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Compact Potentiometric NO_x Sensor

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Project ID #
PM 023

Vehicle Technologies – Annual Review – June 7-11, 2010

Sponsored by ***Propulsion Systems Materials***

Overview

Timeline

- Project start FY08
- Project end FY12
- 50% complete

Budget

- Total project – $390K
- FY09 = $200 K (DOE)
- FY10 = $150 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 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

- 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

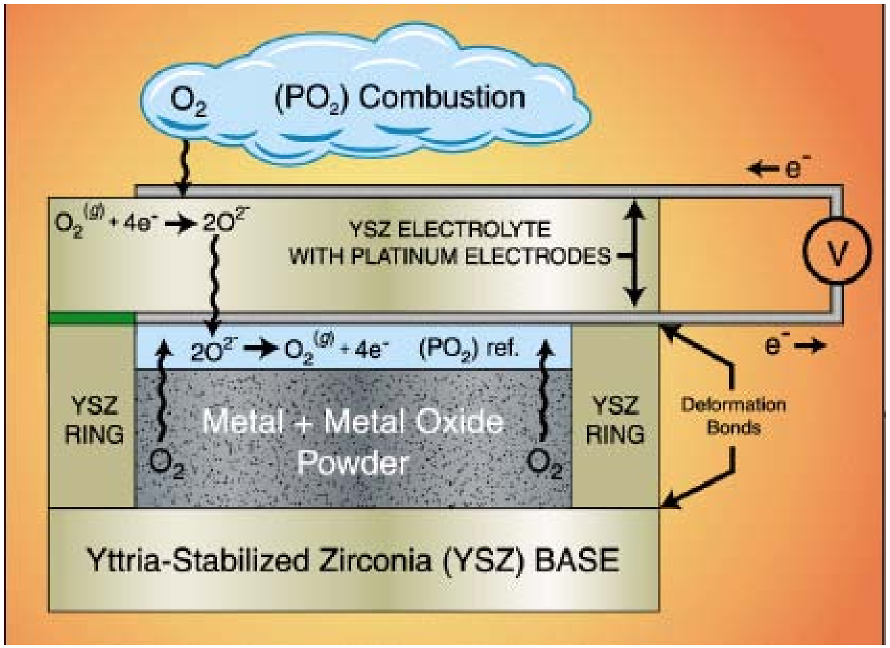
- First develop a high-temperature oxygen sensor and subsequently modify it to sense NO_x concurrently
- Sensor design is based on relatively simple and well-known electrochemical principles. It is a closed end device made from oxygen ion conducting partially stabilized zirconia ceramic (YSZ). At elevated 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 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 strategy to convert oxygen sensor to measure No_x and O_2
  - Demonstrate NO_x sensing capabilities
  - Conduct performance evaluation of the NO_x sensor, including long-term behavior and cross interference with O_2
- FY10
  - Develop high-temperature electrically conducting ceramic electrode material to replace expensive Pt
  - Demonstrate electrical properties of the ceramic electrode
  - Demonstrate joining of ceramic electrode to sensor package material (zirconia)
  - Incorporate ceramic electrode in the sensor package and evaluate 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:

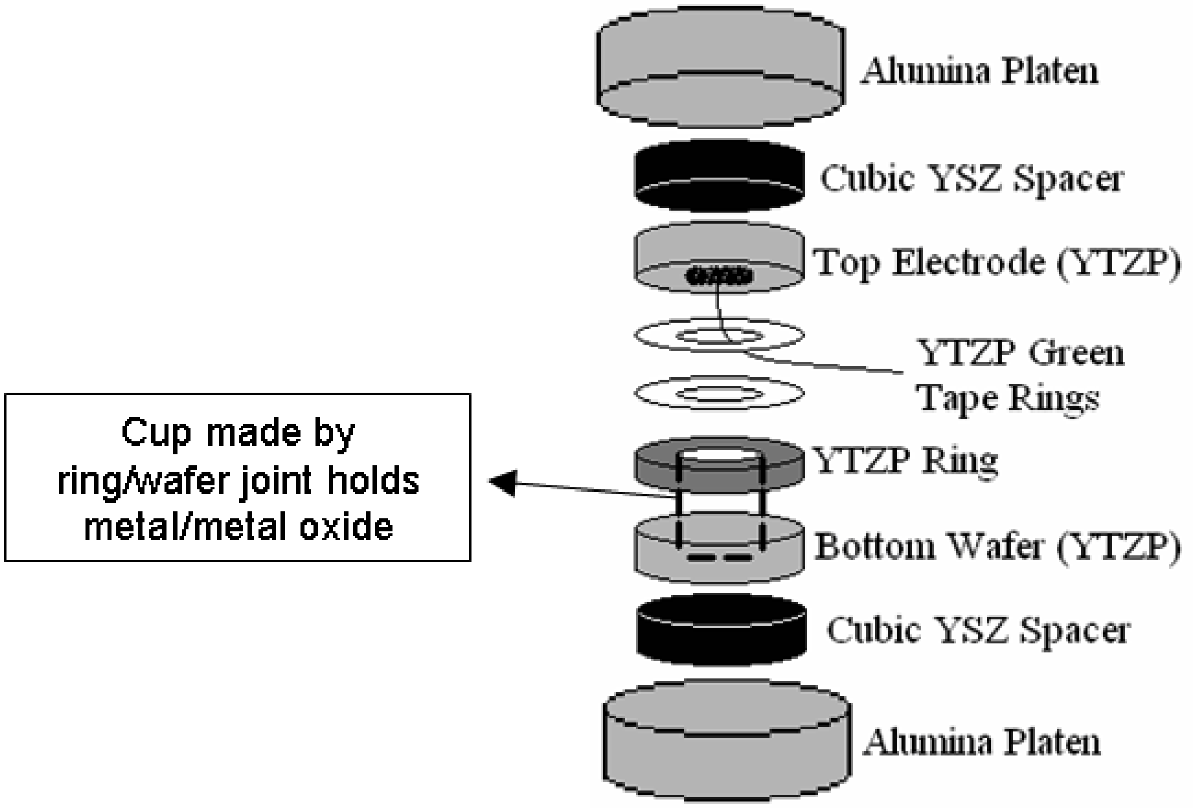
$$E = \frac{RT}{4F} \ln \frac{(PO_2)^{combustion}}{(PO_2)^{int.}}$$

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

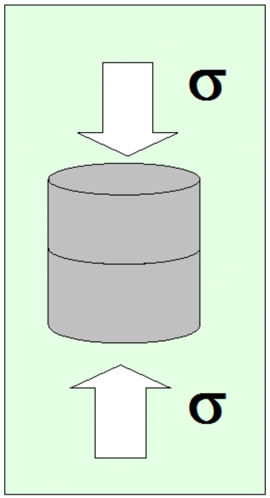
Components of Basic Sensor Package



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

Accomplishments

Joining of Sensor Package YSZ Components



Experiments

- Relatively low joining temperatures:

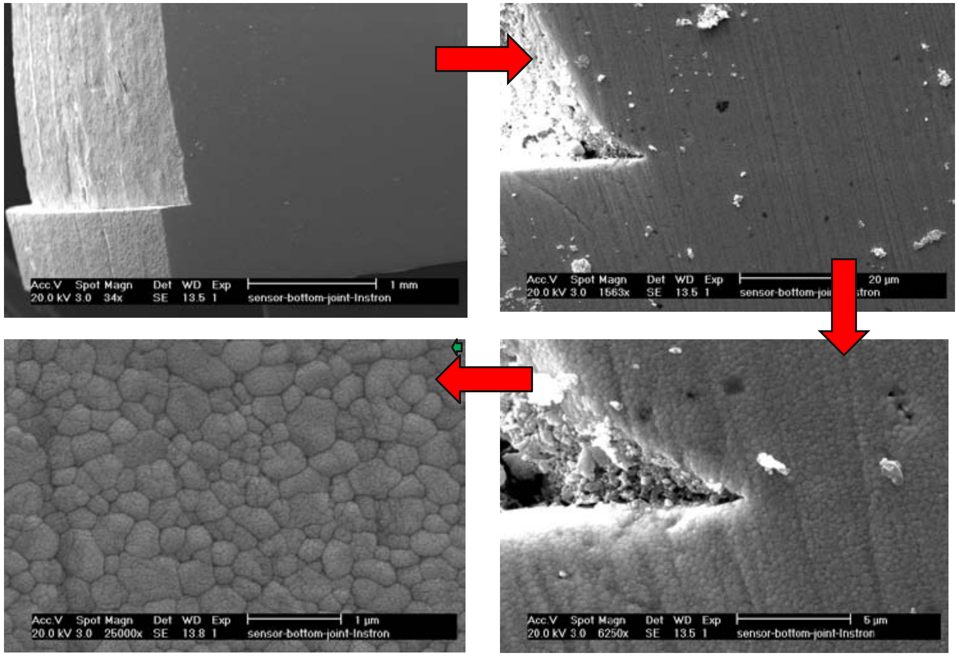
  1100 ² T ² 1350¼C.

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

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

- Near-net-shape process:

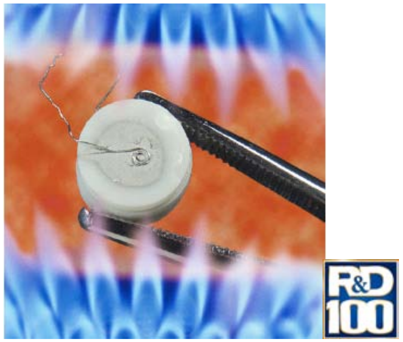
  $\varepsilon_{max} < 10$ %.



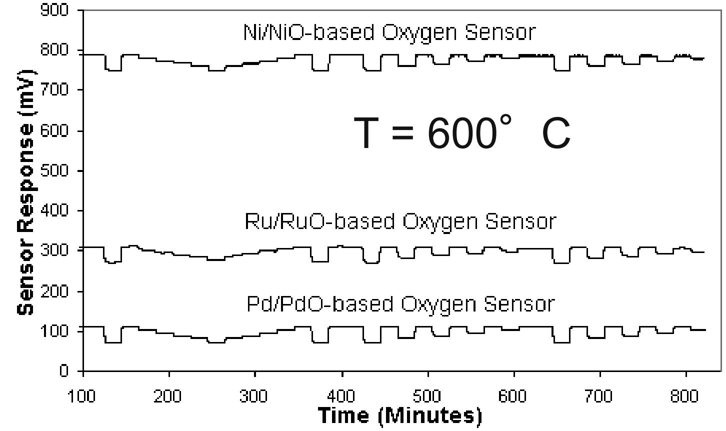
Scanning electron microscopy images of the joint interface shows no porosity; air-tight durable seal

Accomplishments

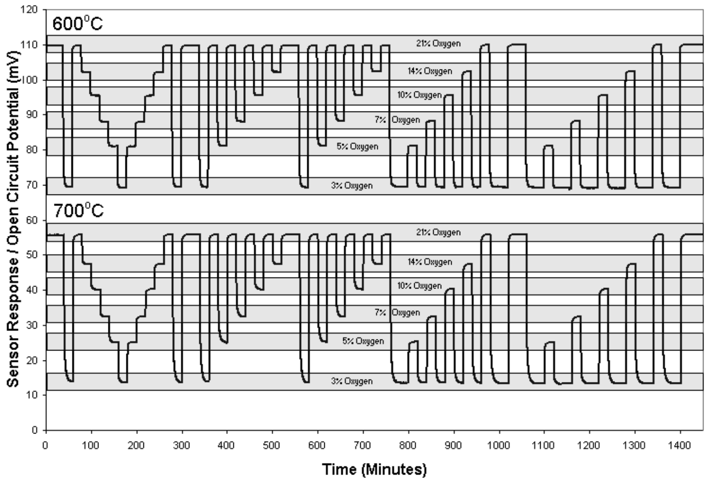
Performance of the Oxygen Sensor



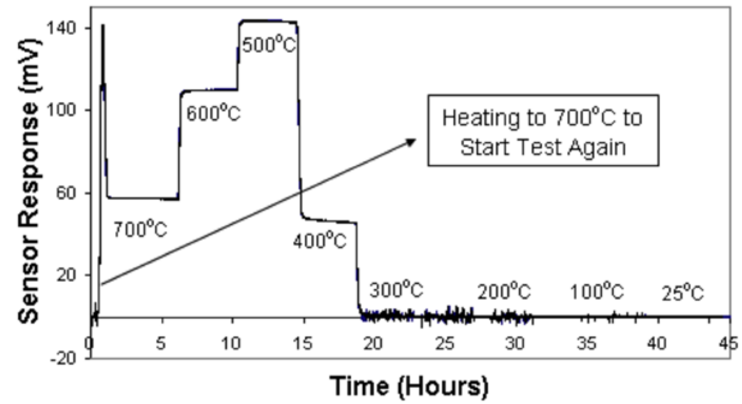
Fabricated Sensor



Output signal for various metal/metal oxide mixtures



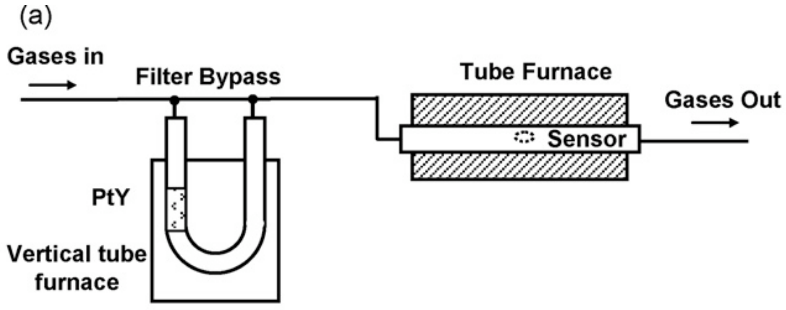
High sensitivity and fast response time



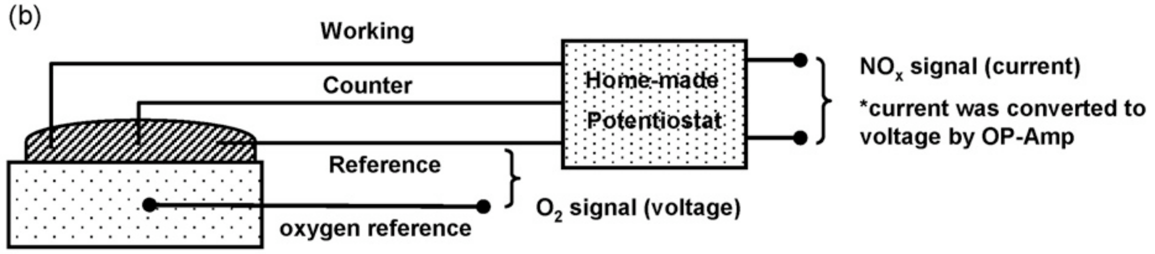
Sensor performance repeatable, trace of four runs overlapping

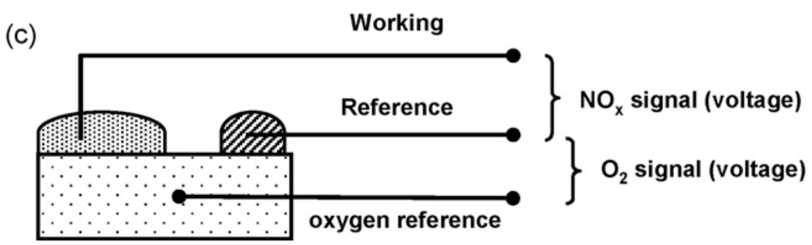
Accomplishments

NO_x Sensor Test Set-up



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



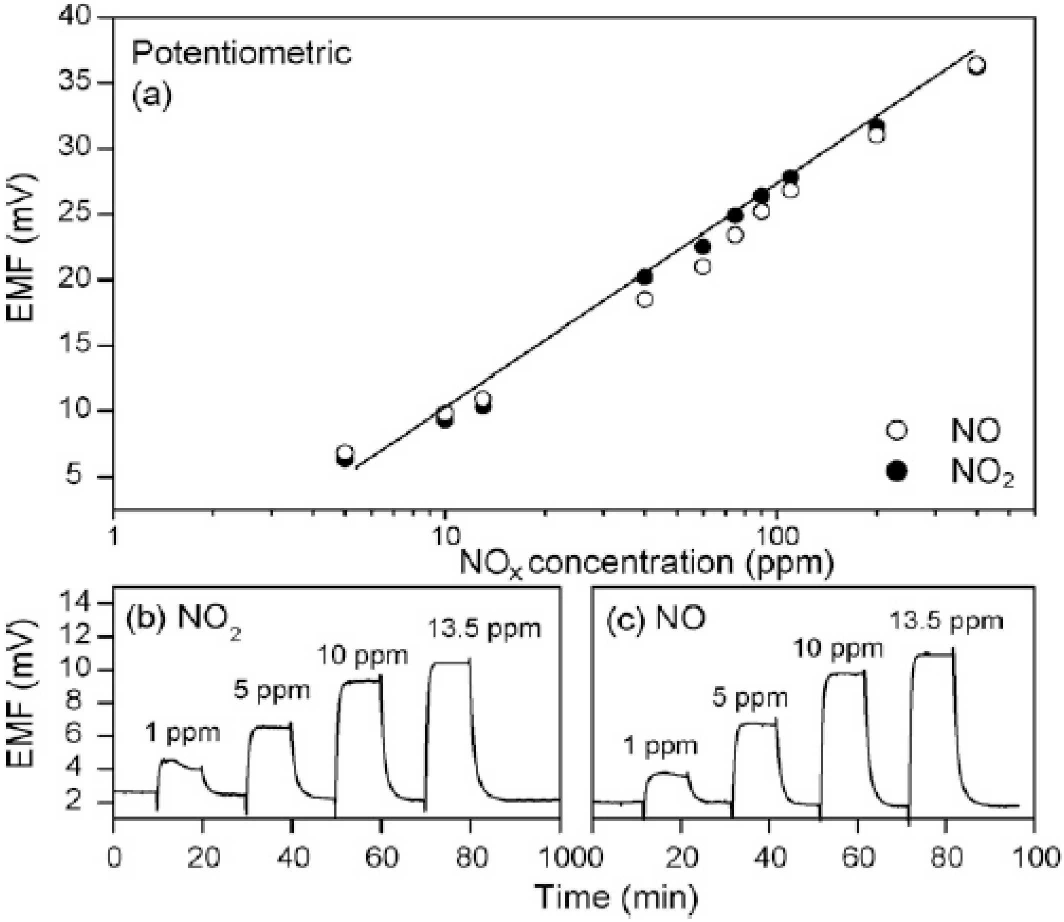


(b) Amperometric mode

(c) Potentiometric mode

Accomplishments

Sensitivity of the Sensor to NO_x in Potentiometric Mode

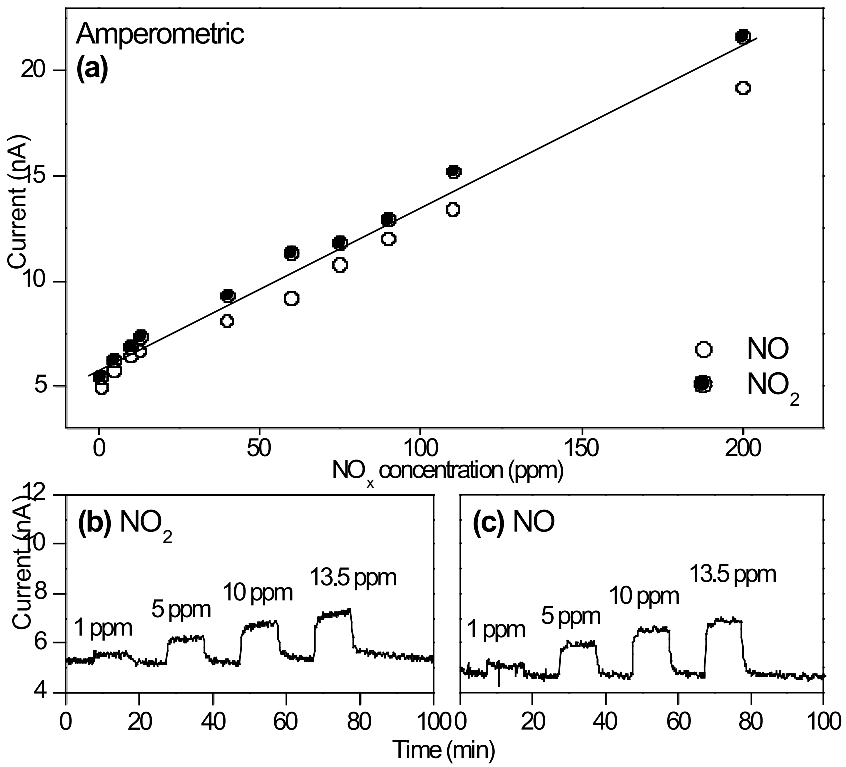


Test Temperature = 600°C
Filter Temperature = 400°C
O_2 level 3% in gas

Response transients for 1-13.5 ppm of NO and NO_2

Accomplishments

Sensitivity of the Sensor to NO_x in Amperometric Mode



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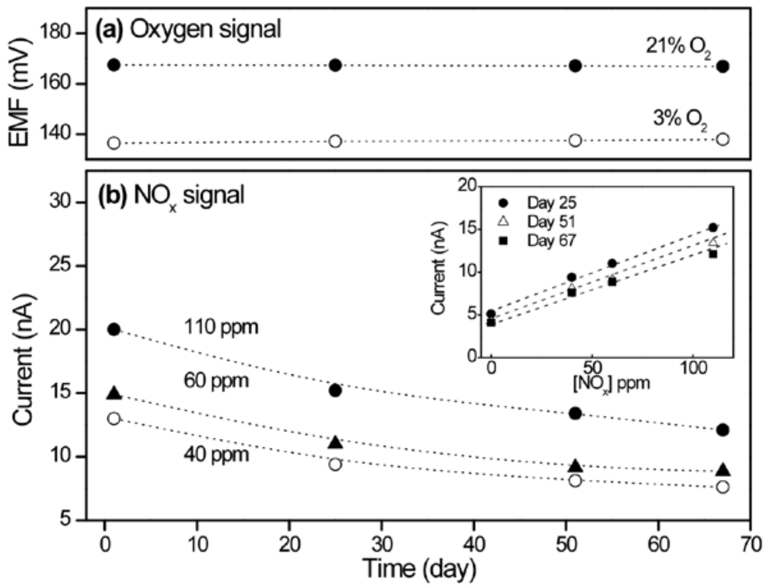
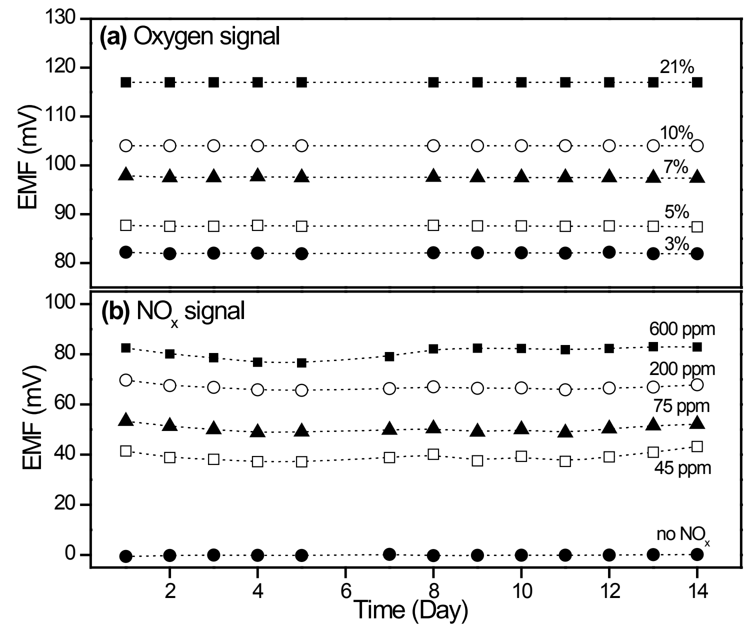
Accomplishments

Long Term Sensor Performance





Amperometric Mode

Potentiometric Mode

Path Forward

- Develop electrically conducting ceramics electrode and evaluate its electrical properties and joining characteristics with zirconia

- 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

- 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
- Modifications made to the basic oxygen sensor design to sense NO_x
- Modified oxygen sensor design has been demonstrated to sense NOx
- Performance of NOx sensing has shown excellent sensitivity, resolution and long-term performance