Compact Potentiometric O_2/NO_x Sensor

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Vehicle Technologies – Annual Review

Project ID - pm043

Sponsored by ***Propulsion Systems Materials***

Overview

Timeline

- Project start FY08
- Project end FY12
- 95% complete

Budget

- Project funding– FY08-11: $830K (DOE)
- FY12-60K (DOE)
- FY08-11: 2 Ph.D. students (OSU)

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
⇒internal reference gas, eliminates the need for pumping an external reference gas
⇒ need a sensor package that is durable and can withstand repeated high temperature cycling

Partners

- Ohio State University

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 that require expensive external plumbing
- 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, robust, inexpensive bifunctional 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.
- Test joints formed by plasticity for strength and fracture toughness
- Develop ceramic electrode formulations that can be directly joined to sensor housing and obviate the need for platinum electrode to produce a robust sensor
- Patent invention so that we can interest potential industrial users.

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 robust, 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 (completed)
  - Demonstrate joining of ceramic electrode to sensor package material (YSZ) (completed)

- FY12
  - Initiate industrial interactions

Accomplishments joining technique

(12) **United States Patent**
Routbort et al.

(10) **Patent No.:** **US 7,722,731 B2**
(45) **Date of Patent:** **May 25, 2010**

(54) **JOINING OF ADVANCED MATERIALS BY PLASTIC DEFORMATION**

(75) Inventors: **Jules L. Routbort**, Naperville, IL (US); **Dileep Singh**, Naperville, IL (US); **Kenneth C. Goretta**, Tokyo (JP); **Felipe Gutierrez-Mora**, Seville (ES)

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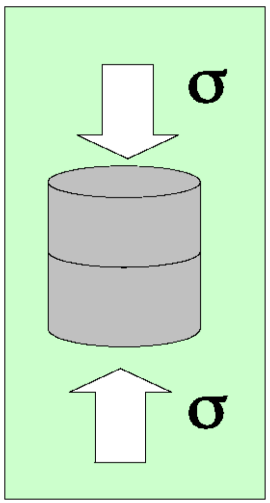


Experiments

- Relatively low joining temperatures:

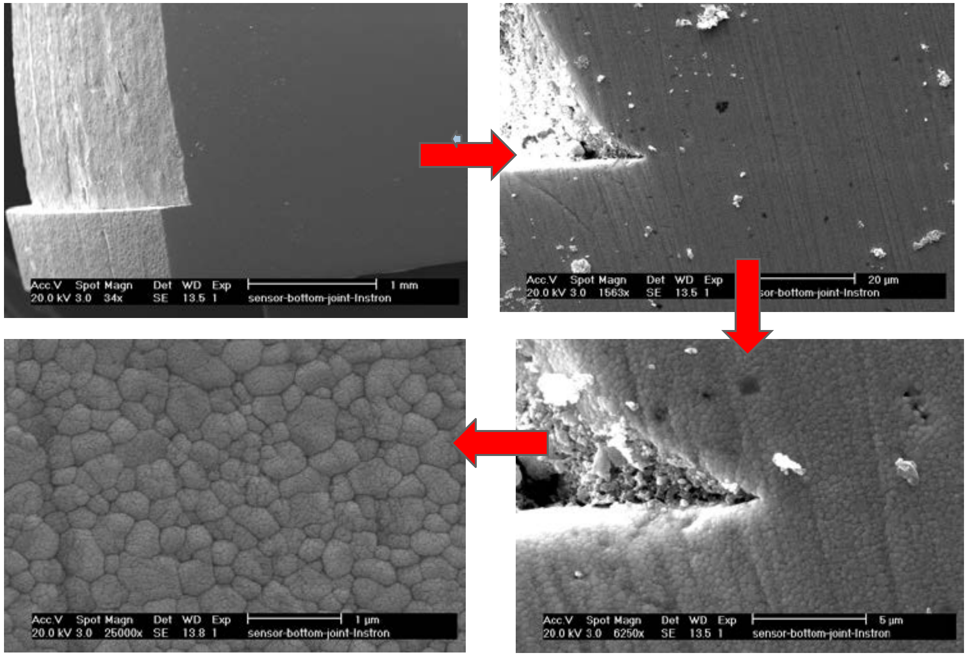
  $1100 \leq T \leq 1350°C$.

- Moderate strain rates in constant-strain-rate tests (Ar or air):

  $\dot{\varepsilon} \approx 10^{-5}\ s^{-1}$.

- Near-net-shape process:

  $\varepsilon_{max} < 10\ \%$.



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

Accomplishments oxygen sensor

(12) **United States Patent**
Routbort et al.

(10) **Patent No.: US 8,057,652 B2**
(45) **Date of Patent: Nov. 15, 2011**

(54) **HIGH-TEMPERATURE POTENTIOMETRIC OXYGEN SENSOR WITH INTERNAL REFERENCE**

(75) Inventors: **Jules L. Routbort**, Hinsdale, IL (US); **Dileep Singh**, Naperville, IL (US); **Prabir K. Dutta**, Worthington, OH (US); **Ramamoorthy Ramasamy**, North Royalton, OH (US); **John V. Spirig**, Columbus, OH (US); **Sheikh Akbar**, Hilliard, OH (US)

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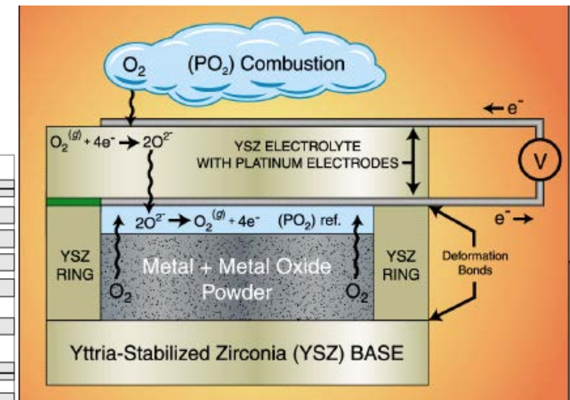
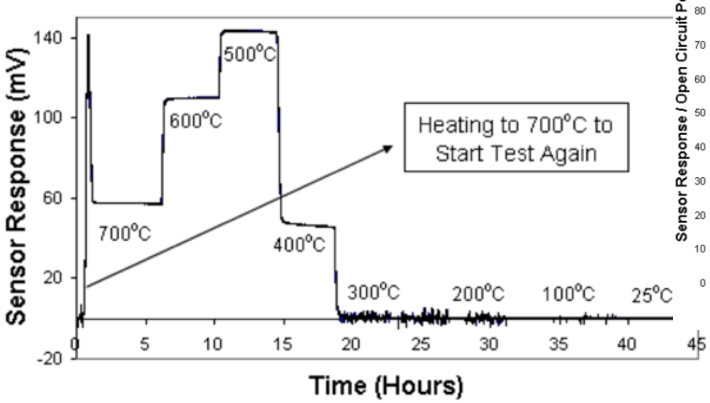
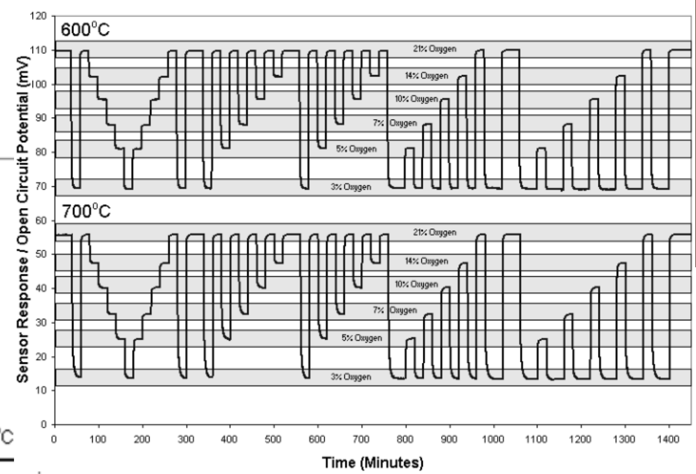


High sensitivity and fast response time





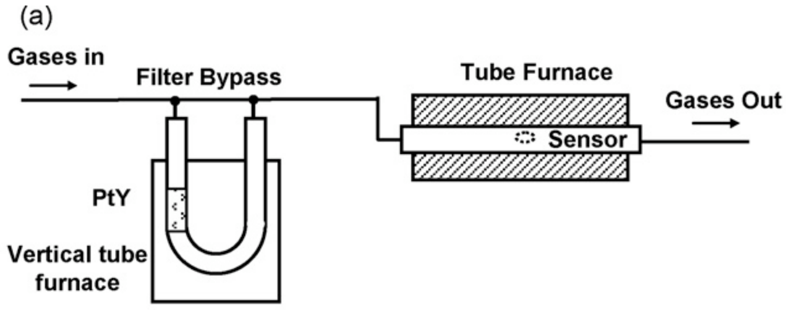
$$E = \frac{RT}{4F} \ln \frac{(PO_2)^{combustion}}{(PO_2)^{int.}}$$

Sensor performance repeatable

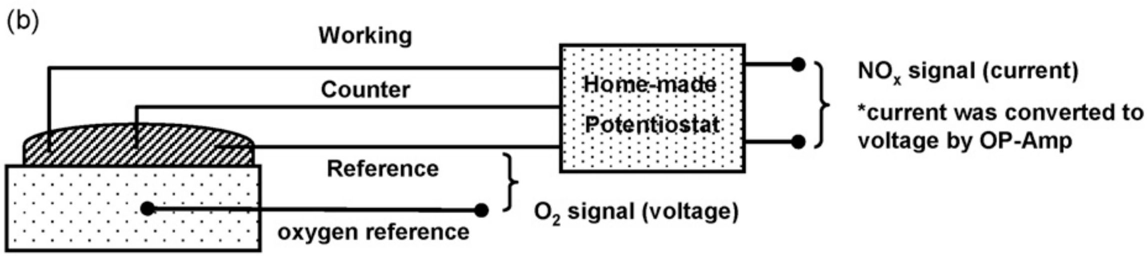
Sensor components are stacked and joined in a one-step process

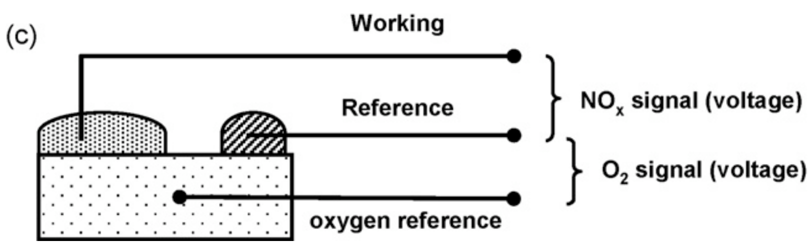
Accomplishments

NO_x Sensor Test Set-up



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





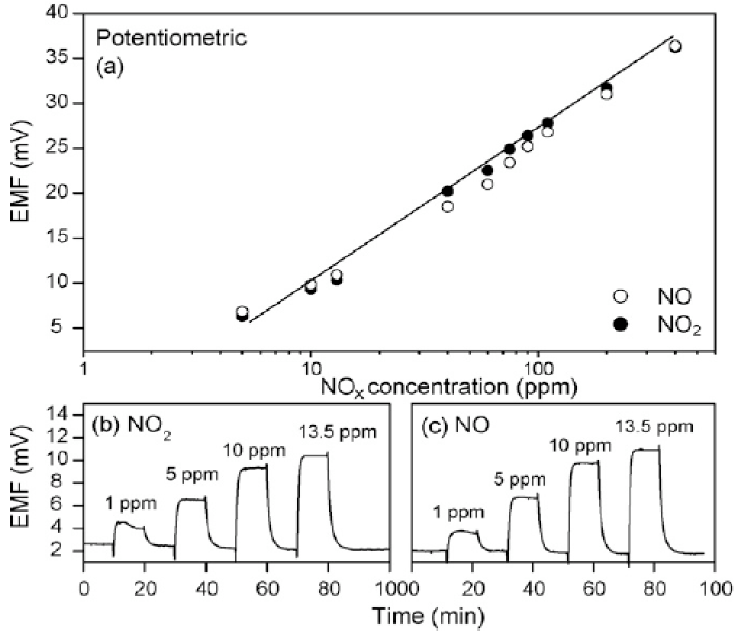
(b) Amperometric mode

(c) Potentiometric mode

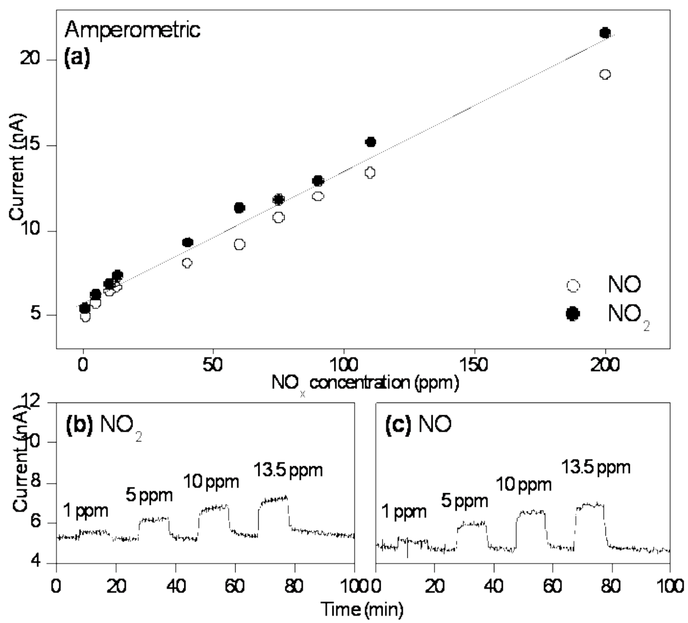
Accomplishments

Sensitivity of the Sensor to NO_x

Potentiometric Mode



Amperometric Mode



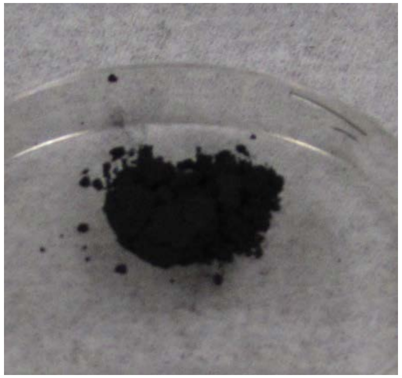
Test Temperature = 600°C, Filter Temperature = 400°C
O_2 level 3% in gas

Response transients for 1-13.5 ppm of NO and NO_2

Accomplishments

Replacing Pt with $La_{0.8}Sr_{0.2}Al_xMn_{(1-x)}O_3$: 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

↓

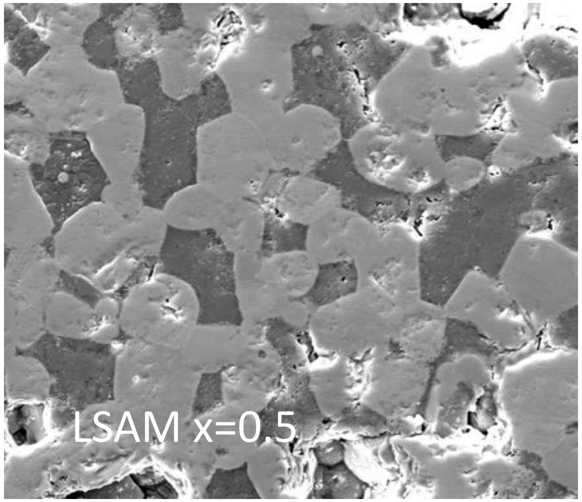
Reduce particle size:
Sieve or planetary mill

↓

Press pellets

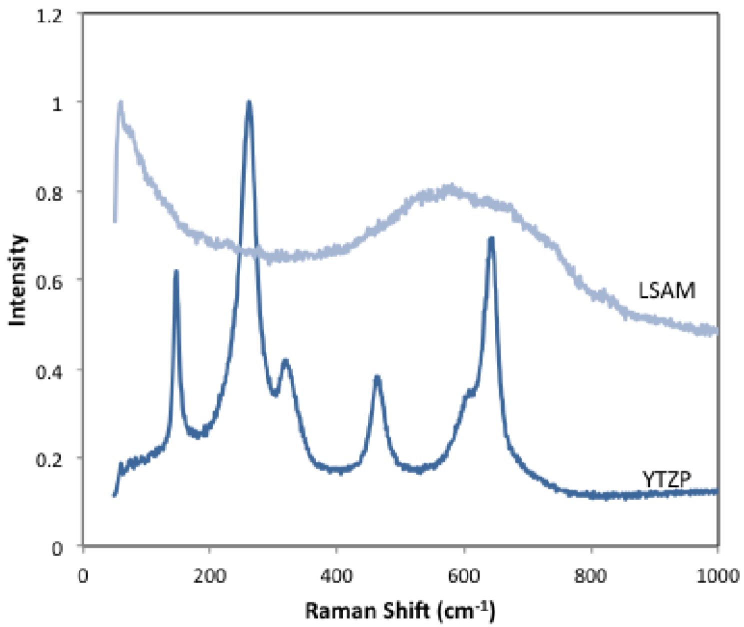
↓

Sinter:
1450°C for 50 hours

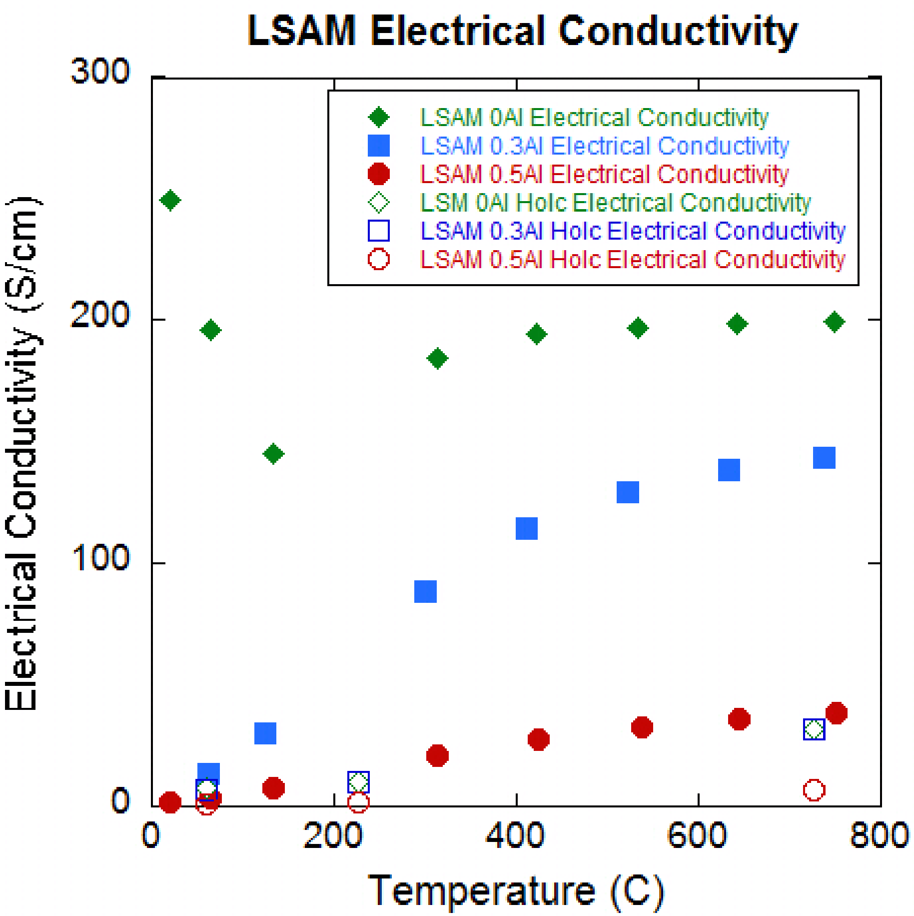


Accomplishments

Optimizing LSAM electrode



Typical Raman spectra

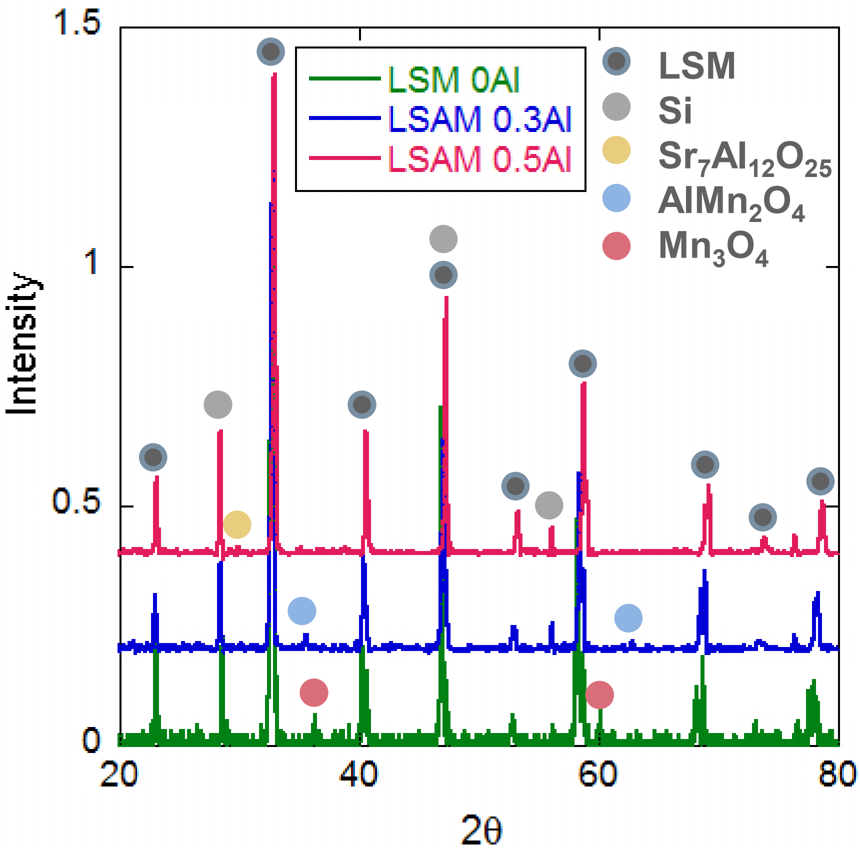


- σ increases with T
  Known LSM discontinuity at 100°C
- Increasing Al content decreases σ
  Not a large decrease between x=0 and 0.3
- Values improved over literature results

Accomplishments

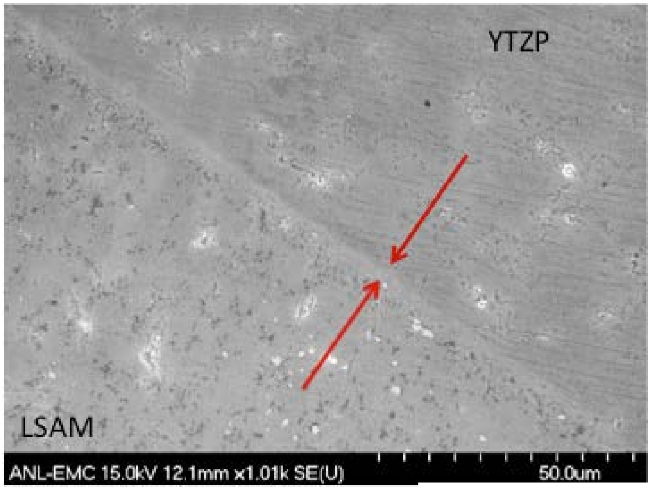
LSAM - X-Ray Diffraction

- 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



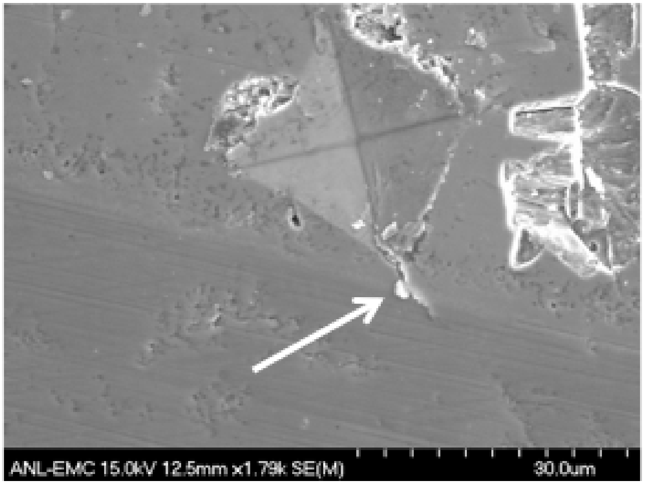
Accomplishments

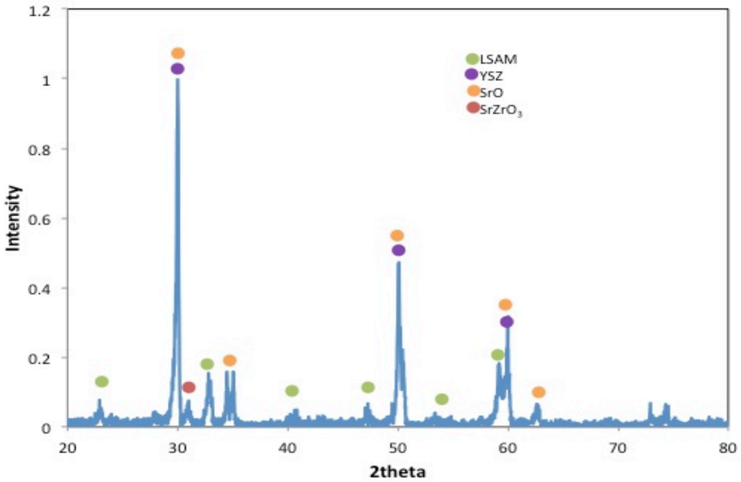
Joining LSAM to YTZP



Interface between LSAM/YTZP

Strength of joint indicated by transverse crack





XRD of interface

Accomplishments

Patent issued September 2011

(12) **United States Patent**
Singh et al.

(10) **Patent No.: US 8,012,323 B2**
(45) **Date of Patent: Sep. 6, 2011**

(54) **COMPACT ELECTROCHEMICAL BIFUNCTIONAL NO_x/O_2 SENSORS WITH INTERNAL REFERENCE FOR HIGH TEMPERATURE APPLICATIONS**

(75) Inventors: **Dileep Singh**, Naperville, IL (US); **Jules Routbort**, Hinsdale, IL (US); **Prabir Dutta**, Worthington, OH (US); **John V. Spirig**, North Brunswick, NJ (US); **Jiun Chan Yang**, Skokie, IL (US)

(73) Assignee: **UChicago Argonne, LLC**, Chicago, IL (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 386 days.

(21) Appl. No.: **12/402,216**

(22) Filed: **Mar. 11, 2009**

(65) **Prior Publication Data**

US 2009/0288961 A1 Nov. 26, 2009

Related U.S. Application Data

(60) Provisional application No. 61/035,962, filed on Mar. 12, 2008.

(51) **Int. Cl.**

G01N 27/26	(2006.01)
G01N 27/27	(2006.01)
G01N 27/407	(2006.01)
G01N 27/409	(2006.01)
G01N 27/417	(2006.01)
G01N 27/419	(2006.01)

(52) **U.S. Cl.** **204/424**; 204/425; 204/426; 204/427; 205/781; 205/782; 205/784; 205/784.5; 205/785.5

(58) **Field of Classification Search** 204/424, 204/425, 426, 427; 205/781, 782, 784, 784.5, 205/785.5

See application file for complete search history.

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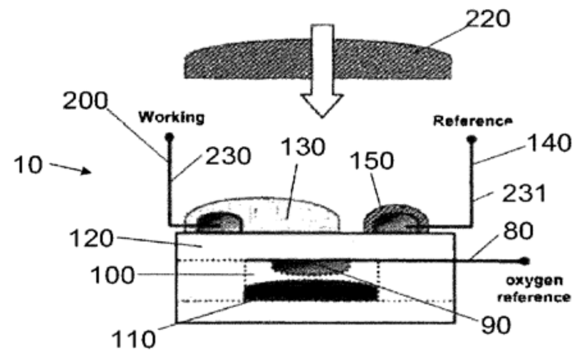
Primary Examiner — Bruce Bell
(74) *Attorney, Agent, or Firm* — Foley & Lardner LLP

(57) **ABSTRACT**

A bifunctional total NO_x and O_2 sensor assembly with an internal reference for high temperature sensing. Two electrochemical total $NO_x(NO+NO_2)$ measuring systems and method were coupled with a metal/metal oxide internal oxygen reference to detect O_2 and NO_x simultaneously in a combustion environment using a single sensor. A Pd/PdO-containing reference chamber was sealed within a stabilized zirconia superstructure by a high pressure/temperature bonding method. An amperometric and potentiometric NO_x sensor assembly was built on the outside of the Pd/PdO chamber. Pt-loaded zeolite Y was used to obtain total NO_x capacity and also to cover the Pt electrodes for detecting oxygen in the presence of NO_x.

20 Claims, 8 Drawing Sheets



Collaborations

- Ohio State University (2 Ph.Ds)
- 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

Path Forward

Project was very successfully <u>completed</u> and with 60K (FY2012) will attempt to develop partnerships with OEMs for technology demonstration and eventual transfer of 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 fabricated 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; optimum composition identified and joined to YTZP