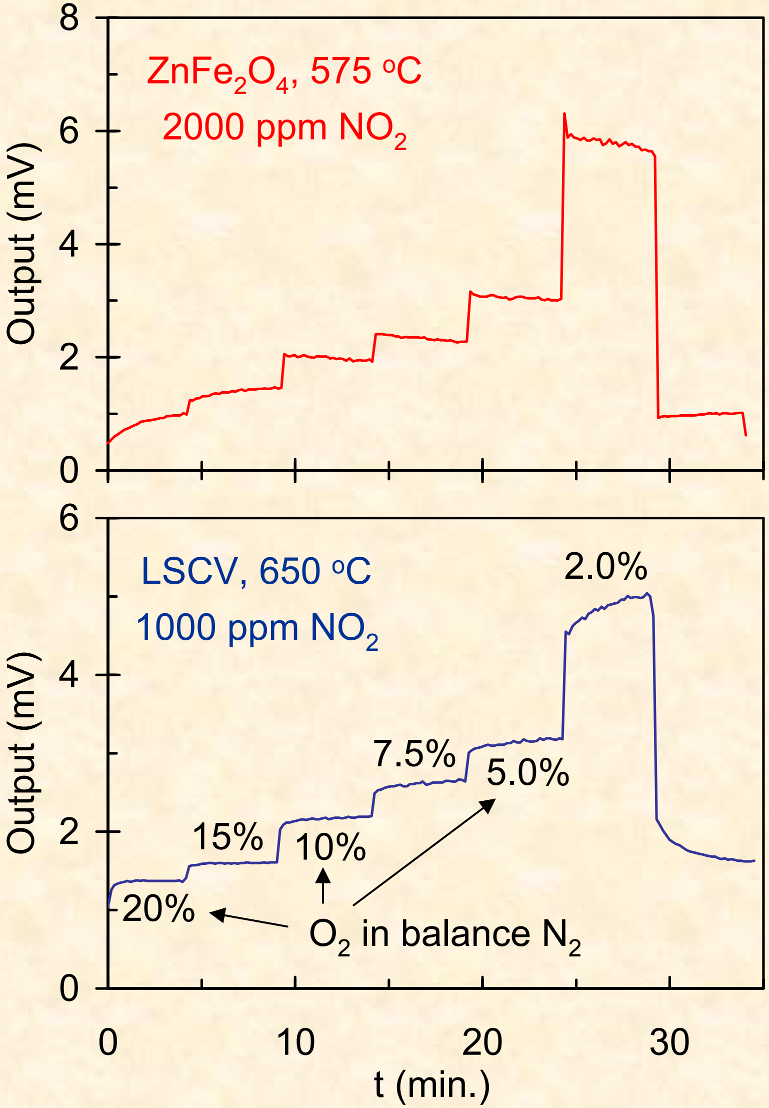


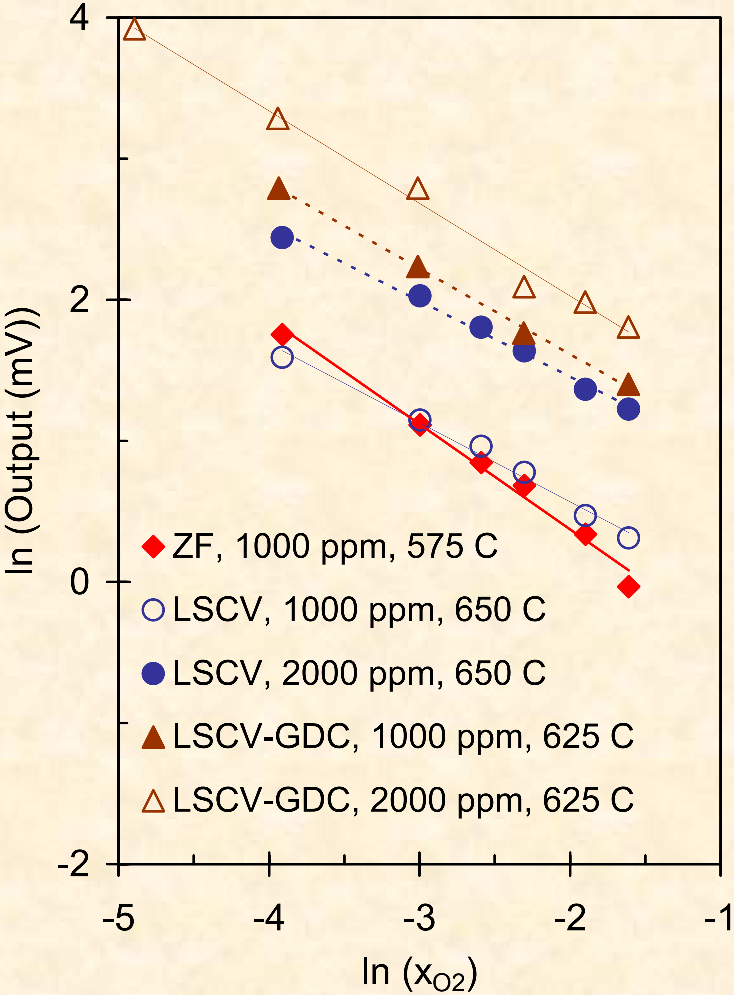
O_2 variations, fixed input NO



Balance gas = N_2.

Oxygen sensitivity with NO_2†





†Sensitivity with NO even more pronounced.

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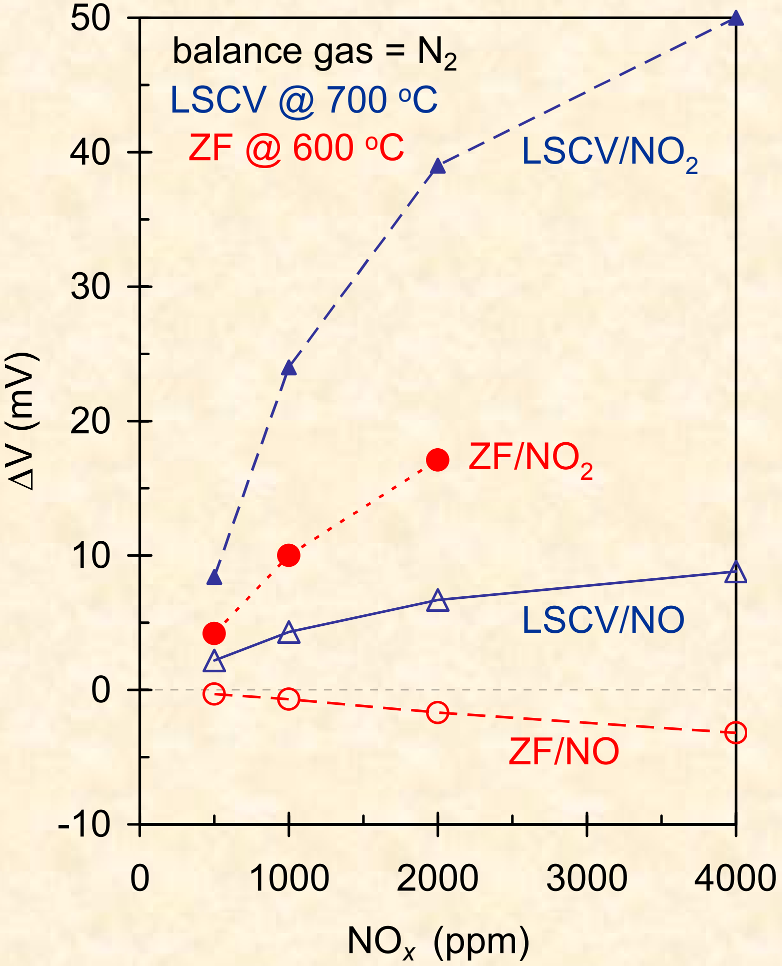
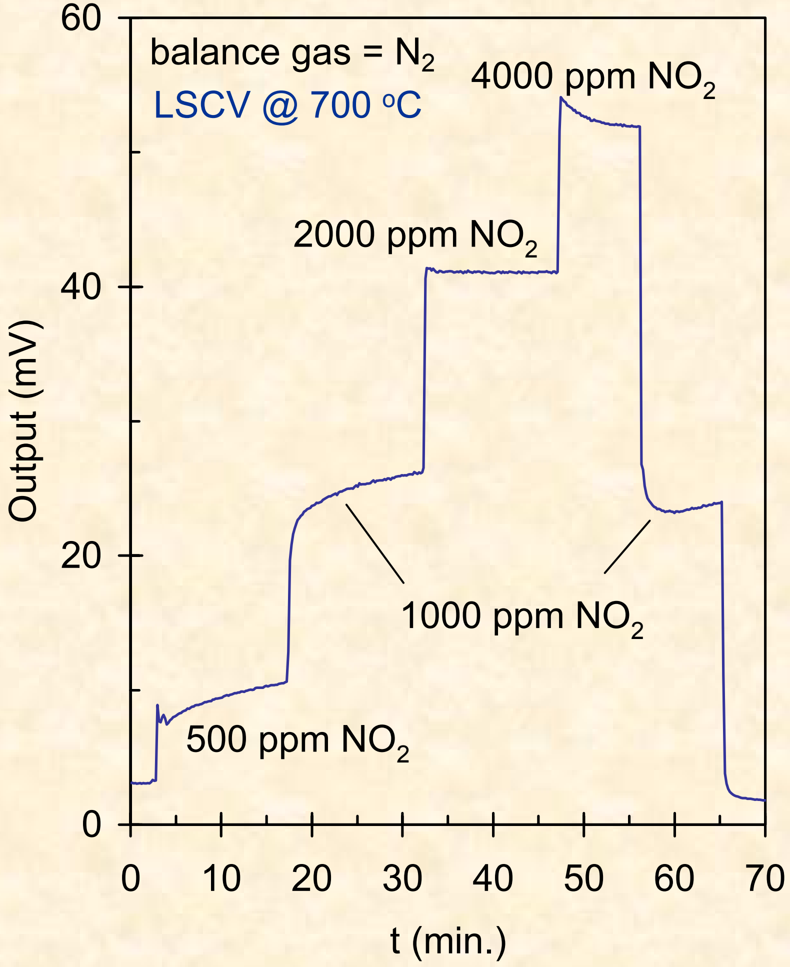
Sensor outputs under NO and NO_2

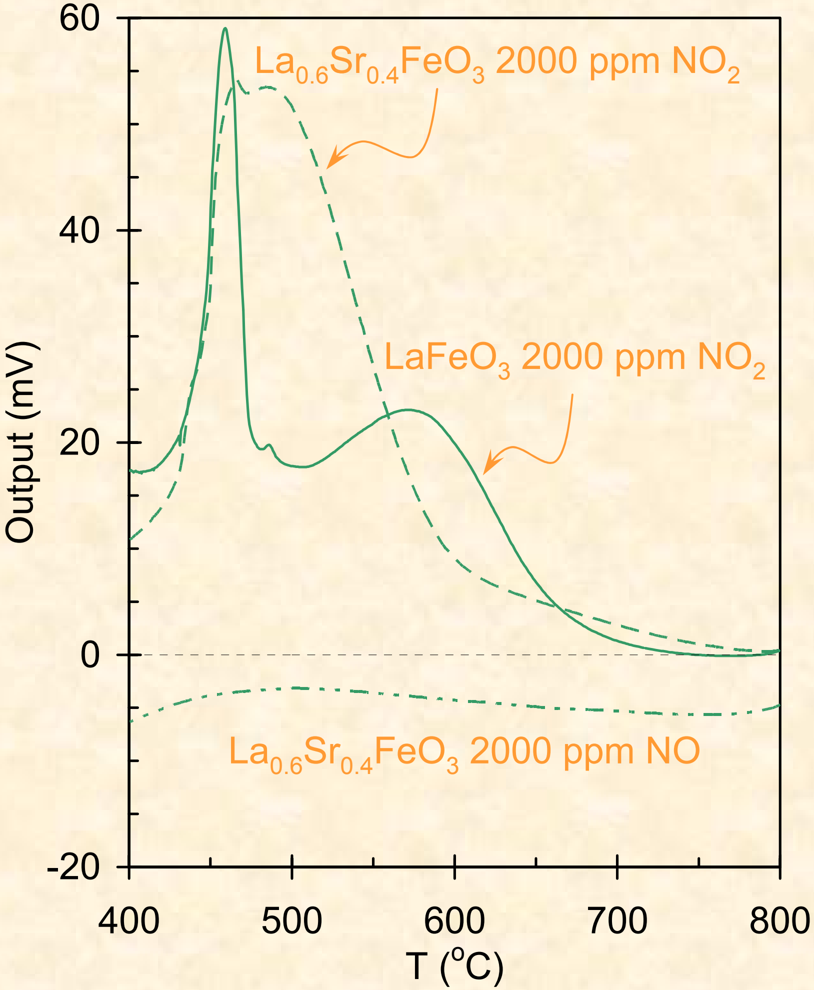
$ZnFe_2O_4$(ZF) and $La_{1-x}Sr_xCr_{1-y}V_yO_{3-\delta}$ (LSCV) electrodes

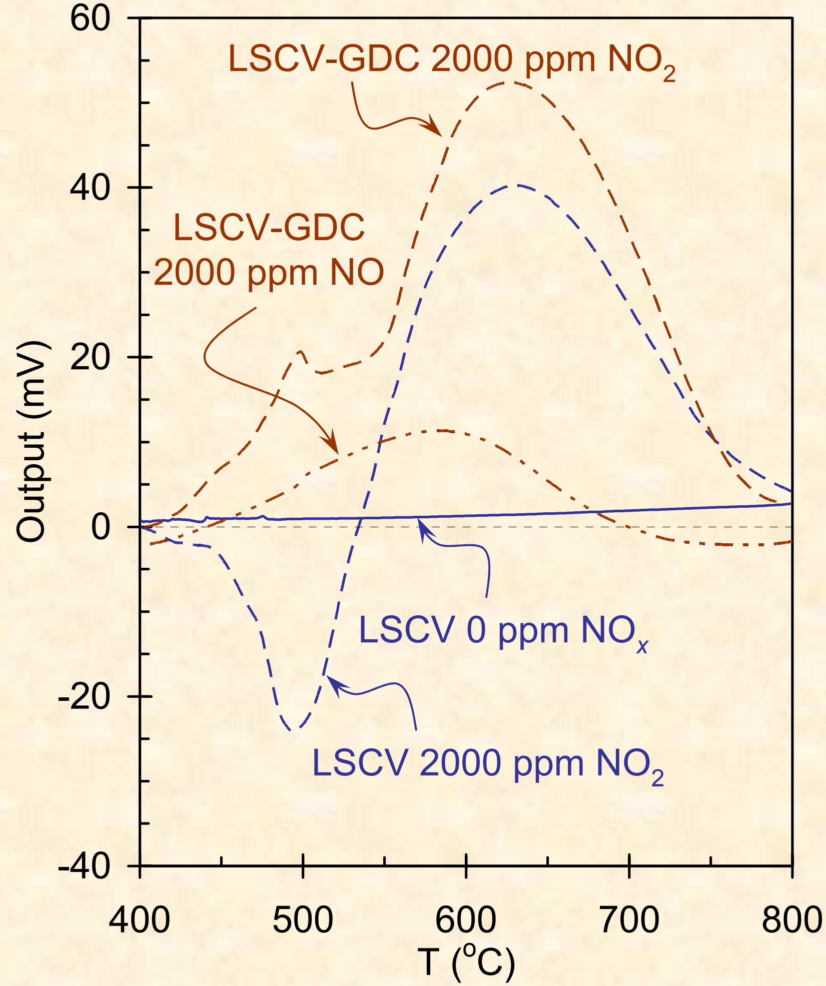




Material response as a function of temperature

All data on cooling, N_2 balance gas





Summary

⇒ Background

- Primary species NO and NO_2, NO dominates at T > 600 ^oC. Present high-T NO_x sensors include mixed-potential and amperometric sensors.

⇒ Experimental progress

- Specimens for investigating material response fabricated, test rig for oxide electrode evaluations constructed.

⇒ Observations

- Responses to NO_2 much stronger than NO. Both are function of O_2 content.

⇒ Proposed future work

- SE electrode material(s) – properties, processing.
- Testing design – improve tailoring for end-user's application.