Title: Linear Air-Fuel Sensor Development

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PART I

Linear Air- Fuel Sensor Development

Final Report

CRADA # LA92C10060

A.PURPOSE

Parties: Parties described hereunder are as follows:

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General Motors, AC Rochester Division (Now GM/Delphi E. Division)

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B.SCOPE

Objectives

This project has the objective of developing a linear output oxygen sensor, based on solid-electrolyte/ thin film electrode technology, that can operate with adequate sensitivity and lifetime under lean-burn engine conditions.

C. Technical Report

INTRODUCTION

The electrochemical zirconia solid electrolyte oxygen sensor, is extensively used for monitoring oxygen concentrations in various fields. They are currently utilized in automobiles to monitor the exhaust gas composition and control the air-to-fuel ratio, thus reducing harmful emission components and improving fuel economy.

Zirconia oxygen sensors, are divided into two classes of devices: (1) potentiometric or logarithmic air/fuel sensors; and (2) amperometric or linear air/fuel sensors. The potentiometric sensors are ideally suited to monitor the air-to-fuel ratio close to the complete combustion stoichiometry; a value of about 14.8 to 1 parts by volume. This occurs because the oxygen concentration changes by many orders of magnitude as the air/fuel ratio is varied through the stoichiometric value. However, the potentiometric sensor is not very sensitive to changes in oxygen partial pressure away from the stoichiometric point due to the logarithmic dependence of the output voltage signal on the oxygen partial pressure. It is often advantageous to operate gasoline power piston engines with excess combustion air; this improves fuel economy and reduces hydrocarbon emissions. To maintain stable combustion away from stoichiometry, and enable engines to operate in the excess oxygen (lean burn) region several limiting - current amperometric sensors have been reported.¹⁻⁶ These sensors are based on the electrochemical oxygen ion pumping of a zirconia electrolyte. They typically show reproducible limiting current plateaus with an applied voltage caused by the gas diffusion overpotential at the cathode.

Figure 1. Schematic illustration of Limiting current oxygen sensor behavior

The sensor current plateau is linearly proportional to the concentration of oxygen in the external environment, and the oxygen concentration. This phenomenon occurs

because the diffusion of the oxygen through the gas diffusion barrier is the rate-determining step. Two types of diffusion barriers are currently being evaluated by

Figure 2. Pinhole type of limiting current sensor

Figure 3. Porous barrier limiting current sensor

the automotive industry : a) a cavity with a small diffusion hole. and b) a porous ceramic layer on the cathode to limit the oxygen transfer rate from the ambient gas. The aperture type of limiting current sensors requires that the hole does not occlude or change dimensions during long term operation and is relatively difficult to manufacture. The porous diffusion layer is easier to fabricate but controlling the porosity of the layer is a difficult step in the manufacturing process. Long term operation of this sensor may suffer from a drift in the response from a changing pore morphology over time.

The problems associated with pore based diffusion barriers may be overcome, however, by using a mixed electronic and oxygen ion-conducting solid membrane as a diffusion barrier. The diffusion of oxygen through the mixed conducting solid materials is much slower than in a gas. This slower diffusion will reduce the oxygen flux to the cathode and, consequently, will upgrade the sensor performance. By applying a thin, or thick, film of mixed conductor layers, the entire area will be an effective diffusion barrier.⁶ As the mixed conductor also

exhibits very high electronic conductivity, it will also act as a cathode, and the charge transfer reaction will occur across the entire mixed conductor and solid electrolyte interfacial area. A number of mixed conducting compounds have been identified and used as fuel cell cathode materials. The lanthanum transition metal oxide perovskite structure ceramics represent the largest class of suitable materials. Other suitable compounds include rare earth and transition metal doped ceria and zirconia based fluorite and pyrochlore oxides. These materials are selected for high thermal and chemical stability, and good thermal expansion coefficient match with zirconium oxide.

In this document, we report on the fabrication and testing of limiting-current oxygen sensors that utilize mixed conductors as diffusion barriers.

Experimental Aspects

Materials:

Yttria-doped tetragonal zirconia polycrystals (TZP) ceramic substrates (RC334) and single crystal yttria stabilized zirconia (YSZ) substrates were obtained from A. C. Rochester and Enprotech respectively. A single 50mm diameter, hot-pressed target of $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ were purchased from SSC (Seattle Specialty Ceramics) for use as solid oxide mixed conducting diffusion barriers. Lanthanum strontium manganese materials for screen printing were SSC powders, ground and sieved to pass through a 600 mesh screen. Phase purities were confirmed with Bragg Bretano X-ray powder diffraction.

Figure 3. Limiting current sensor configuration

Sensor preparation:

The basic geometric configuration of the limiting-current sensor is shown in Fig. 3. Typical thicknesses of the TZP disks and YSZ substrates were about 0.07 cm and

0.05 cm. The mixed conductors were deposited by a 90° off-axis radio-frequency (RF) magnetron sputtering technique. The substrate was mounted to a quartz lamp heated plate using silver paste, and the substrate heater temperature was measured using an IR camera. All the depositions were carried out at an RF power of 100 W at a temperature of 700° C. After the depositions, the chamber was flooded with pure oxygen to a pressure of 5 Torr, and the films were allowed to cool. Films from 0.5 to 10 microns in thickness were produced using this technique.

Metal oxide diffusion barrier electrodes were also applied as screen printed thick films (50-150 μm) where glycerol was used as the screen printing vehicle. The thick films were dried at approximately 150°C to remove the vehicle and the fired at 1350°C to densify the electrodes. For electrical testing, platinum contact pads were sputtered to both faces of the devices and thin platinum wires were parallel-gap-welded on both electrodes, as shown in Fig. 3. Electrochemical oxygen leakage from the edges of the devices was reduced by the application of a glass seal around the circumference of the sensors. The sensors were placed inside a quartz tube mounted inside the furnace to provide a controlled Ar/O₂ atmosphere and a controlled temperature.

Oxygen and argon gas mixtures of controlled oxygen pressures, ranging from 0.01 to 20% were applied to the sensors. The mixing and the flow rate of the gas were controlled by a MKS Instruments mass flow controlling system (Model 129A and Model 24C 4-channel readout). All oxygen partial pressures were checked and monitored by an oxygen analyzer (Ametek) connected the exhaust tube of the system. The gas flow rate was approximately 150 cc/min.

DC polarization measurements:

The sensor current voltage characteristics we measured using a Solartron 1286 Electrochemical Interface or an EG&G Princeton Applied Research 273 Potentiostat/Galvanostat and the data was recorded using a digital computer. An oxygen partial pressure was fixed with the gas mixing apparatus and measured using the Ametek oxygen analyzer. Polarization potentials were incremented from 0 - 4 volts and the corresponding electrochemical current was recorded for each device. The furnace temperature was then changed and the measurements were repeated. Figures 4 and 5 illustrate the constant temperature sensor responses. Figures 6, 7 and 8 illustrate the sensor responses at various temperatures.

Figure 4. O_2 sensor response for a $La_{0.84}Sr_{0.16}MnO_3$ film/ yttria stabilized zirconia/platinum device operating at $600\text{ }^{\circ}\text{C}$

Figure 5. $La_{0.84}Sr_{0.16}MnO_3$ /tetragonal zirconia /Pt oxygen sensor response at $800\text{ }^{\circ}\text{C}$

Current-voltage characteristics of the limiting-current sensors:

The i - V characteristic curve of a typical sensor has four regimes that represent different electroactive processes similar to the response observed in other types of limiting current sensors.⁸⁻¹⁰ In the initial region, the current increases exponentially with the applied voltage. This increase is believed to be caused by Butler Volmer type charge transfer kinetics at the mixed conductor / solid electrolyte interface. The second regime displays an ohmic slope where the output current increases with increasing applied voltage. This behavior is related to the combined ionic transport in the mixed conductor and the solid electrolyte. Taking the slopes as an indication of the total DC resistivities and subtracting the contribution from the mixed conductors, the DC resistivity of the solid electrolyte can be determined. the mixed conductors have electronic and oxygen ion conductivities that are several orders of magnitude higher than those of the solid electrolyte, the slopes are predominantly caused by the ohmic behavior of the solid electrolyte.

Figure 6. $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ thin film/ yttria stabilized zirconia/platinum device response at varying temperatures

Figure 7. $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ thin film / tetragonal zirconia / Pt sensor response as a function of temperature

The third regime features the limiting-current plateau, which is determined by the gas diffusion through the mixed conductor diffusion barrier. This current can be described using the following relationship:

$$i_l = \frac{4FD_{\text{O}_2}SC_{\text{O}_2}(0)}{L} \quad (1)$$

where i_l , F , D_{O_2} , S , $C_{\text{O}_2}(0)$, and L are the limiting current, the Faraday constant, the oxygen diffusion coefficient through the mixed conductor at the given temperature, the surface area of the mixed conductor (diffusion barrier), the oxygen concentration in ambient gas, and the thickness of the mixed conductor, respectively.

The characteristics of the limiting-current plateau has been studied extensively in devices that use physical diffusion barriers.¹⁻⁶ In this region, the rate determining step of our devices is based on the diffusion of oxygen atoms through the lattice of the mixed conductors. Since the electronic conductivity of mixed conductors is so high, the gradient of electric potential is very small. Therefore, oxygen transport through these materials occurs only due to an oxygen chemical potential gradient.

Figure 8. $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3/\text{tetragonal zirconia}/\text{Pt}$ oxygen response

Our current - voltage characteristics show that the limiting-current plateaus have a slight slope with increasing applied voltage. The observed results are believed to be caused by a mixture of ohmic current proportional to the applied voltage and by a current based on the diffusion restriction of atomic oxygen through the mixed conductors. The ohmic current is believed to be caused by edge leakage.^{4, 11} The glass seal applied to the exposed three-phase contact area (mixed conductor, electrolyte, gas) may not be completely dense, and may, therefore, allow a short diffusion length pathway

Another feature of i - V characteristics of the sensors is the observation of a peak at the beginning of the limiting-current plateau. This peak is observed only at the low P_{O_2} current plateaus. Recent unpublished cyclic voltammetry experiments by the authors indicate that the peak is that it caused by a partial reduction in oxygen stoichiometry of the metal oxide upon application of reducing potentials.

The fourth regime is the current - voltage behavior beyond the limiting-current plateau. This region is expected to be caused by the electrochemical decomposition of the zirconia electrolyte expressed by:¹²

This effect appears to be a thermally activated process and is most dramatic at the highest operating temperatures.

The dynamic measurement range for these limiting current sensors is determined by a number of device parameters. The highest oxygen concentration detected by our thin film sensors is about 2000 to 3000 ppm. Figures 6, 7, and 8 show that the range of oxygen concentration detected is larger with higher temperature. As the

temperature is lowered, the detection range of the sensor gets narrower due to the higher conductivity of the solid electrolyte with increasing temperature. The ionic conductivity of the solid electrolyte predominately determines the slope in the second regime of the i - V curve. The conductivity of the electrolyte determines the highest possible intercept of the ohmic part in the i - V plot. To increase the range of measureable oxygen concentration, a more conductive or thinner solid electrolyte can be used. The range can be increased significantly by using thin-film solid electrolyte technology.

The oxygen sensor response can be further optimized by tailoring the thickness of the barrier layer for the oxygen concentration range that is desired. The mixed conductors used as diffusion barriers for our oxygen sensor have a relatively high oxygen diffusion coefficient. The high mobility of oxygen through the mixed conductor diffusion barrier limits the sensor's detection range at the currently used thicknesses. To increase the operating concentration range, the thickness of the diffusion barrier layer can easily be increased with currently available thick film technology such as screen printing. Figures 9 and 10 illustrate the response of such a device fabricated by the authors. The device displays excellent response characteristics from 0.5% oxygen concentrations to ambient air oxygen partial pressures. Alternatively dense diffusion barrier materials with a lower diffusion coefficient for oxygen can also be used.

Stability issues

Our sensors based on $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ diffusion barriers, displayed a long term drift in the limiting current plateaus when subjected to polarization voltages of over 2 volts and temperatures of 800°C . Optical examination of the devices revealed significant morphological changes of layers and XRD analysis confirmed phase decomposition. The $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ material proved to be a more stable material, exhibited better chemical stability and thus proved to be the diffusion barrier of choice of these perovskites.

Figure 9. I-V data for sensors based on La-Sr-Mn-O diffusion barrier film ink deposited on tetragonal zirconia ceramics.

Figure 10. Oxygen pressure-current output data for La-Sr-Mn-O diffusion barrier film ink deposited on tetragonal zirconia solid electrolytes with platinum counter electrodes.

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Table 1. Summary of Technical Tasks and Milestones

Task	Primary party	STATUS
Phase 1: Planning		
1. Research Plan Formulation. Definition of performance over useful life, approach.	LANL/LLNL/ AC -Rochester	completed
2. AC Rochester will provide information about the status of its planar sensor technology.	AC Rochester	completed
3. Strategic planning for integrated solid state sensor package for exhaust gas multisensor.	LANL/LLNL/ AC-Rochester	completed
Phase2:Materials Development		
4. Development of substrate and heater technology.	AC Rochester	completed
5. Development of Electrolyte material (identification of suitable materials, deposition technology, characterization)	LANL/LLNL/ AC Rochester	completed
6. Development of diffusion barrier layer. (identification of suitable materials, deposition technology, characterization)	LANL	completed
7.Development of metallization, inter-connects etc.	LANL	completed
8. Development of packaging and encapsulation.	LANL/ AC Rochester	completed
Phase 3: Prototype Device Development		
10. Fabrication of prototype devices.	LANL/LLNL	completed
11. Development of experimental testbed at Los Alamos.	LANL	completed
12. Electrochemical characterization of sensor response under laboratory conditions.	LANL / AC Rochester	completed
Phase 4: Device Testing		
13. Evaluation using simulated exhaust gas environment.	AC Rochester	completed

D. Partner Contributions

GM /Delphi E (formerly AC Rochester) has contributed to the project by providing the advanced ceramics processing research and technology to produce the solid electrolyte and sensor structure. They have also developed the self heating technology and the encapsulation technology required to package the devices. No subject inventions were created during the CRADA project.

Intellectual property

Background Property: LANL Patent applied for and allowance granted by US Patent Office Application attached

E. Document Reference List

a) CRADA Quarterly Reports

b) Patent Application

c) No subject Inventions developed

d) Licensing status: Two US manufacturers have expressed interest in license agreements

F. Acknowledgements

Participants signature on the final report indicates the following:

1) The Participant has reviewed the final report and concurs with the statements made therein;

2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project;

3) The Participant certifies that all reports either completed or in process are listed and all subject inventions and the associated intellectual property protection measures attributable to the project have been disclosed or are included on a list attached to this report:

4) The Participant certifies that proprietary information has been returned or destroyed by LANL

Carl Miller 25 Nov 96

Carl Miller (GM-Delphi E) Date

Fernando Garzon 10-24-96

Fernando Garzon MST-11 LANL Date

PART II FINAL ABSTRACT

A new type of miniature oxygen sensor has been developed under this CRADA. Unlike conventional oxygen sensors that exhibit a logarithmic response to oxygen concentration, the new devices respond linearly to oxygen concentration. The sensors are high temperature micro-electrochemical devices that use a dense diffusion barrier of a special class of materials that readily transport oxygen and conduct electrons, deposited in thin film form on top of a zirconia-based electrochemical pump. When a voltage is applied to the pump, oxygen is depleted from one side of the diffusion barrier and the ionic current is proportional to the flux of oxygen across the thin film layer. If the pumping voltage reaches a high enough value, the transport of oxygen across the membrane, and hence the device's output current, will be limited by the external oxygen concentration and the transport characteristics of the diffusion barrier. Past design diffusion limited current sensors have previously used porous layer diffusion barriers. The dense diffusion barriers developed here offer key advantages over the porous diffusion barriers. The dense layers utilize intrinsic materials properties such as oxygen diffusion coefficients, as opposed to an extrinsic materials property - porosity. This enables easier device manufacture, removes the need to calibrate the devices individually, and solves the problem of the sensor response changing over time due to pore clogging and porosity decreasing due to anneal effects. These sensors may have widespread applications in transportation technology, chemical process control and workplace monitoring

In conclusion we have developed linear oxygen sensor prototypes that:

- a) demonstrated linearity over multiple decades of oxygen partial pressure
- b) demonstrated sustained operation at high temperature ($>1000^{\circ}\text{C}$)
- c) are corrosion resistive
- e) are self heated less than 3 seconds to operation temperature
- f) can be manufactured economically
- g) exhibit a fast (millisecond) response

Figure 1. Photograph of the LANL-GM sensors developed under this CRADA

Figure 2. Response of the sensor device to change oxygen pressures

D. Partner Contributions

GM /Delphi E has contributed to the project by providing the advanced ceramics processing research and technology to produce the solid electrolyte and sensor structure. They have also developed the self heating technology and the encapsulation technology required to package the devices. No subject inventions were created during the CRADA project.

PART III Project Accomplishments Summary

Background

Increasingly stringent regulations regarding average fuel economy and exhaust emissions are an important factor contributing to the difficulties facing US. auto makers in the area of international competitiveness. Engines of the future will require increasingly sophisticated electronic systems to monitor and control various engine functions. Among these engine subsystems, exhaust gas monitoring is of critical importance, both from the point of view of emissions control (including catalyst diagnostics) and fuel economy. At the present time, an oxygen monitor is incorporated into the exhaust system of every new gasoline-powered automobile. This sensor, based on electrochemical principles, monitors the air/fuel ratio and allows feedback to the fuel supply, giving control of the engine combustion processes. This sensor works well if the engine is operated at the stoichiometric point: that is, at an air-to-fuel ratio that is determined by a strict chemical balance in the combustion process. There are, however, considerable advantages in operating an engine in the lean-burn region, not the least of which is an improvement in fuel economy. Unfortunately, for fundamental reasons, the present generation of oxygen sensors is insufficiently sensitive in the lean-burn region. The principal objective of the joint work is the development of a Linear Air-Fuel Ratio Sensor, that would have adequate sensitivity in the lean-burn region. In the approach we propose to take, other advantages would also be accrue, such as better temperature stability and faster response time. In the long term we wish to work towards a comprehensive approach to exhaust gas monitoring, which would include solid-state sensors for additional species such as hydrocarbons, carbon monoxide and oxides of nitrogen.

Description

This project has the objective of developing a linear output oxygen sensor, based on solid-electrolyte film technology, that can operate with adequate sensitivity and lifetime under lean-burn engine conditions. This project is part of a coordinated effort between General Motors/AC Rochester and the four Defense Programs Laboratories to develop sensors and systems for engine management. Besides Exhaust Gas Monitoring, there are three other main areas: Combustion Monitoring, Engine Fluid Condition Monitoring and Engine Control. Los Alamos is coordinating the research efforts in the area of exhaust gas monitoring, and each of the Laboratories has a similar role in one of the other areas.

Los Alamos National Laboratory's primary tasks were the development of the oxygen diffusion barrier materials and the laboratory testing of devices. GM's contribution was the development of solid electrolytes, heating technology and packaging of the sensors.

The Overall rating of this project by our industrial partners during review was given the highest possible rating

Economic impact

Several companies are currently interested in various aspects of the technologies developed by LANL. These include Fisher/Rosemont Analytical, one of the worlds largest suppliers of combustion control equipment, and Englehard Industries a major supplier to the chemical and transportation industries. The expected benefits to the tax payer include key components of technologies that reduce air pollution and thus decrease the health effects of transportation technologies and also improve fuel economy and improve automobile engine performance.

Benefits

Industry Area

General Motors/ AC-Rochester has benefited from the expertise of Los Alamos in the areas of solid-state electrochemistry, thin film deposition and characterization, electronic materials and modeling.

DOE Benefits

Los Alamos has benefit from association with a company able to define its technological and market objectives clearly, and which is able to provide sophisticated device testing in a fully operational environment. Other intangible benefits include that of exposing LANL personnel to new technologies and materials, and having them work with GM personnel in product development.

Benefit to DOE Programs

Chemical and combustion sensing is becoming an increasingly important aspect of the reconfigured DOE complex. We have developed spin off chemical sensing technologies of importance to the Fossil Fuel Energy programs, Energy Efficiency Programs and transportation Programs.

DOE Facility/LANL Point of Contact for Project Information

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Company Size and Points of Contact

General Motors is one of the 10 largest corporations in the United States.

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