Compact Potentiometric NO_x Sensor

Dileep Singh
Nuclear Energy Division
May 10, 2011

coworkers:
K. Pappacena, J.L. Routbort
P. Dutta, J. Spirig, and J. C. Yang (Ohio State University)

Vehicle Technologies – Annual Review

Project ID - pm023

Sponsored by ***Propulsion Systems Materials***

Overview

Timeline

- Project start FY08
- Project end FY12
- 75% complete

Budget

- FY09 = $200 K (DOE)
- FY10 = $150 K (DOE)
- FY11 = $101 K* (DOE)

*Continuing resolution, funds received

Barriers

- Critical need for low-cost high temperature sensors to monitor combustion gases (NO_x, O_2, CO, CO_2) for an internal combustion engine to optimize the combustion process (maximize fuel efficiency) and minimize pollutants

⇒ accurate, real-time, and cost-effective monitoring
⇒ sensing at close proximity to the combustion process for accurate monitoring
⇒ require internal reference gas, thus eliminating the need for pumping an external reference gas
⇒ need a sensor package that is durable and can withstand repeated high temperature cycling

Partners

- Marathon Sensors
- McDaniel Ceramics
- Integrated Fuel Technology

This project complements the overall goal for fuel efficiency for vehicle combustion systems

Relevance

- Optimum operation of vehicle combustion system *will increase fuel efficiency and reduce emissions,* both are high priority goals for the vehicle technology program
- Efficiency of the combustion process can be monitored by the make-up of the combustion exhaust gases (O_2, NO_x, CO, CO_2)
- Most state-of the-art gas sensors require external reference gas source and are expensive
- Compact NO_x sensor (or multiple sensing capability) with an internal reference can be placed close to the combustion process and will provide more rapid and accurate information of the gas compositional make-up
- Need for a compact, reliable, inexpensive NO_x sensor technology that is amenable for mass production

Objectives

- Modify and develop the compact oxygen sensor design to sense NO_x concentrations at ppm levels
- Fabricate compact NO_x sensor package using the plastic deformation joining technology; optimize joining conditions, electrode formulations, sensing materials
- Test the fabricated sensors for sensitivity, selectivity, stability, cross interference from other gases, etc. In addition, explore options for expanding the sensing capabilities to other combustion gases
- Develop ceramic electrode formulations that can be directly joined to sensor housing and obviate the need for platinum electrode to produce a robust sensor
- In collaboration with an industrial partner, demonstrate the sensor performance in an actual combustion environment and transfer technology to an OEM or the end user

Approach

- First develop a high-temperature oxygen sensor and subsequently modify it to sense NO_x concurrently
- Sensor design is based on relatively simple and well-known electrochemical principles. It is a closed end device made from oxygen ion conducting partially stabilized zirconia ceramic (YSZ). At elevated temperatures, differences in oxygen partial pressures across the ceramic produces a voltage that can be measured by attaching electrodes
- Develop high temperature plastic joining technology to join the YSZ sensor components & ceramic electrode to produce a leak–proof package. This allows creating a known internal reference gas atmosphere at the measuring temperatures
- Using appropriate filter(s) and sensing materials, modify the oxygen sensor such that NO_x concentrations are measured
- Conduct extensive tests to validate the performance of the sensor

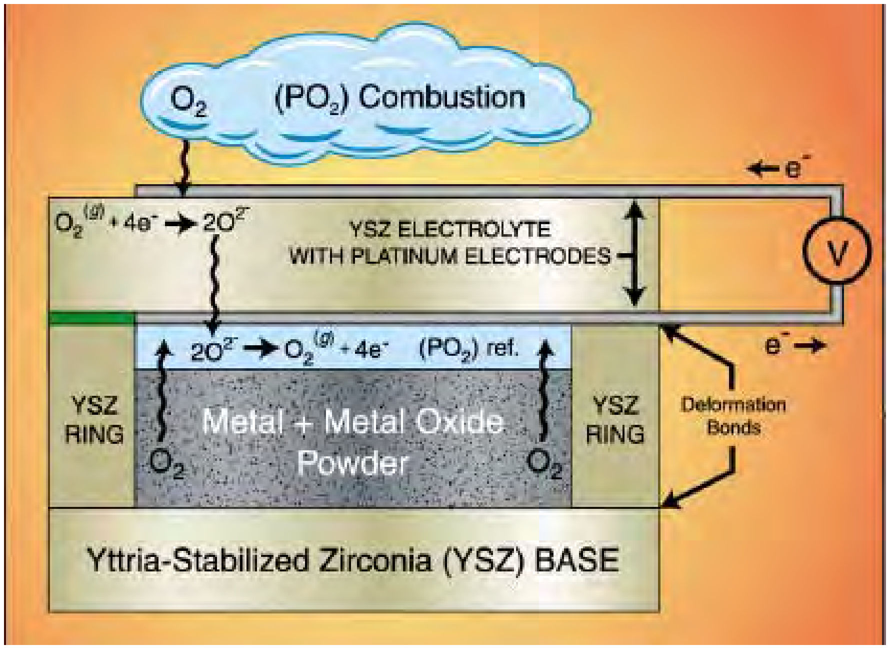
Milestones

- FY10
  - Develop high-temperature electrically conducting ceramic electrode material to replace expensive Pt (completed)
  - Demonstrate electrical properties of the ceramic electrode (completed)
  - Conduct preliminary deformation studies on the ceramic electrode material to identify the optimum compositions (completed)

- FY11
  - Develop optimum composition of the ceramic electrode for the sensor package
  - Demonstrate joining of ceramic electrode to sensor package material (YSZ)
  - Incorporate ceramic electrode in the sensor package and evaluate preliminary sensor performance
  - Initiate collaborations with industry

Accomplishments

Basic Package Design to Sense O_2



- At T>450°C, a specific oxygen partial pressure $(pO_2)^{int.}$ from M+MO is generated within the sensor package.

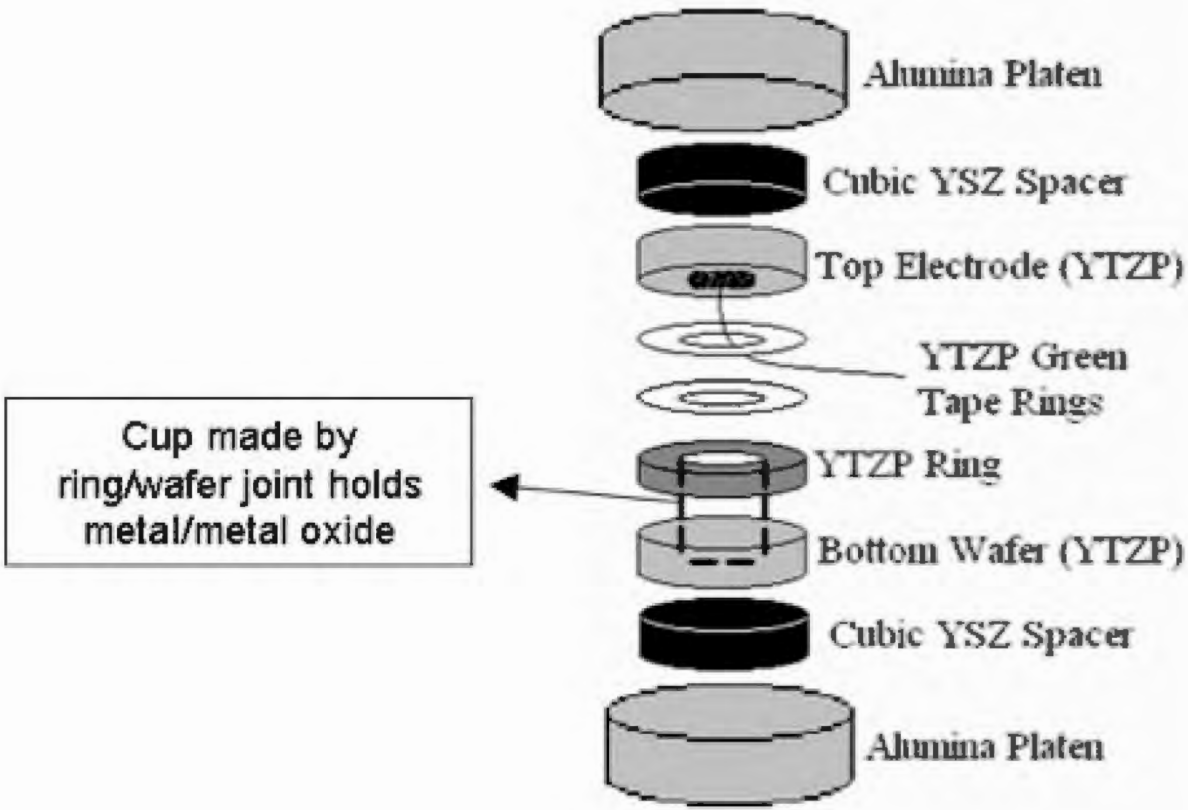
- Because of the difference in the oxygen partial pressures between combustion environment, $(pO_2)^{combustion}$, and $(pO_2)^{int.}$ a voltage, E, as give by the equation below, is generated across the YSZ electrolyte:

R = gas constant
T = absolute temperature
F = Faraday’s constant

Knowing the temperature, metal/metal oxide mixture, and voltage, oxygen concentration in combustion environment can be determined

Accomplishments

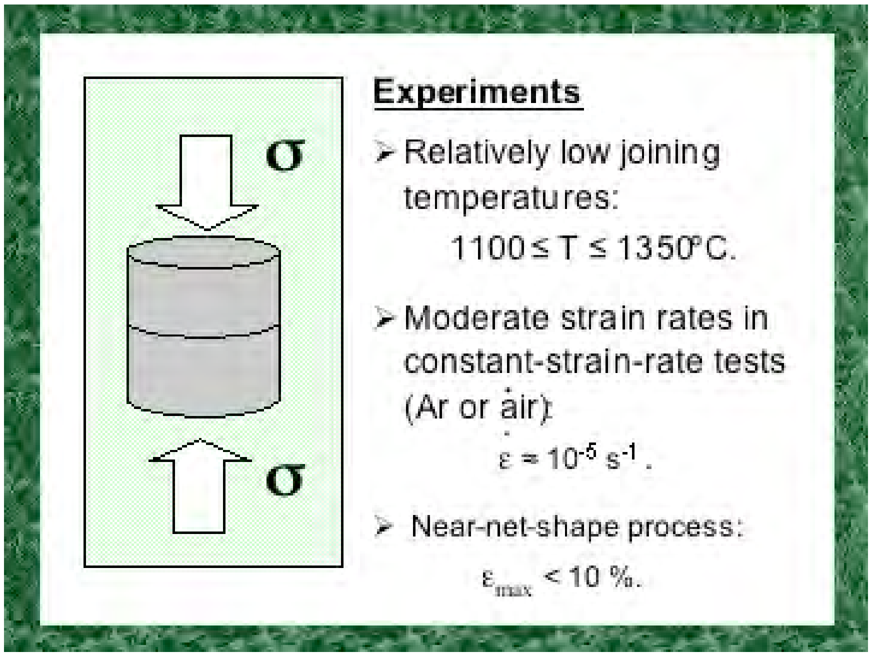
Components of Basic Sensor Package

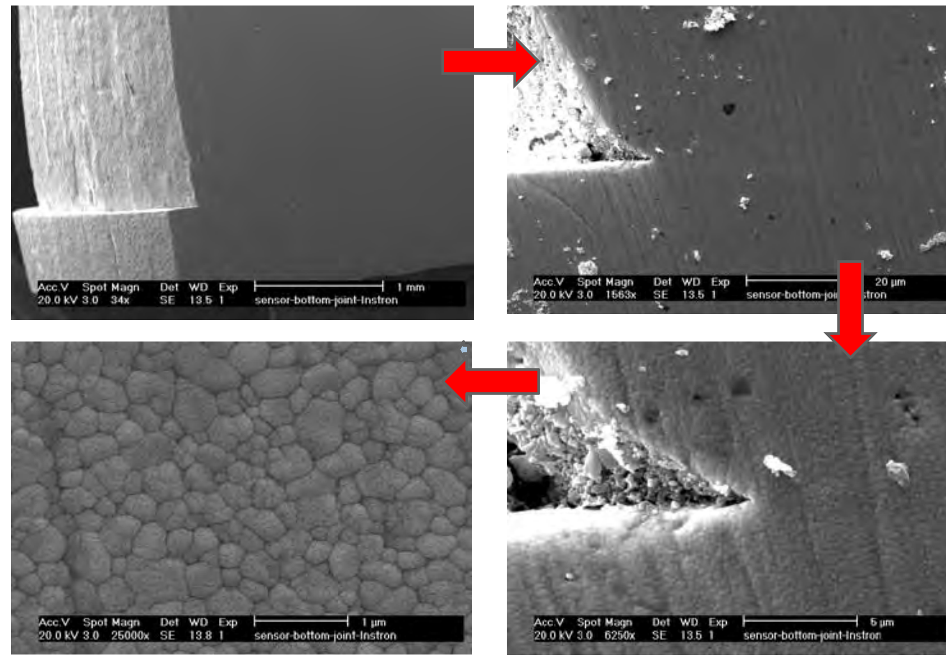


Sensor components are stacked and joined in a one-step process

Accomplishments

Joining of Sensor Package YSZ Components

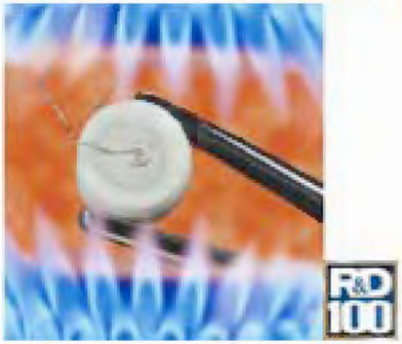




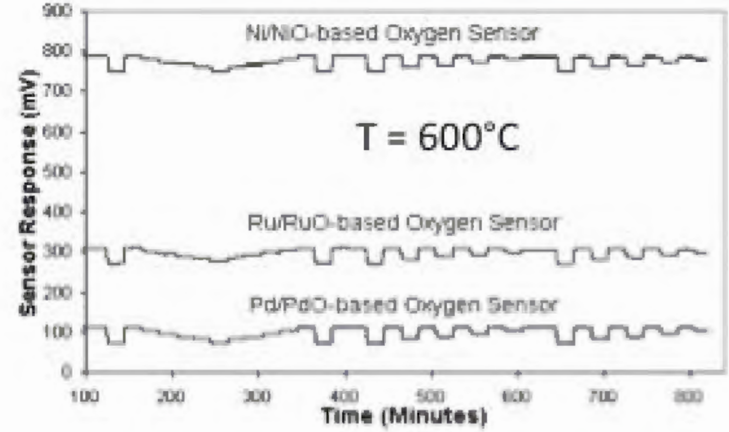
Scanning electron microscopy images of the joint interface shows no porosity; air-tight durable seal

Accomplishments

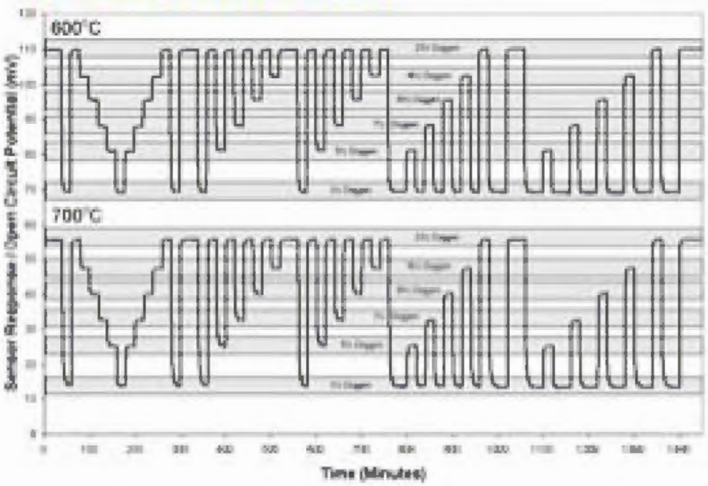
Performance of the Oxygen Sensor



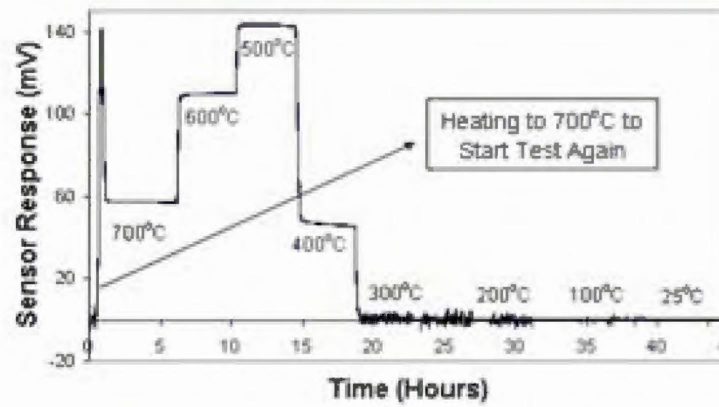
Fabricated Sensor



Output signal for various metal/metal oxide mixtures



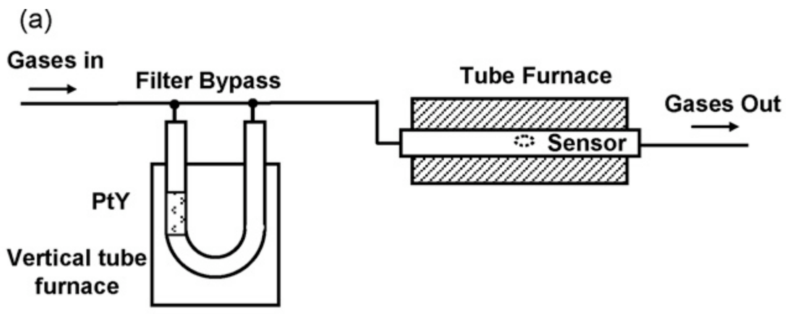
High sensitivity and fast response time



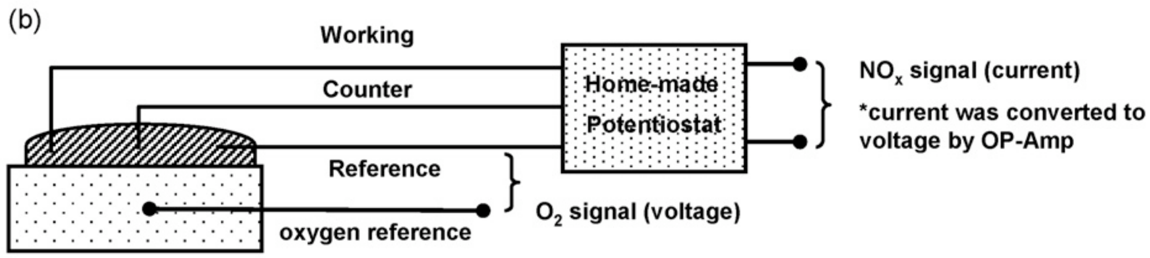
Sensor performance repeatable, trace of four runs overlapping

Accomplishments

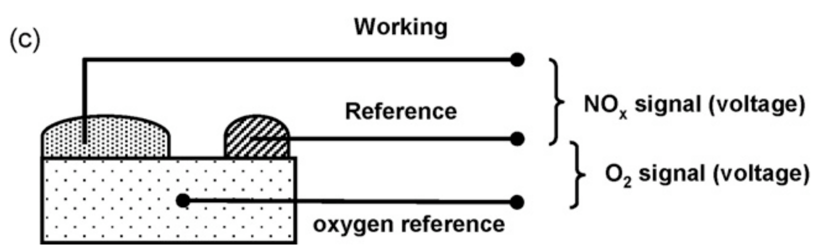
NO_x Sensor Test Set-up



Pt-Y filter equilibrates the gas and allows measurement of total NO_x



(b) Amperometric mode

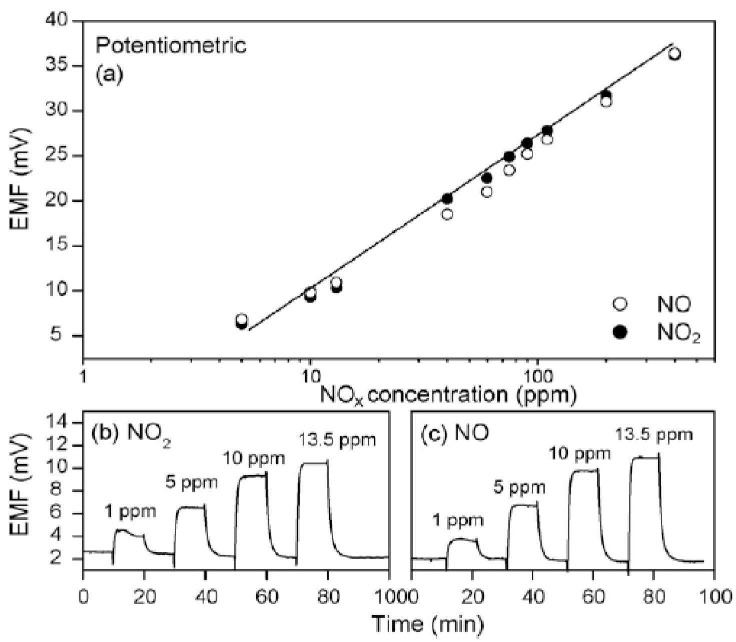


(c) Potentiometric mode

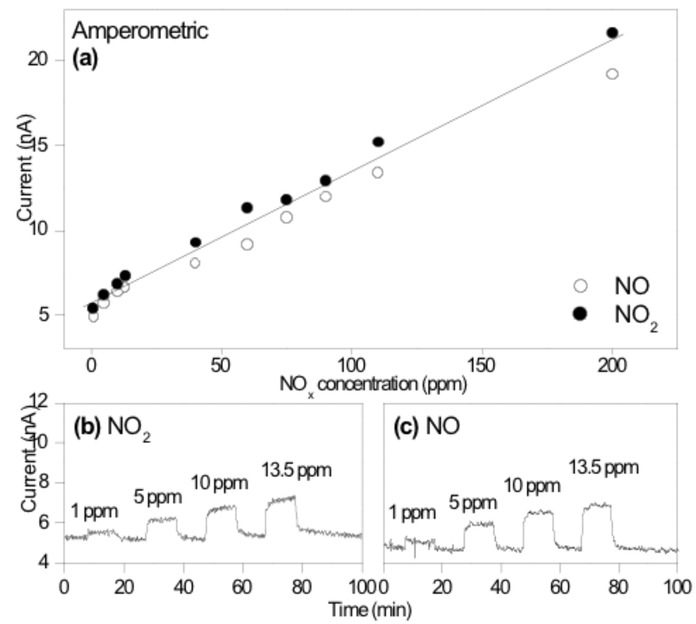
Accomplishments

Sensitivity of the Sensor to NO_x

Potentiometric Mode



Amperometric Mode



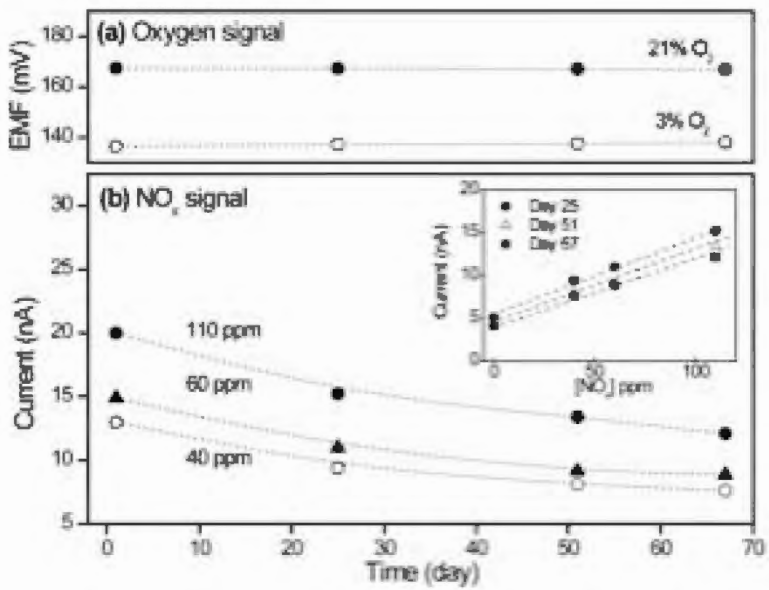
Test Temperature = 600 ℃, Filter Temperature = 400 ℃

O_2 level 3% in gas

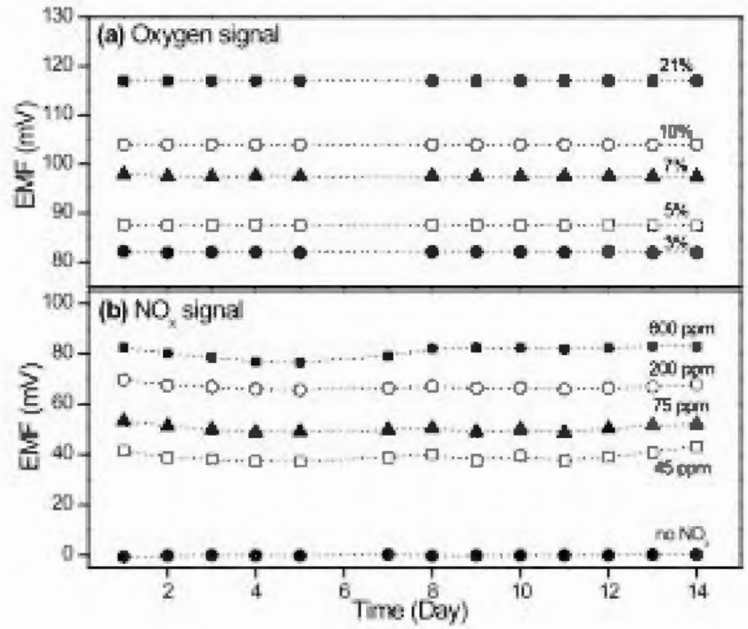
Response transients for 1-13.5 ppm of NO and NO_2

Accomplishments

Long Term NO_x Sensor Performance



Amperometric Mode



Potentiometric Mode

Accomplishments

$La_{0.8}Sr_{0.2}Al_xMn_{(1-x)}O_3$: Electrode material

Al added to prevent reaction of the electrode material to zirconia

Mix powders in proper proportions (x=0, 0.3, 0.5)

↓

Calcination:
1000°C for 4 hours,
1200°C for 50 hours

↓

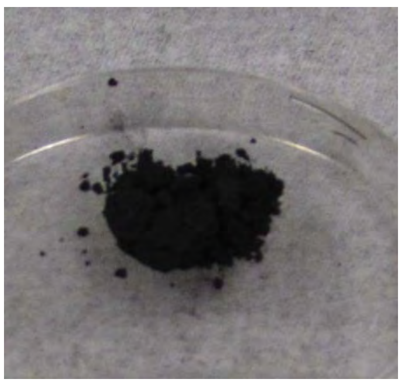
Reduce particle size:
Sieve or planetary mill

↓

Press pellets

↓

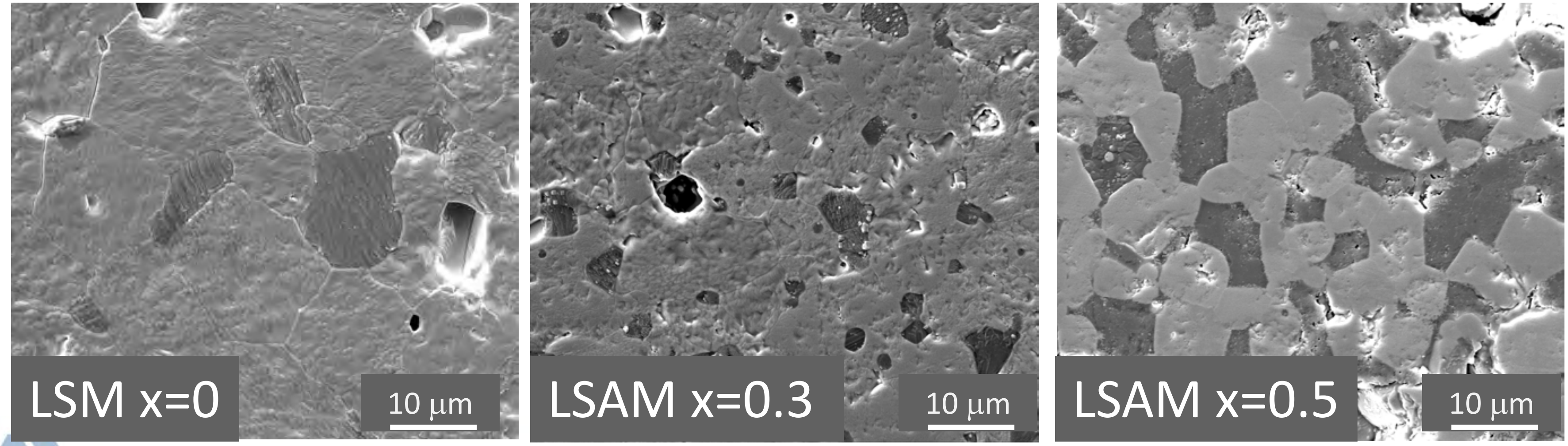
Sinter:
1450°C for 50 hours



Accomplishments

LSAM - SEM Analysis

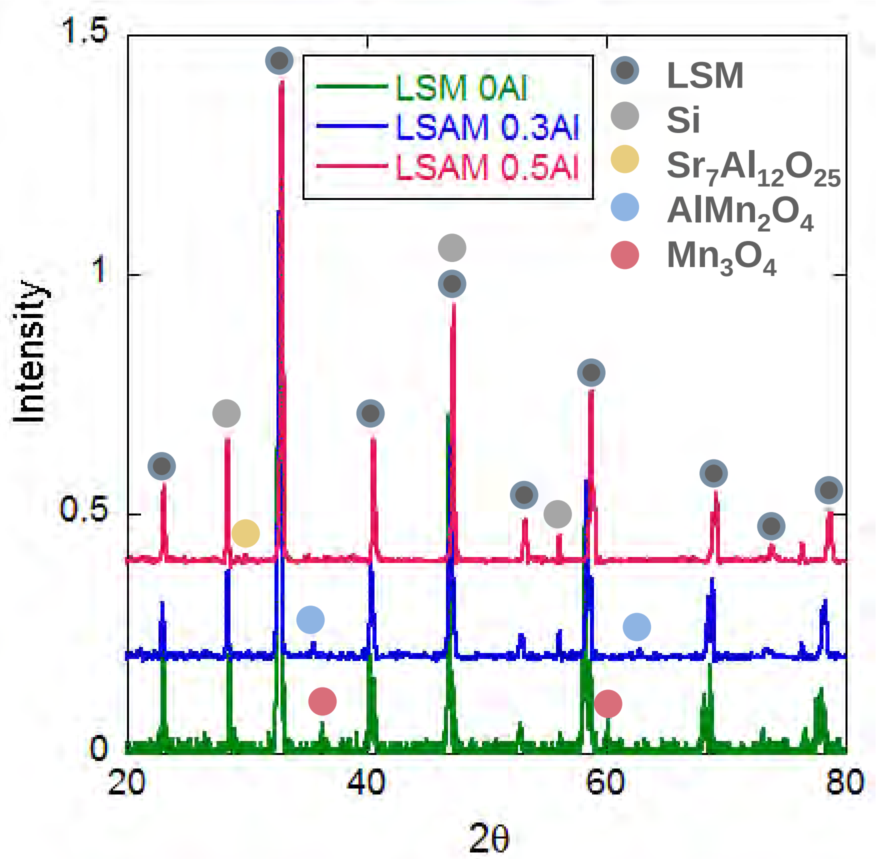
- SEM images with EDS indicate phase segregation in darker grains
  - LSM- Mn_3O_4 segregation, grain size 7.4 μm, open porosity 1.5%
  - LSAM 0.3Al- Al_2MnO_4 segregation, grain size 4.7 μm, open porosity 0.97%
  - LSAM 0.5Al- $Al_7Sr_{12}O$ segregation, grain size 5.3 μm, open porosity 1.3%



Accomplishments

LSAM - X-Ray Diffraction

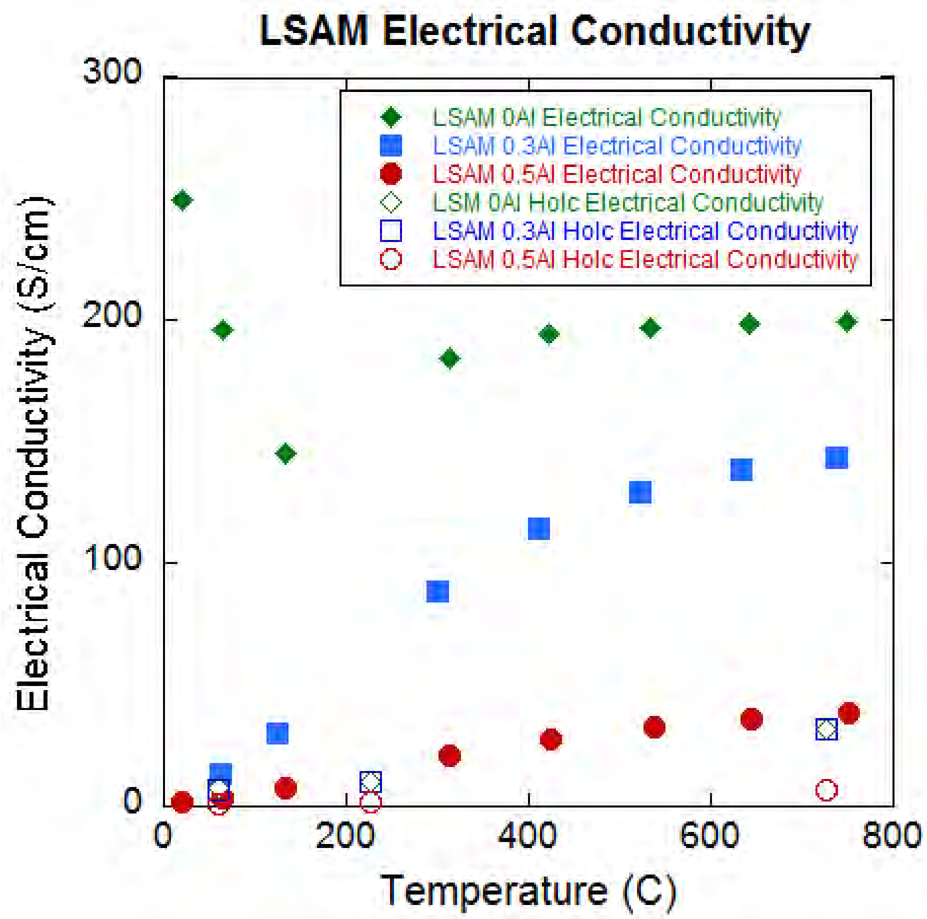
- X-Ray diffraction indicates peak shifts toward the right for increasing Al content
- Second phases seen with EDS are confirmed with x-ray diffraction
  - Mn_3O_4 peaks in x=0
  - Al_2MnO_4 peaks in x=0.3
  - $Sr_7Al_{12}O_{25}$ peaks in x=0.5



Accomplishments

LSAM - Electrical Conductivity

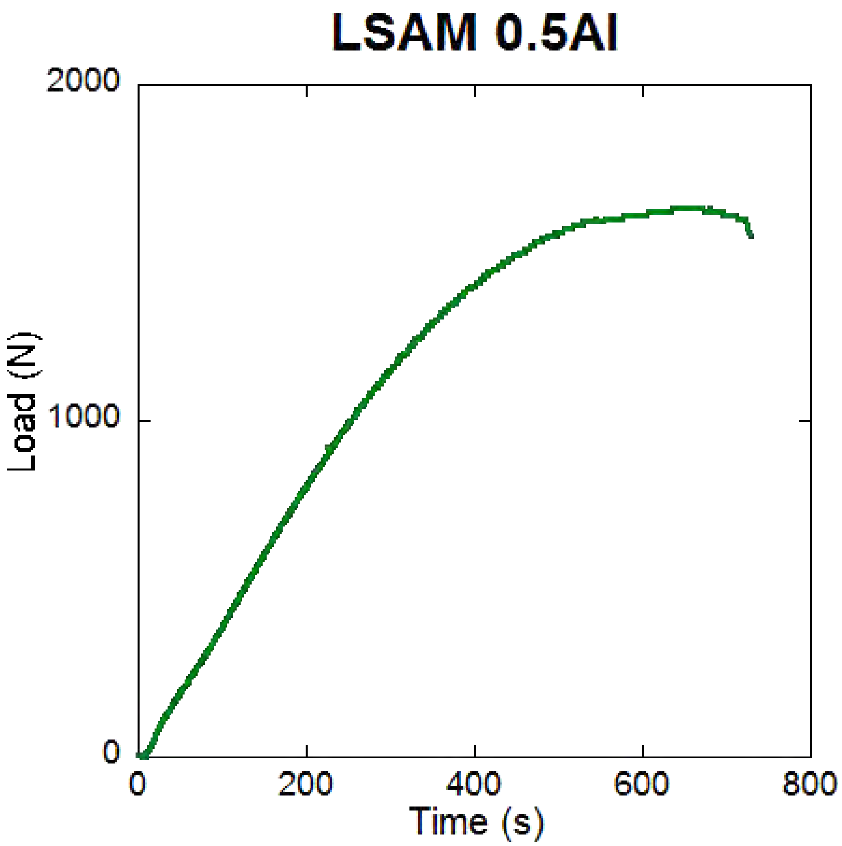
- Electrical conductivity (σ) determined
- σ increases with T
  - Known LSM discontinuity at 100°C
- Increasing Al content decreases σ
  - Not a large decrease between x=0 and 0.3
- Values improved over literature results



Accomplishments

LSAM - Deformation Testing

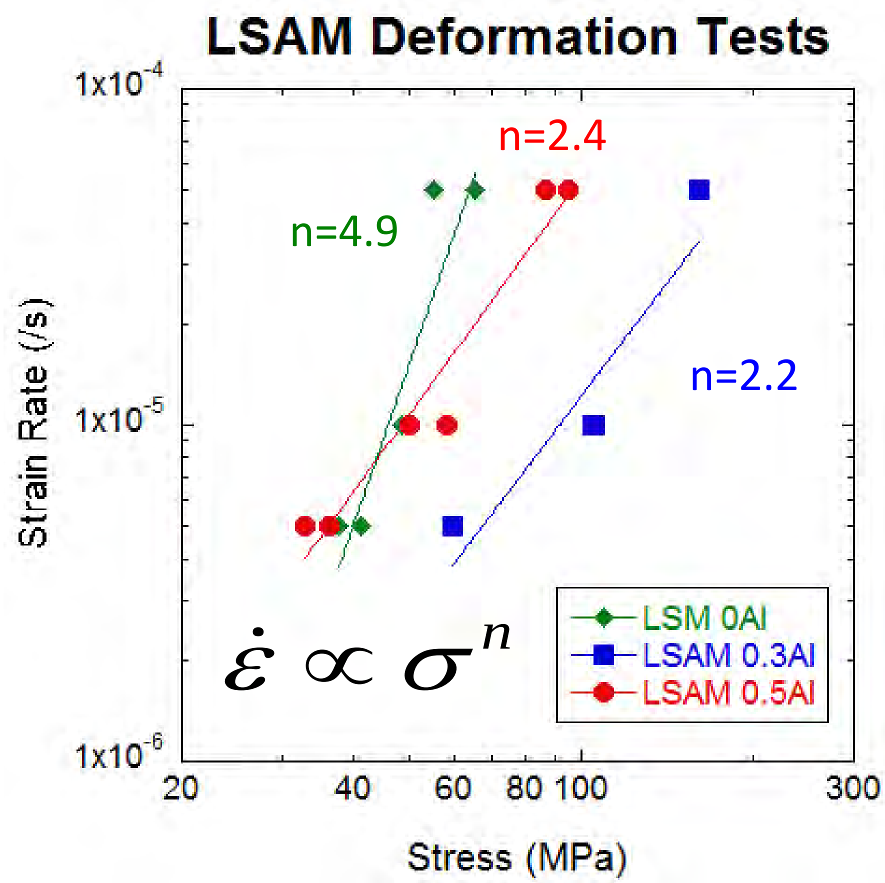
- Deformation testing performed
  - Test temperature: 1270°C
  - Compositions: x=0, 0.3, 0.5
  - Strain rates (ε): $5x10^{-6}/s$, $1x10^{-5}/s$, $5x10^{-5}/s$
- Flow stress (σ_f) determined in plateau region on the load-time curve



Accomplishments

LSAM - Deformation Testing

- Strain rate plotted versus flow stress
  - σ increases with increasing ε
  - σ increases with increasing Al content
- Stress exponent (n) determined
  - $n_{x=0.3,\ 0.5}$ agree with diffusion mechanism values (n=1-2)
  - $n_{x=0}$ much higher, larger grain size
- Flow stresses at $\varepsilon = 5x10^{-5}$/s
  - LSAM 0.3Al: 160 MPa
  - LSAM 0.5Al: 91 MPa
  - YSZ : <40 Mpa



Similar flow stress regime indicates potential ability of LSAM 0.5 Al for deformation joining to YSZ

Path Forward

- Optimize the ceramics electrode properties, including electrical properties and joining characteristics with YSZ
- Include the ceramic electrode in the sensor package design and fabricate a sensor
  - characterize the sensor performance
  - establish durability of the sensor
- Develop strategies to include CO and CO_2 sensing on the current sensor platform
- Develop partnerships with OEMs for technology demonstration and eventual transfer of technology

Collaborations

- General Electric – sent oxygen sensors for evaluation
- Marathon Sensors – contacted ANL for a possible licensing agreement
- Integrated Fuel Technology – contacted ANL for a licensing agreement
- Honeywell International – expressed interest in the technology

Conclusions

- Based on YSZ ceramic, a basic sensor package design developed
- Using the the sensor package design, an oxygen sensor with an internal reference developed and demonstrated
- Modifications made to the basic oxygen sensor design to sense NO_x
- Performance of NOx sensing has shown excellent sensitivity, resolution and long-term performance
- LSAM based electrode formulations developed and evaluated for electrical and deformation properties; optimum composition identified