Compact Potentiometric NO$_x$ Sensor

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May 10, 2011

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Vehicle Technologies – Annual Review

Project ID - pm023

Sponsored by Propulsion Systems Materials

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Overview

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

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

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

*Continuing resolution, funds received

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\textsubscript{2}, NO\textsubscript{x}, CO, CO\textsubscript{2}).

- Most state-of-the-art gas sensors require external reference gas source and are expensive.

- Compact NO\textsubscript{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\textsubscript{x} sensor technology that is amenable for mass production.
Objectives

- Modify and develop the compact oxygen sensor design to sense NO\textsubscript{x} concentrations at ppm levels

- Fabricate compact NO\textsubscript{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\textsubscript{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\textsubscript{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 \( \text{O}_2 \)

- At \( T > 450^\circ \text{C} \), a specific oxygen partial pressure \((p_{O_2})_{\text{int.}}\) from M+MO is generated within the sensor package.

- Because of the difference in the oxygen partial pressures between combustion environment, \((p_{O_2})_{\text{combustion}}\), and \((p_{O_2})_{\text{int.}}\) a voltage, \(E\), as given by the equation below, is generated across the YSZ electrolyte:

\[
R = \text{gas constant} \\
T = \text{absolute temperature} \\
F = \text{Faraday’s constant}
\]

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 $\text{NO}_x$

**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

Long Term NO\textsubscript{x} Sensor Performance

![Graphs showing long term NO\textsubscript{x} sensor performance in amperometric and potentiometric modes.](image-url)
La_{0.8}Sr_{0.2}Al_xMn_{(1-x)}O_3: Electrode material

Accomplishments

Al added to prevent reaction of the electrode material to zirconia
Accomplishments

**LSAM - SEM Analysis**

- SEM images with EDS indicate phase segregation in darker grains
  - LSM- Mn₃O₄ segregation, grain size 7.4 µm, open porosity 1.5%
  - LSAM 0.3Al- Al₂MnO₄ segregation, grain size 4.7 µm, open porosity 0.97%
  - LSAM 0.5Al- Al₇Sr₁₂O 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$_3$O$_4$ peaks in $x=0$
  - Al$_2$MnO$_4$ peaks in $x=0.3$
  - Sr$_7$Al$_{12}$O$_{25}$ peaks in $x=0.5$
Accomplishments

**LSAM - Electrical Conductivity**

- Electrical conductivity ($\sigma$) determined
- $\sigma$ increases with $T$
  - Known LSM discontinuity at 100°C
- Increasing Al content decreases $\sigma$
  - 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
  - $\sigma$ increases with increasing $\varepsilon$
  - $\sigma$ 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 $\varepsilon = 5\times 10^{-5}/s$
  - 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\textsubscript{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 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