Development of Novel NOx Sensors and System Integration with Alumina Heater Elements

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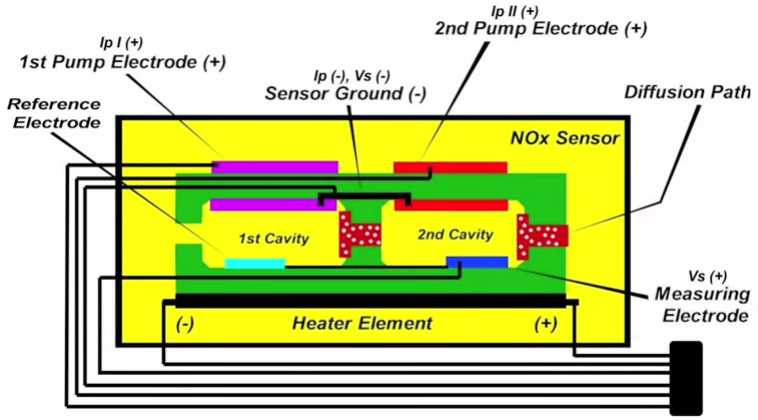
NOx sensors currently in vehicles and our novel method both related to O_2 sensor technology

- In vehicles now – amperometric operation (dc current) of solid-state electrochemical cell
  - Multiple cells to pump out O_2 and measure remaining NOx
  - Difficulty detecting sub 5 ppm and poor durability of complex probes



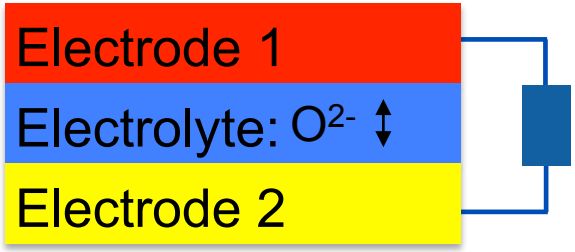
https://www.youtube.com/watch?v=VsR_P-14K0U

- Our method – novel single-cell 'impedancemetric' operation
  - Two electrodes with specific oxygen catalyst properties covered with porous yttria-stabilized zirconia (YSZ) O^{2-} conducting ceramic electrolyte placed directly in gas
  - Applied oscillating signal with resulting wave distortion analyzed
  - Potential for lower cost and better performance

System integration with alumina heater elements

Impedancemetric sensing: Yttria-stabilized zirconia (YSZ) electrolyte conducts O^{2-} >600°C

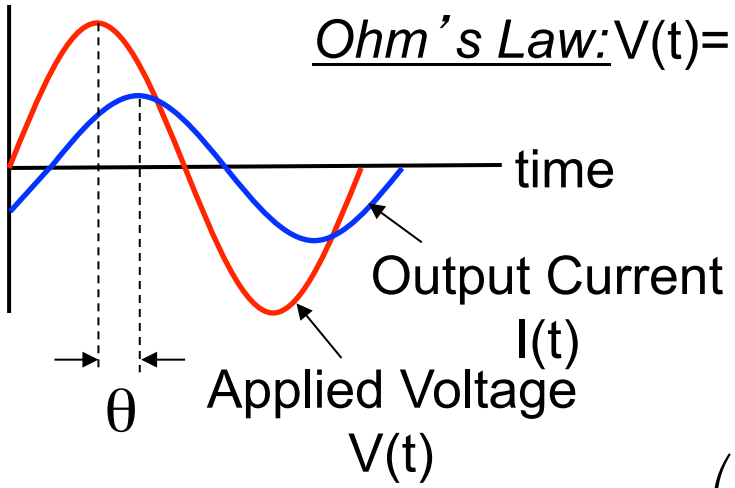
Requires at least one sensing electrode: symmetric or asymmetric cells with design flexibility



$$\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}$$

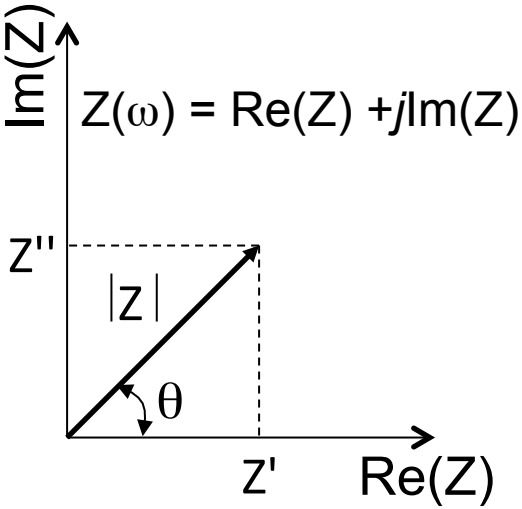
$$NO_2 + 2e^- \leftrightarrow NO + O^{2-}$$

Non equilibrium multiple reactions



Ohm's Law: $V(t)=I(t)\bullet Z(\omega)$

Complex impedance:
AC response to small amplitude signals over a range of frequencies



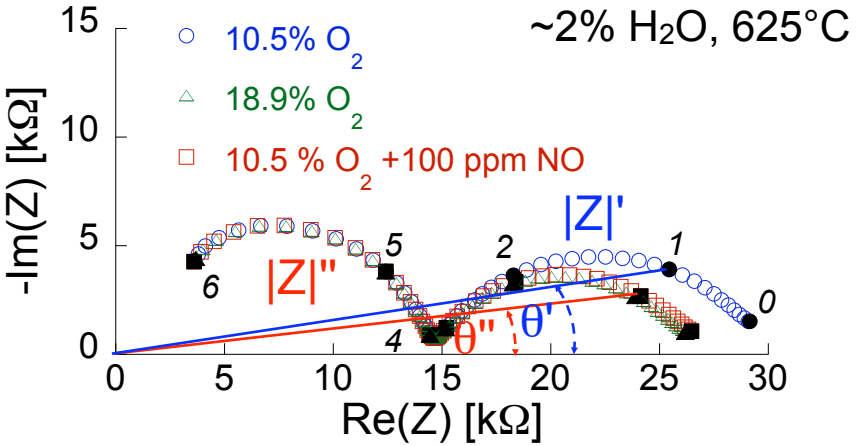
$$\theta = \tan^{-1}\left(\frac{Im(Z)}{Re(Z)}\right)$$

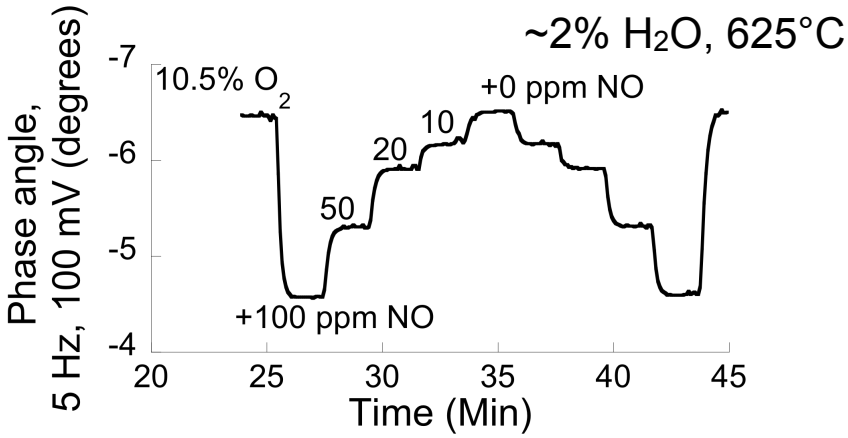
Phase angle

$$|Z| = \sqrt{(Re(Z))^2 + (Im(Z))^2}$$

Magnitude

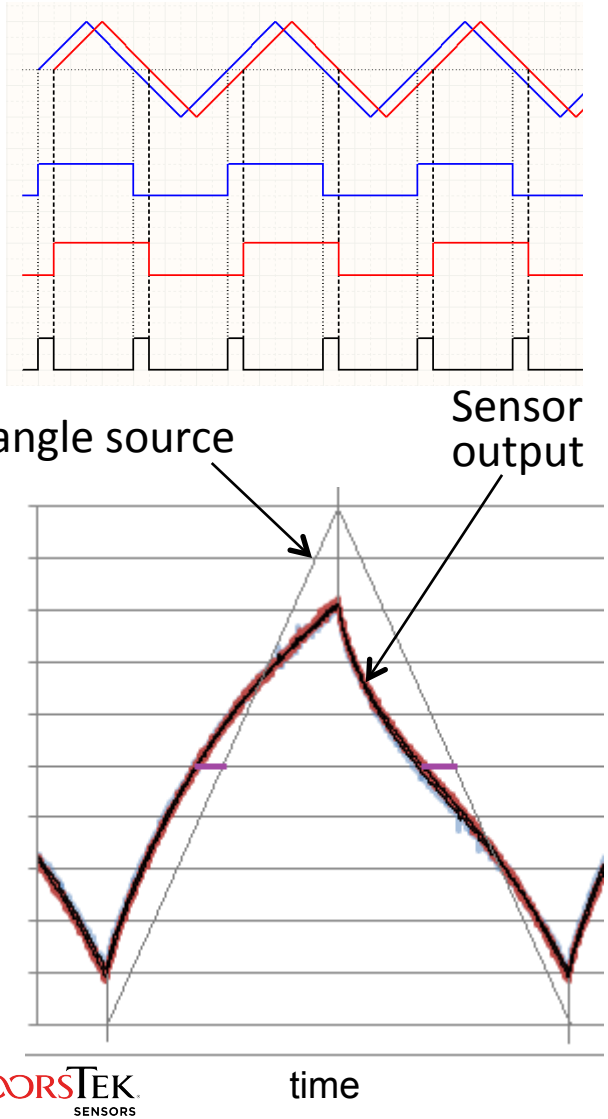
For operation, choose phase angle (θ) at 5-50 Hz and 100 mV excitation





- Less than ~1 kHz: Impedance (phase angle, θ, and magnitude, |Z|) decrease with increasing NOx and O_2
  - Oxygen – methods for extraction
  - Phase angle (θ) – better stability and sensitivity than |Z|

Development of lower cost electronics led to surprising discovery about sensor response



- Precision laboratory equipment (Solartron 1260) costs ~ $50k
- For portable low-cost digital electronics, explored triangle wave form and zero-crossing detection
- Complex response to triangle wave source showed peak relatively unchanged – no phase shift!
- Digital voltage-current time differential method using complex changes in asymmetric wave form
- NOx and O_2 concentration alter different portions of wave in time – basis for extracting oxygen

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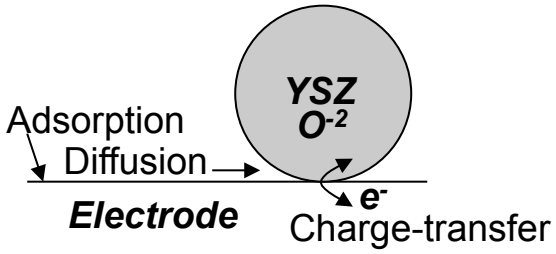
Sensing relies on electrochemical reaction rates at the electrode/electrolyte interfaces

electrolyte	***electrode***
O^{2-} $\longleftrightarrow$	$\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-}$
	$NO_2 + 2e^- \leftrightarrow NO + O^{2-}$

- Impedance – reaction rates with different frequency dependencies
  - NOx and O_2 influence < 1 kHz
  - Parallel contributions from both

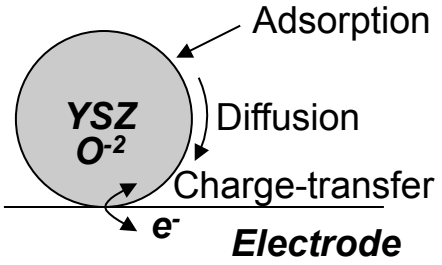
- Resolve ppm NOx changes in large 2-21% O_2 background by limiting O_2 reaction rate with porous YSZ electrolyte

Low sensitivity



Minimal NOx response when electrode surface dominates

High sensitivity

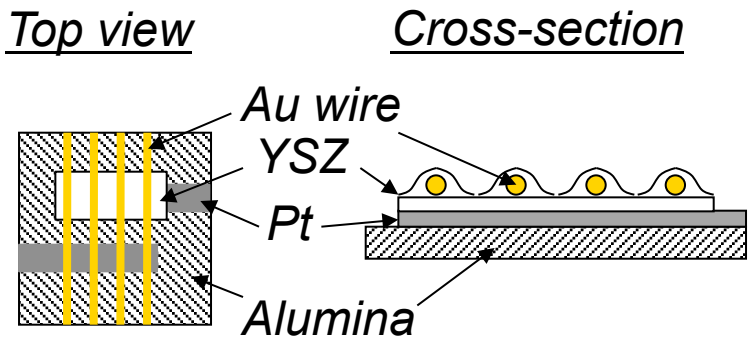


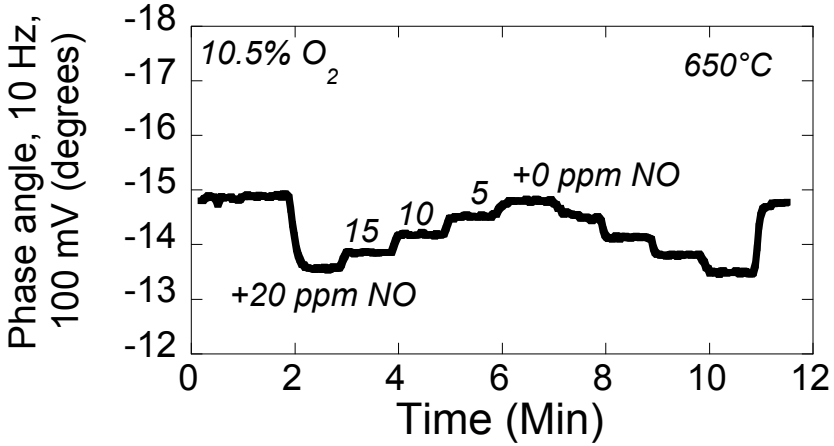
Larger NOx response: controlling microstructure and composition is key

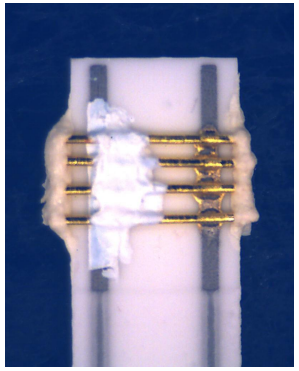
System integration of NOx sensor designs with Al_2O_3 heater for more deployable prototypes

- More advanced designs suitable for single higher temperature cofiring step with Al_2O_3 for easier processing and improved robustness
- Bonding of porous YSZ electrolyte to Al_2O_3
- Incorporating more desirable processing techniques such as screen-printed electrodes
- Packaging and electrical connections to heater and sensor

Continued evolution of designs starting with hand-assembled single-cell lab prototypes

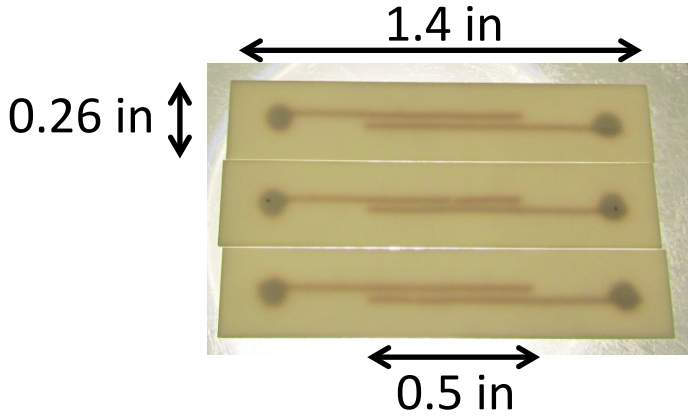






- Al_2O_3 substrates and Pt leads fired ~ 1500°C
- Followed by separate lower temperature (1000 °C) post-firing step for Au wire and porous YSZ
- Sensitivity < 5 ppm, response < 5 sec for 10 ppm
- Stable reproducible signal > 1000 hours and durability > 3800 hours
- Low cross-sensitivity to water

More advanced designs: Au ribbon constrained by YSZ layers suitable for cofiring with Al_2O_3

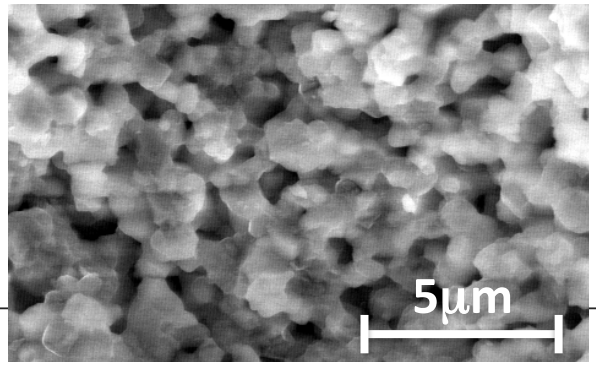


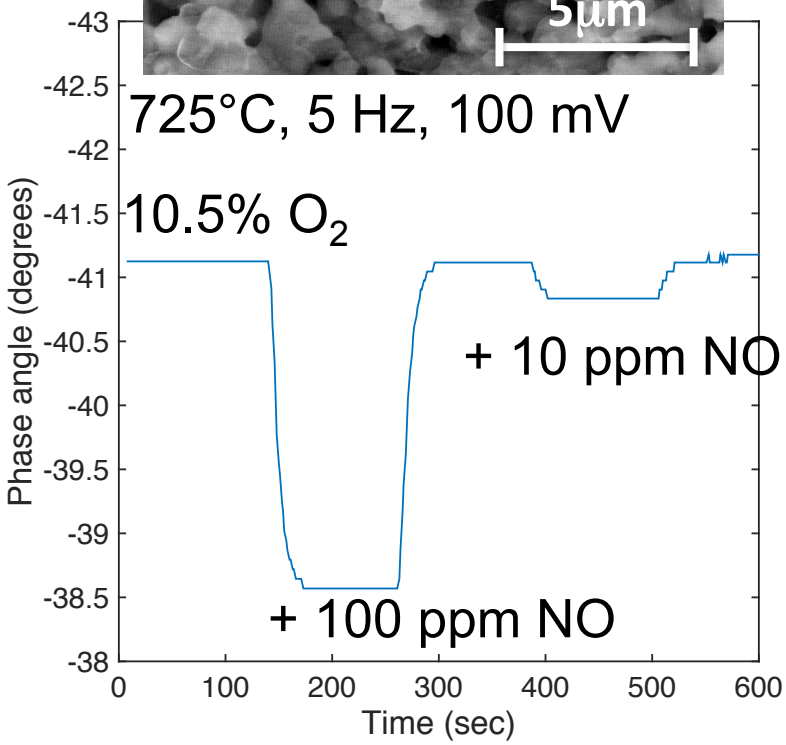
Polish to expose contact pads at ends for electrical leads

- 1450°C as target minimum for cofiring with Al_2O_3
- Tape cast YSZ thickness (before firing) ~10 mils: laminated 2 layers above and 2 layers below Au ribbons
- Au ribbons: ~11 mils width x 5 mils thickness with 25 mil spacing between
- Fugitive material added to Au ribbon channels to account for larger shrinkage of ceramic

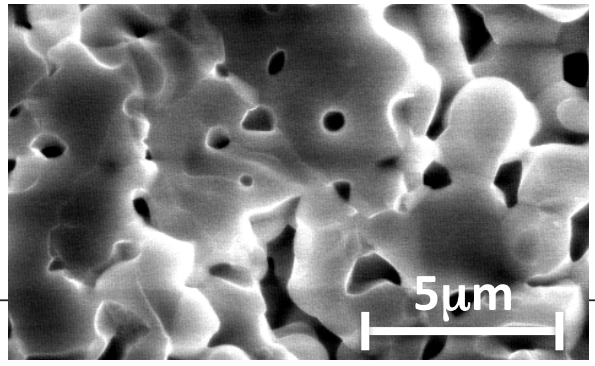
Previously, two different porous YSZ studied for constraining Au at 1450 °C (no Al_2O_3 heater)

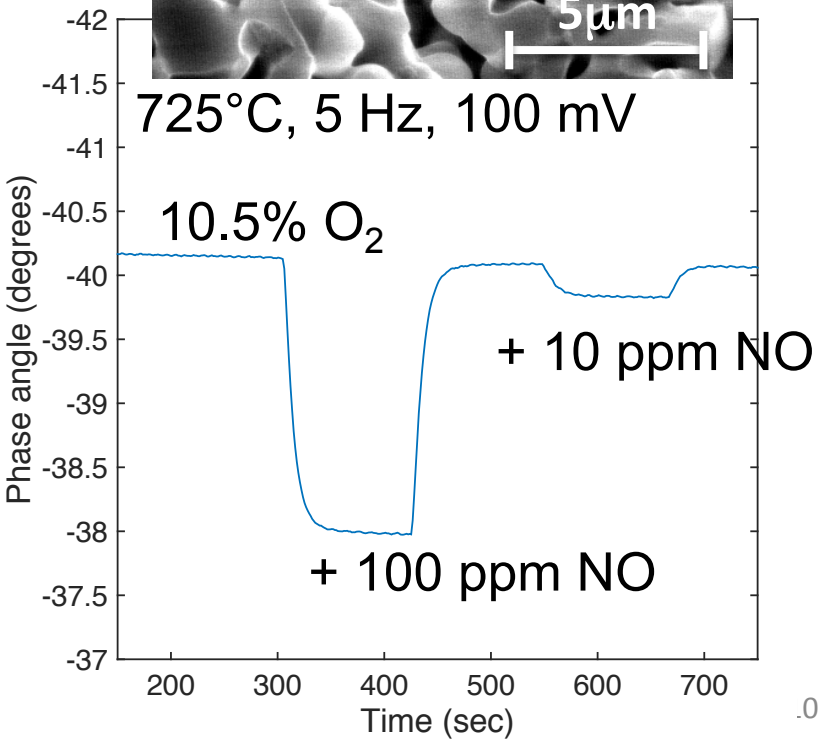
Adding 22 vol% carbon black as pore former; ~23% porosity



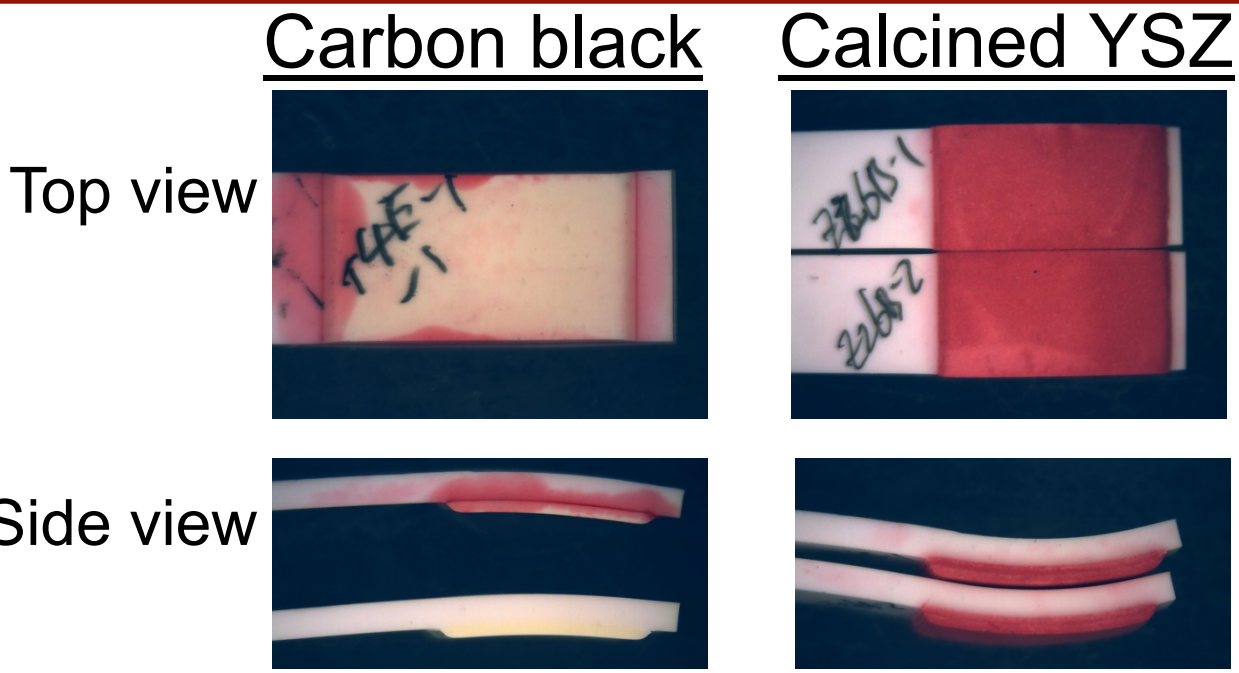


Calcined YSZ at 1300 °C to reduce sintering kinetics; ~16% porosity



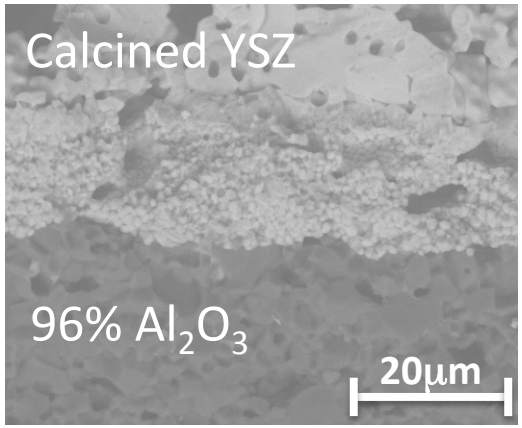


Investigate cofiring two different porous YSZ with Al_2O_3 at 1450°C



- Both types of porous YSZ bonded to Al_2O_3
- Densification of porous YSZ near interface with Al_2O_3
- More porosity (indicated by uptake of red dye) in calcined YSZ – better sensor performance

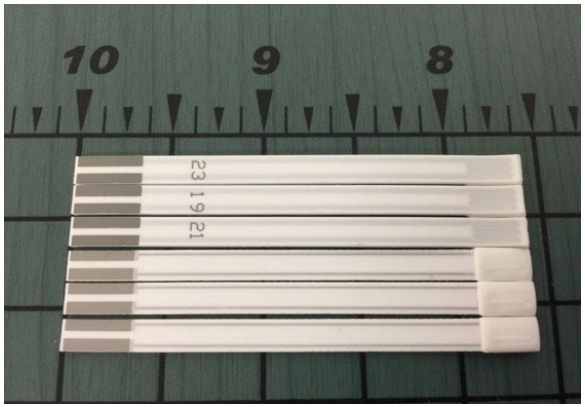
Evidence of interfacial structure and strong bonding in calcined YSZ with Al_2O_3

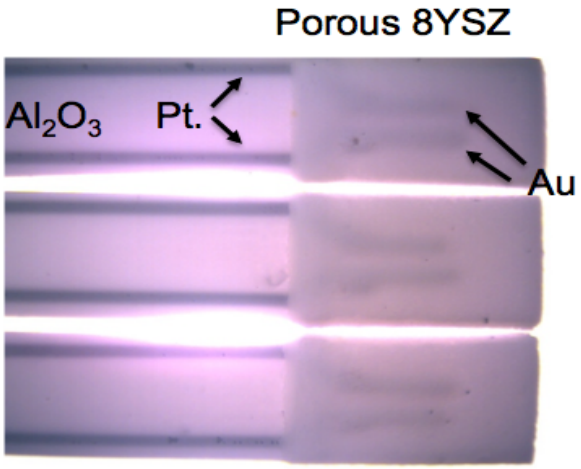


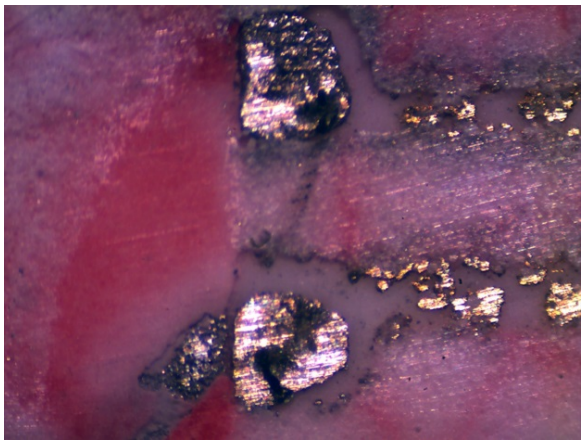
"Fine-grain" structure in calcined YSZ near interface with Al_2O_3

- Thermal cycling and autoclave testing indicated strong durable bonding at YSZ/Al_2O_3 interface
- Due to strong bonding and better porosity than carbon black, used calcined YSZ for developing working sensors with Au electrodes and Pt leads integrated with Al_2O_3 heater elements

1450 °C cofiring of Au electrode and Pt lead showed poor electrical continuity



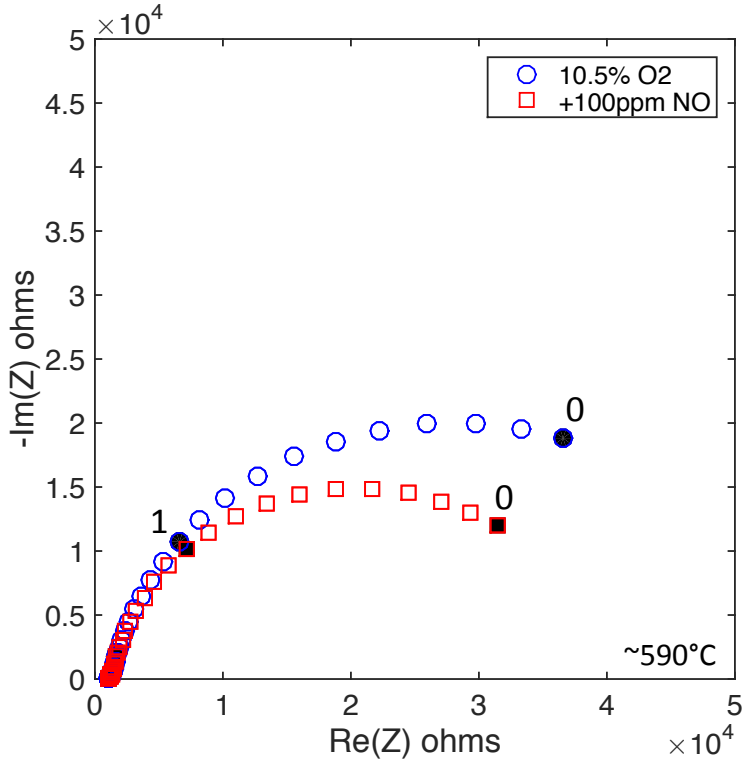


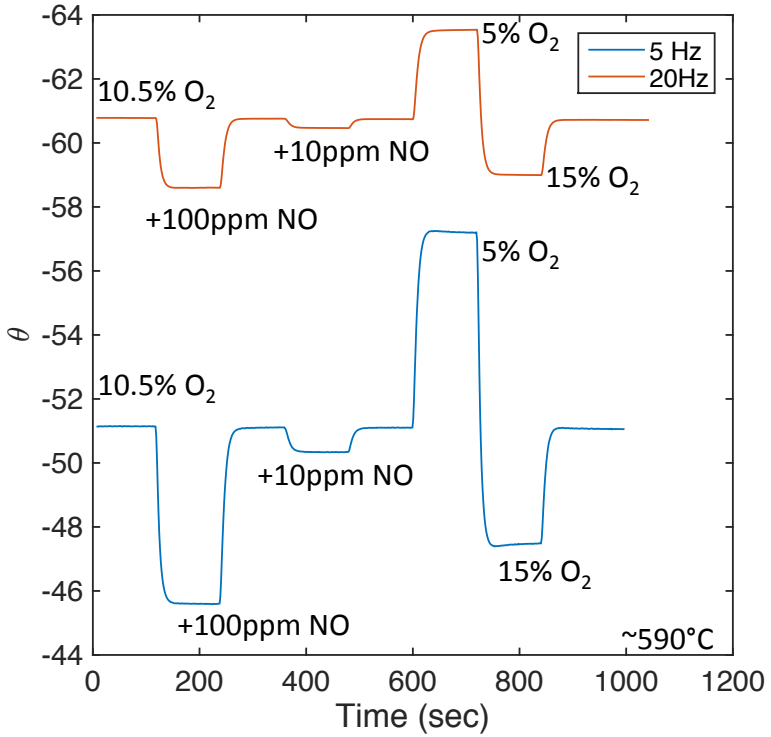


- Novel material interconnect developed to allow electrical contact between Au electrode and Pt lead

Verified performance of sensor designs using novel material interconnect solution

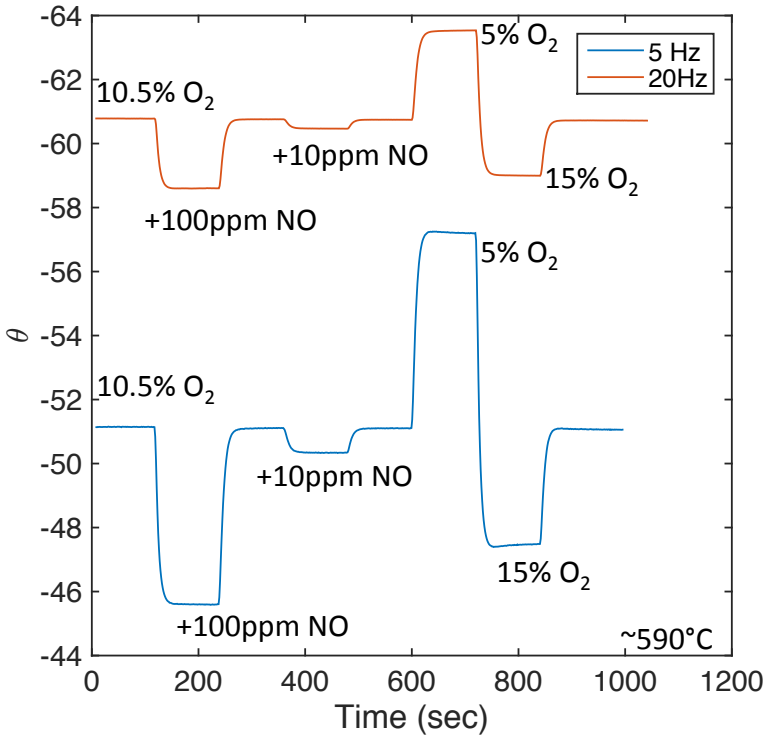
Au ribbon/YSZ/Al_2O_3



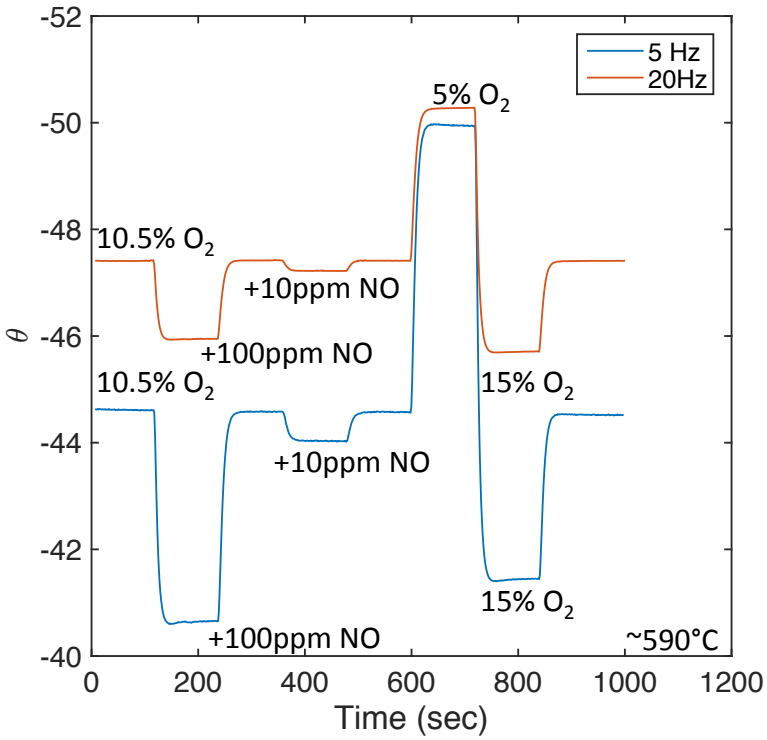


Replace Au ribbon electrode with Au paste for all screen-printed sensor prototype

Au ribbon/YSZ/Al_2O_3

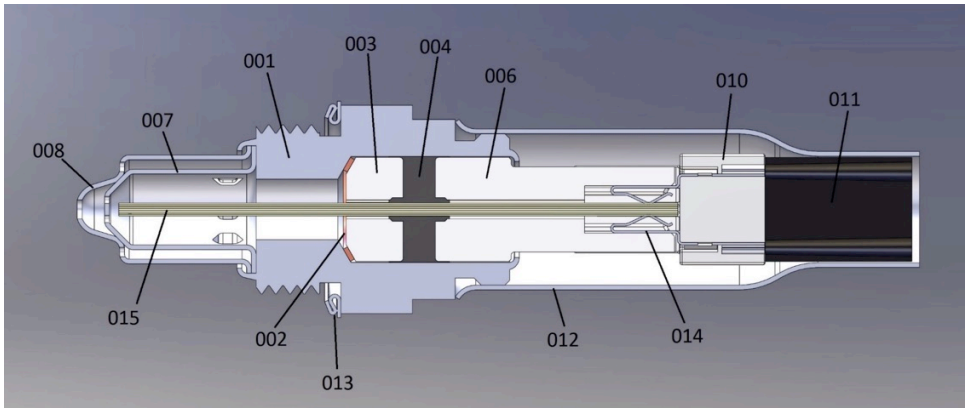


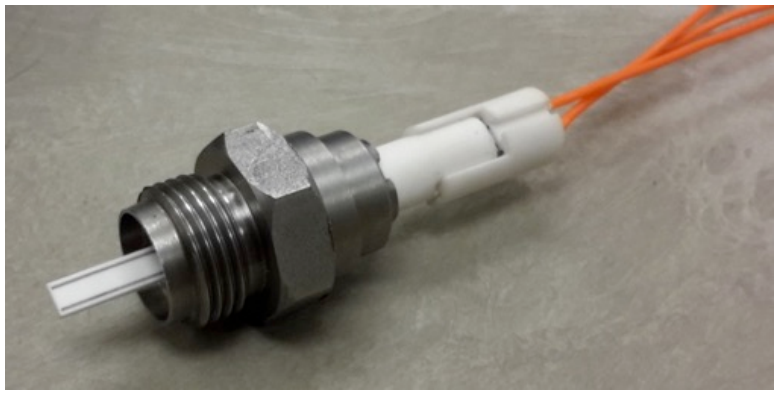
Au paste/YSZ/Al_2O_3



Development of packaging for operating NOx sensor prototypes with Al_2O_3 heaters

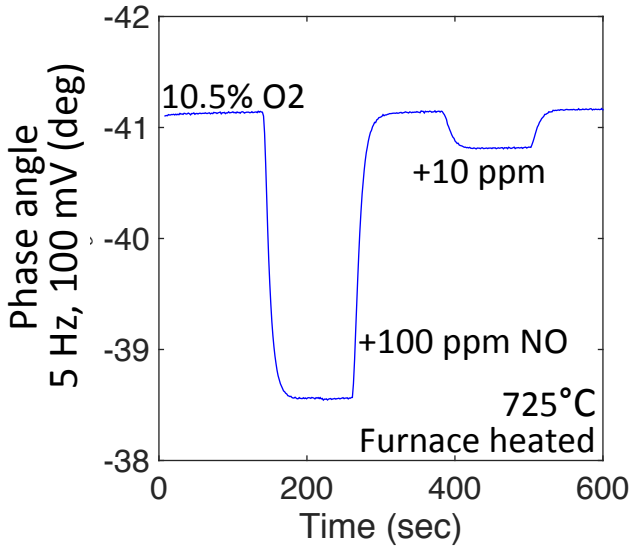
- Concept design to understand role of:
  - Venturi tip
  - Crushable gas seal
  - Electrical connection



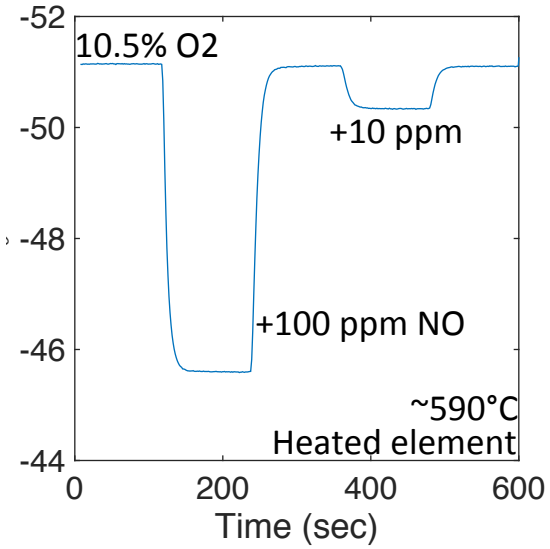


Maintaining sensor performance as designs evolve towards more deployable prototype

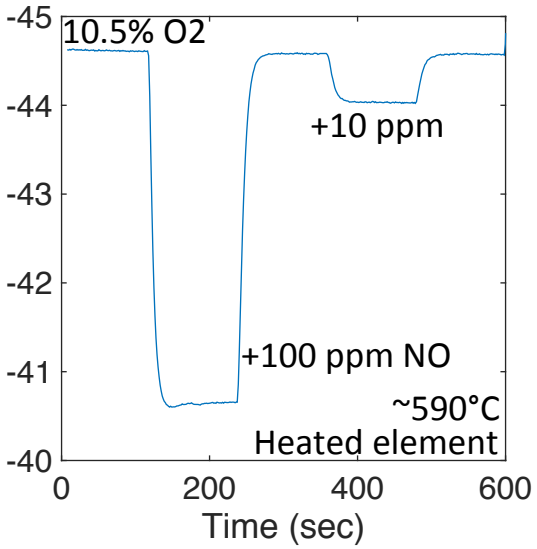
Cofired constrained Au ribbon/porous YSZ



Cofired Au ribbon/YSZ/Al_2O_3



Cofired Au paste/YSZ/Al_2O_3



Next steps

- Improving shrinkage match to reduce bowing
- Optimizing novel interconnect material solution
- Re-evaluating aging/drift and sensitivity to NO_2, H_2O, and NH_3 in more advanced designs to compare with previous data from earlier designs
- Modifying electronics for compatibility with more advanced designs
- Continuing to improve Al_2O_3 heater operation and develop packaging

Summary

- Novel single-cell ‘impedancemetric’ sensor
  - Wave distortion from applied oscillating signal – digital voltage-current time differential
  - Potential for lower cost and better performance
- System integration of NOx sensor designs with Al_2O_3 heater for more deployable prototypes
  - Constrained gold electrodes suitable for cofiring with Al_2O_3 for easier processing and improved robustness
  - Good bonding of calcined YSZ to Al_2O_3
  - Novel material interconnect solution for Au and Pt
  - All screen-printed design and packaging development

Questions? Thank you for you attention! lw@emisense.com