Argonne NATIONAL LABORATORY
... for a brighter future

Compact Potentiometric NO_x Sensor

Dileep Singh
Nuclear Engineering Division
May 21, 2009

Coworkers:
J. Routbort (Argonne National Lab)
P. Dutta, J. Spirig, and J. C. yang (Ohio State University)

Project ID #
pmp_16_singh

Vehicle Technologies – Annual Review – May 18-22, 2009

Sponsored by ***Propulsion Systems Materials***

U.S. Department of Energy
UChicago Argonne LLC
A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

Timeline

- Project start FY08
- Project end FY12
- 20% complete

Budget

- Total project – $240 K
- FY08 = $40 K (DOE)
- FY09 = $200 K (DOE)

Barriers

- Critical need for 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 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 systems

Why a Need for a Compact NO_x Sensor with Internal Reference?

- Optimum operation of vehicle combustion system will increase fuel efficiency and control 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 sensors) 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

- Develop and modify 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
- 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

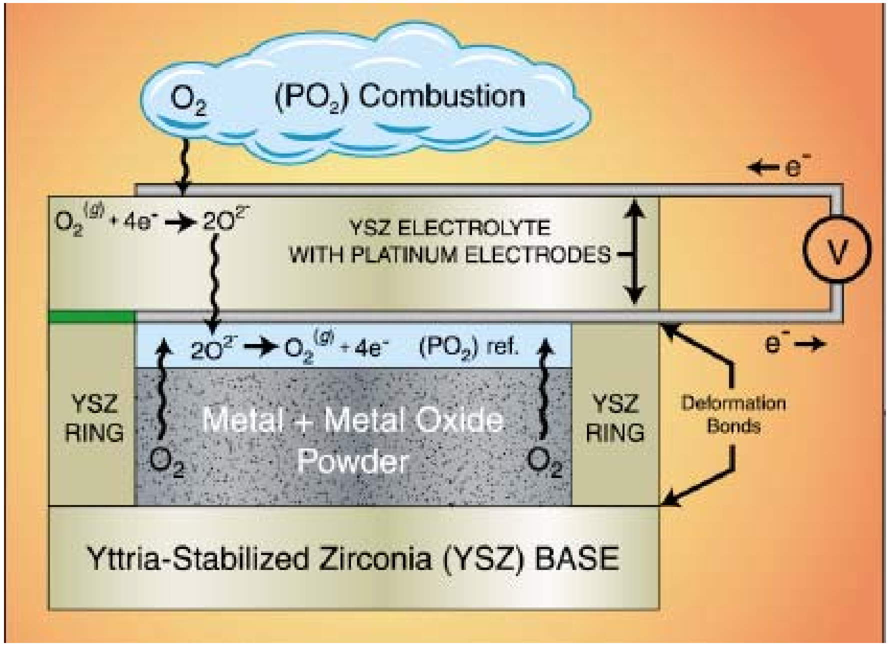
- First develop a high temperature oxygen sensor and subsequently modify it to sense NO_x and/or O_2 in combustion environments
- Sensor design is based on relatively simple and well-known electrochemical principles. It is a closed end device made from oxygen ion conducting partially stabilized zirconia 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 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

- FY09
  - Develop optimum joining conditions for sealing sensor package components
  - Demonstrate internal reference of the compact sensor and demonstrate it for O_2 sensing
  - Develop high temperature electrically conducting electrode material
  - Develop strategy to convert oxygen sensor to measure NOx
  - 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:

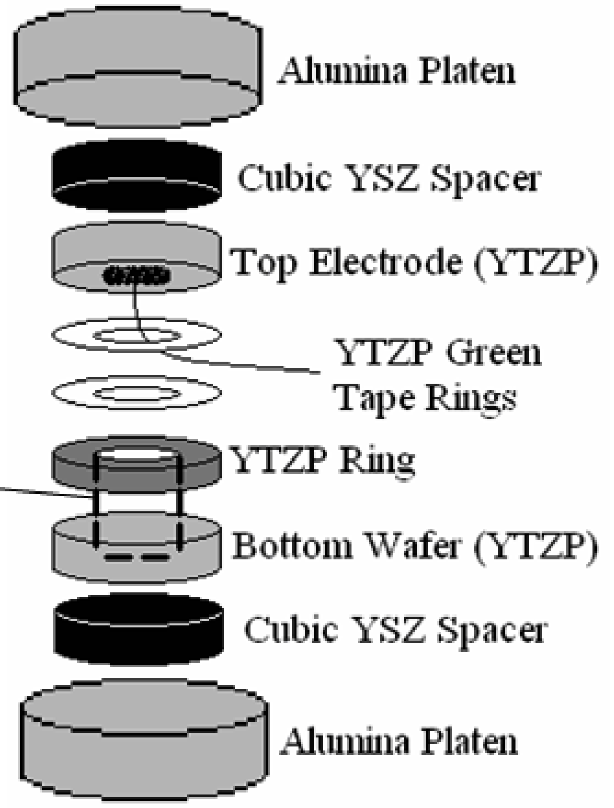
$$E = \frac{RT}{4F} \ln \frac{(PO_2)^{combustion}}{(PO_2)^{int.}}$$

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

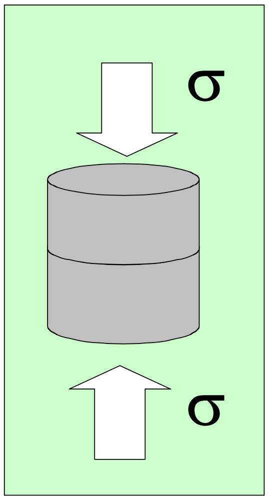


Cup made by ring/wafer joint holds metal/metal oxide

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

Accomplishments

Joining of Sensor Package YSZ Components



Experiments

- Relatively low joining temperatures:

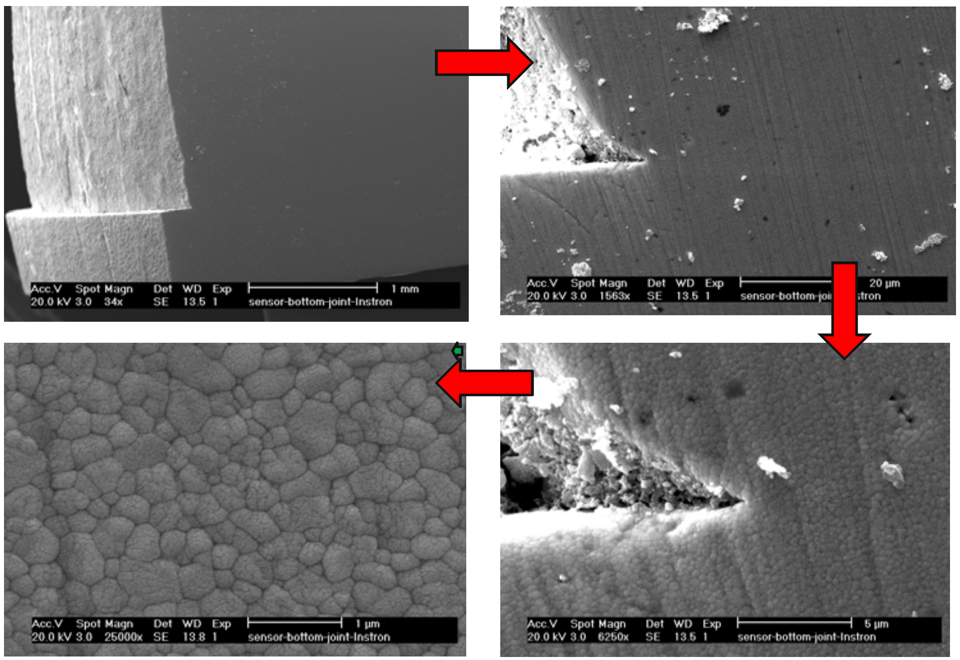
  $1100 \le T \le 1350$ °C.

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

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

- Near-net-shape process:

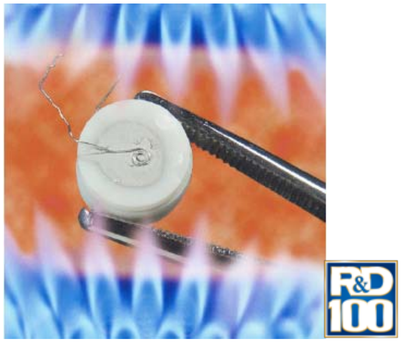
  $\varepsilon_{max} < 10$ %.



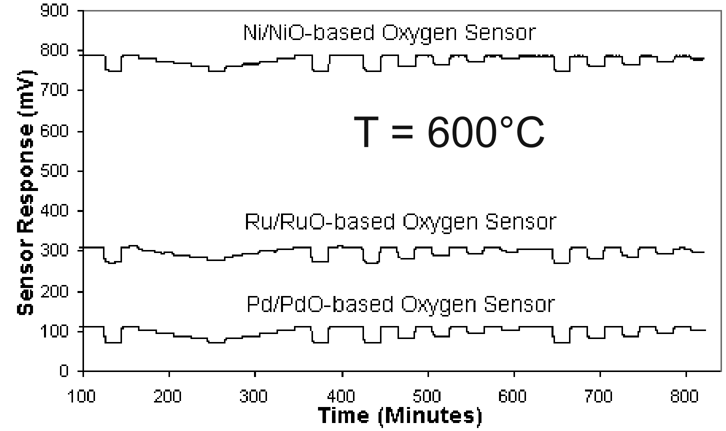
Scanning electron microscopy images of the joint interface shows no porosity; air-tight durable seal

Accomplishments

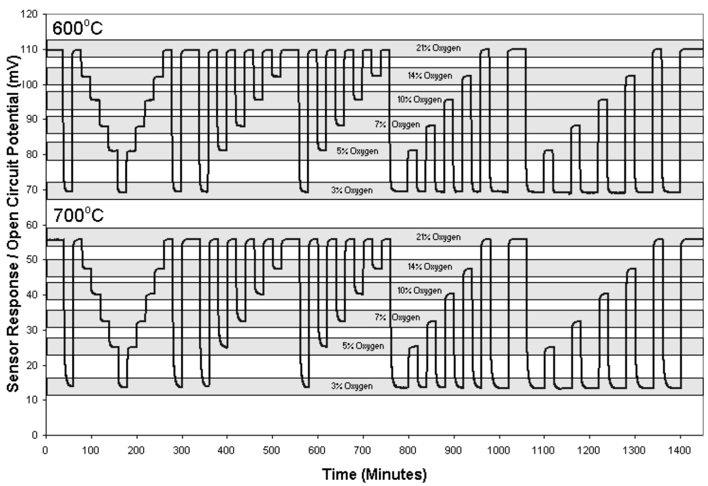
Performance of the Oxygen Sensor



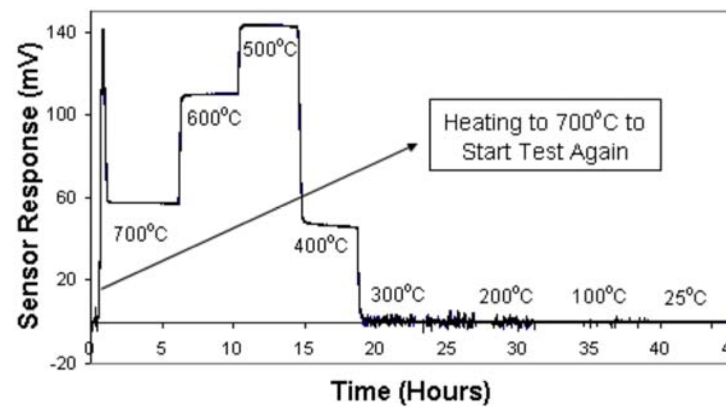
Fabricated Sensor



Output signal for various metal/metal oxide mixtures



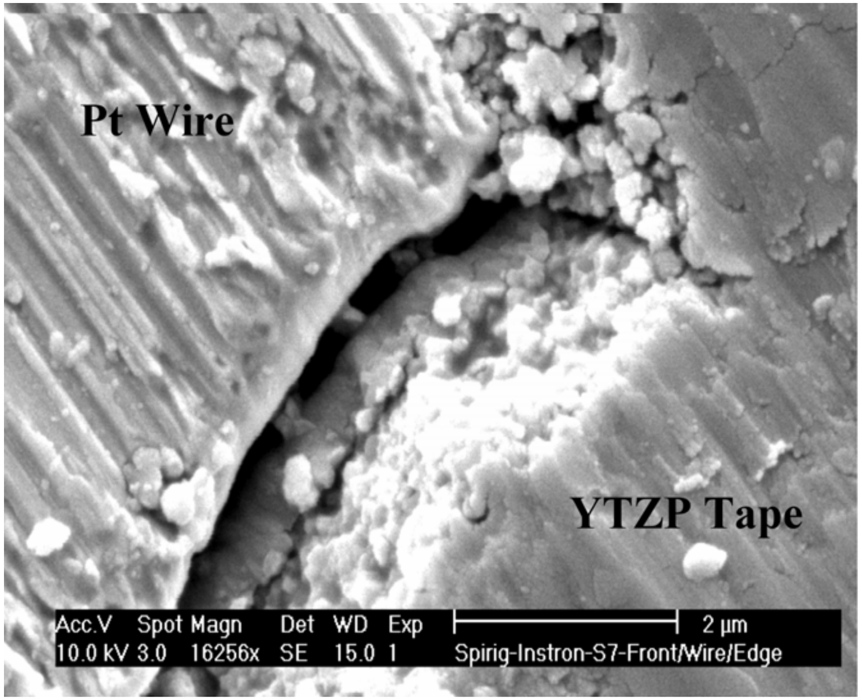
High sensitivity and fast response time



Sensor performance repeatable, trace of four runs overlapping

Accomplishments

Long-term Performance of the Oxygen Sensor



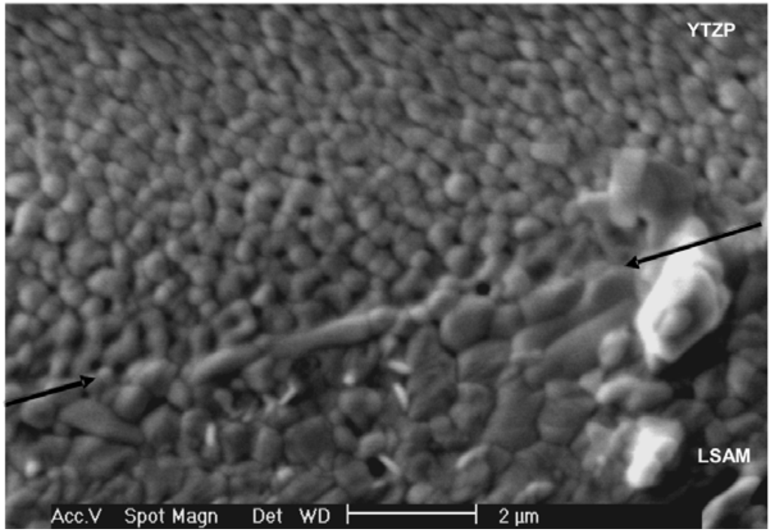
Over repeated temperature cycling, glass used to seal the region around Pt wire (interior electrode) exiting from the sensor chamber can possibly degrade and affect the sensor performance

Need for the development of a high temperature electrically conducting ceramic that can join to YSZ by ANL's patented high temperature plastic joining technique

Accomplishments

Development of a High Temperature Ceramic Electrode

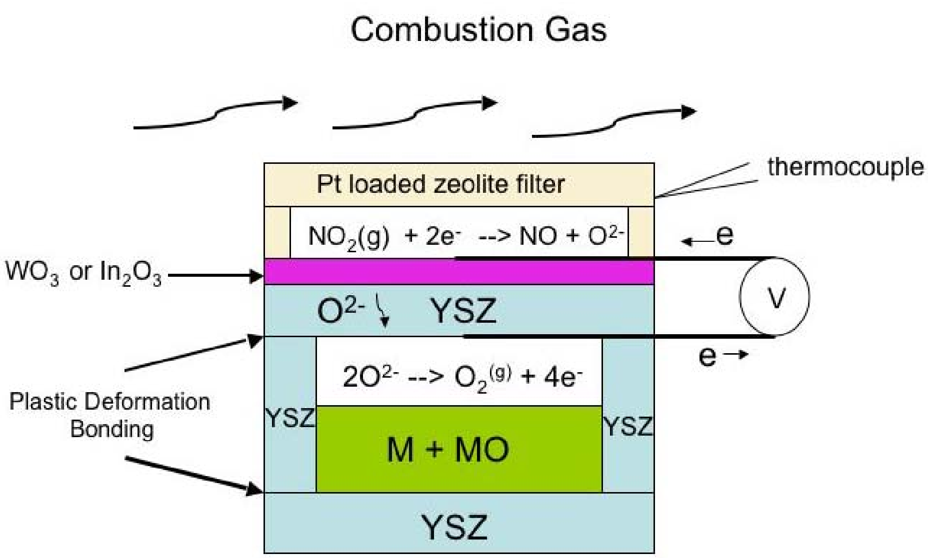
- New material developed: Aluminum-doped lanthanum strontium manganese oxide ($La_{0.77}Sr_{0.20}Al_{0.9}Mn_{0.1}O_3$)
- Joining of LSAM to YTZP demonstrated by plastic joining
- Aluminum doping minimizes reaction with YTZP
- Electrically conducting at sensor operating temperatures



Need to incorporate LSAM electrode into sensor design and evaluate sensor performance

Accomplishments

Proposed Modifications to Oxygen Sensor to Measure NO_x:



- A Pt-loaded zeolite filter will be placed before the sensor that will equilibrate NOx
- By measuring temperature of the catalytic filter and the known characteristic of filter, conversion efficiency of NO to NO_2 can be determined
- Sensor will measure concentration of NO_2 in equilibrated gas by the reduction of NO_2 at WO_3 or In_2O_3 interface that produces a specific O_2 partial pressure
- Because of the difference in the oxygen partial pressures across the oxygen conducting zirconia a voltage will be generated; internal reference oxygen is used
- By measuring filter temperature and voltage, total NO_x concentration in combustion gas can be determined
- Both potentiometric and amperometric approaches for NOx sensing will be investigated

Path Forward

- Continue to develop the sensor package, particularly incorporate the LSAM electrode and test the long-term performance
- Include the sensing components for NO_x
- Fabricate the NO_x sensor based on the proposed design
  - characterize the sensor performance
  - optimize the sensing catalyst formulations for enhanced signals
  - establish durability of the sensor
  - investigate the cross interference with other combustion gases
- Initiate discussions 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 developed and demonstrated
- Progress made in the development of a novel high temperature ceramic electrode material (LSAM)
- Joining of LSAM to YSZ ceramic demonstrated, thus use of Pt electrode as the internal reference gas electrode is obviated
- Modifications of the basic oxygen sensor design to sense NO_x have been proposed