LAWRENCE LIVERMORE NATIONAL LABORATORY

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On-Board Sensor Diagnostics for Catalytic Converters Final Report CRADA No. TC-0882-94

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On-Board Sensor Diagnostics for Catalytic Converters

Project Accomplishments Summary
CRADA No. TC-0882-94

Date: July 1, 1999 Revision: 4

A. Parties

The project is a relationship between the Lawrence Livermore National Laboratory (LLNL) and Chrysler Corporation (Chrysler), General Motors Corporation (GM), Ford Scientific Research Laboratory.

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B. Background

General background:
The auto industry is one of the largest and most important sectors of the U.S. economy. At the time of the CRADA, the Big Three U.S. auto makers (Chrysler, Ford and GM) alone employed 600,000 workers in this country and marketed some eight million new cars and trucks worth approximately $200 billion in sales revenues. When the impact of part

suppliers, steel, aluminum, and electronics producers were included, the effect of a downturn in U.S. car manufacturing had a nationwide impact on jobs and the economy. For example, U.S. auto makers used 1/7 of all U.S. steel production and 1/6 of all U.S. aluminum production. Transplant Japanese factories cannot be expected to compensate for reductions by U.S. auto makers; in fact, transplants resulted in a net loss of U.S. jobs. In 1991, the Big Three U.S. auto makers sold 8.8 million new cars and trucks with over 620,000 employees while the Big Three Japanese firms (Toyota, Nissan, and Honda) sold 2.4 million new cars and trucks with only 37,000 U.S. employees. It was estimated that the Japanese-owned, U.S.-located, auto assembly facilities enjoyed an $8-$9 an hour labor cost advantage over the U.S. Big Three by building new plants in rural areas and hiring young workers with smaller health care and pension needs. Most of the parts in the 2.4 million cars and trucks sold by Japanese auto makers come directly from Japan and the engineering activities were mostly performed in Japan before U.S. assembly began. The effect of these issues was reflected in the U.S. Japan trade imbalance; about two-thirds of Japan's trade surplus was attributable to autos and auto parts.

This project enhanced the competitiveness of U. S. auto manufacturers by improving the U.S. technology base in sensors for engine control. At the time of the CRADA, it was perceived that the Japanese currently led in this area. It was the objective of this project to give U. S. manufacturers a "leap frog" advantage.

Technology Background:
In 1994, the California Air Resources Board (CARB) and the U.S. EPA began implementing regulations that require automakers to incorporate comprehensive on-board diagnostics into new vehicles. The intent of these regulations is to inform the vehicle operator when emission control systems are no longer performing adequately. The most important measure of the operational capacity of the catalytic converter is the concentration of non-methane hydrocarbons (NMHCs) in the exhaust. California regulations limit NMHC concentrations to approximately 25 ppm over the Test Protocol Cycle (FTP) in tailpipe exhaust for the mandated Low Emission Vehicles (LEVs).

The objective of the LLNL work is to develop novel solid-state electrochemical sensors for NMHCs and carbon monoxide (CO) for automobile emissions monitoring. Currently, the electrochemical oxygen sensor is by far the one most commonly used for automobile emissions control. Therefore, electrochemical sensors are a proven technology in terms of reliability, durability, cost, and integration. Solid-state electrochemical sensors are based upon ceramic materials, and are typically layered structures consisting of an ion conducting electrolyte sandwiched between two electrodes. One side of the device is exposed to a reference gas (e.g., air) and the other is exposed to the exhaust. The voltage developed across the sensor corresponds to the concentration of the gas phase component of interest in the exhaust.

In this CRADA our initial effort has been directed towards the development of a sensor for NMHCs, since their measurement is of primary importance with regard to evaluating the performance of the catalytic converter. In FY98, building upon the accomplishments of FY97, work will also begin on the development of a sensor for CO. In the final stage of this work, we will combine the two sensors on a single substrate. Potential for mass fabrication will be considered so that this technology can be easily transferred to industry for commercialization. Completion of this work, and preparation for commercialization will occur in FY00.

Some remarkable progress has been made in FY97, including the development of a new sensing approach based upon proton conducting materials; the development of a novel, stable catalyst; and, a new thin film sensor electrolyte fabrication method. As evidence of our progress, prototype LLNL hydrocarbon sensors are now undergoing rigorous dynamometer testing in the CRADA partners laboratories. This will be summarized below. However, several technology barriers remain to be overcome. These include further improvements of the sensor to achieve even lower sensitivity (ability to measure down to 25 ppm NMHCs in exhaust); an all-thin-film sensor fabrication method (catalyst layer included); further investigation and improvements in catalyst stability; investigation and elimination of potential sensor cross-sensitivity to other exhaust gases; investigate the potential for resistance to sulfur poisoning; understanding the relation of sensor results to the standard industry exhaust gas certification laboratory measurement using a flame ionization detector (FID) (which operates on very different principles from any sensor); and, packaging and mass fabrication considerations.

C. Description

The goal of this collaboration was to develop a prototype sensor, or a sensor array, which could be used for monitoring the performance of the catalytic converter system. It would demonstrate the potential to quantify the level of deterioration, to ensure compliance with environmental regulations. This work involved a collaboration between LLNL, LANL, ORNL, Y-12, and USCAR. Collectively, the project focused on the development of solid-state electrochemical sensors based upon fast ion conductors and semiconducting oxides. LLNL considered both potentiometric and amperometric devices.

Program Activities and Summary of Accomplishments:

In order to better understand the technical objectives accomplished in FY97, a schematic of the LLNL hydrocarbon sensor with identification of sensor components is shown in Fig. 1. The sensor consists of four active parts: a catalyst layer, two electrodes (an anode on the left and a cathode on the right), and a ceramic oxide proton conductor electrolyte. In addition, a porous ceramic material is used to protect the catalyst from direct contact with the exhaust. A voltage measured across the two electrodes is proportional to the concentration of NMHCs in the exhaust gas. Additional general

information regarding solid-state electrochemical sensors, and the LLNL design can be found elsewhere (1). In Fig. 1, the proton conducting electrolyte used is $SrZr_{0.9}Y_{0.1}O_3$, the electrodes are made of gold, and a proprietary catalyst has been developed to promote the sensing mechanism. The materials science used to develop the catalyst was the crowning achievement of FY97, and patents are in preparation for this technology (2). Using the design shown in Fig. 1, sensitivity to NMHCs at levels below 100 ppm has been accomplished.

The primary goals for FY97, all of which were accomplished with great success, were to:

1. Reduce the proton conducting electrolyte resistance by developing a thin film processing technology.

2. Develop a catalyst that is stable in reducing environments found in exhaust gas.

3. Fabricate and test a prototype hydrocarbon sensor in realistic exhaust gases (dynamometer testing) and initiate testing of an improved thin-film electrolyte sensor.

Very promising results for the hydrocarbon sensor have been demonstrated both in the laboratory and under realistic automobile exhaust testing (dynamometer) at Ford Research Laboratories. Fig. 2 shows the response of a recent sensor (using a thin film electrolyte, see below) to varying concentrations of hydrocarbons (using ethane, C_2H_6, as a model). The sensor is reproducible and has a moderate and workable response time (less than 15 s). Data for an earlier prototype sensor (which used the less sensitive thick film ceramic electroyte) challenged in dynamometer testing is shown in Fig. 3. As is seen in this figure, there is a direct correlation between the sensor response (Emf) and the hydrocarbon concentration measured downstream using the FID method. Additional information regarding the laboratory and dynamometer testing of the LLNL NMHC sensor is provided elsewhere (3,4).

In addition to good hydrocarbon sensitivity and reproducibility for the sensor, the LLNL NMHC sensor has several other desirable attributes. These include: relative insensitivity to temperature variation; no cross-sensitivity to CO or hydrogen; the sensor shows no response to methane, as desired; the catalyst is stable up to at least 900 °C; durability; simplicity; potential for low cost manufacturability; and, small size.

Recently, we have developed a thin film sensor fabrication method which should make the sensor even more sensitive to NMHCs. The thin film method has involved developing a process to create sub-micron powders of the electrolyte and a subsequent novel processing method to create self-standing thin films. Initial testing indeed shows higher sensor sensitivity and a much faster response time has been noted. The schematic for the thin film sensor and an actual sensor now being used in the laboratory and dynamometer tests is shown in Fig.4.

To summarize, during FY97 we have accomplished the following major objectives:

- We have prepared a ceramic NMHC sensor with improved stability
- A new dehydrogenation catalyst has been prepared and characterized
- A thin film sensor fabrication method has been developed
- The first generation thin film electrolyte NMHC sensor has been demonstrated

- An improved LLNL ceramic (thick film) sensor was dynamometer tested at Ford and showed promising results

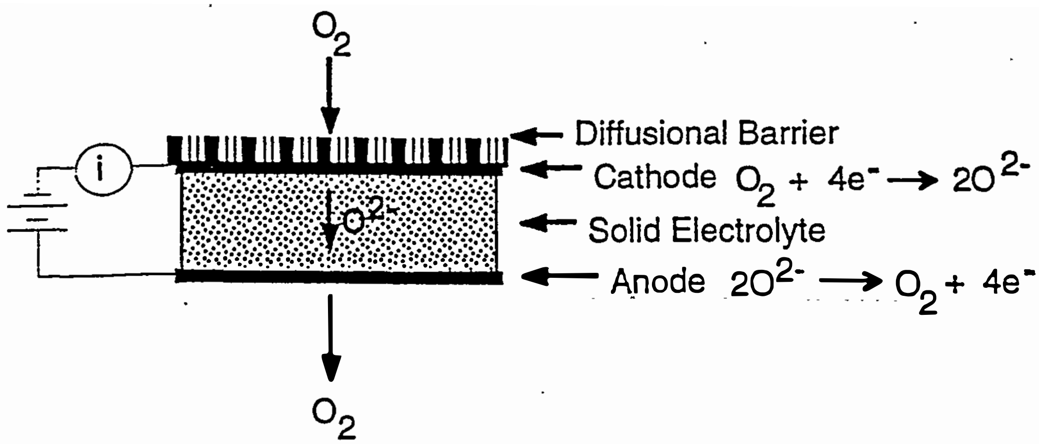

Figure 1. Linear amperometric O_2 sensor using a diffusion barrier.

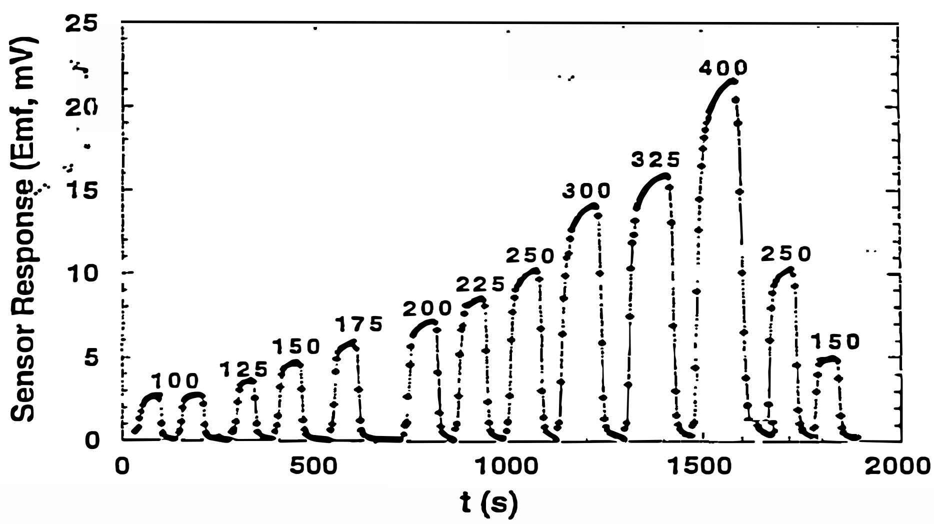

Figure 2. Response of LLNL thin film electrolyte sensor to varying ethane concentration. The numbers in the figure correspond to the concentration of ethane in parts-per-million.

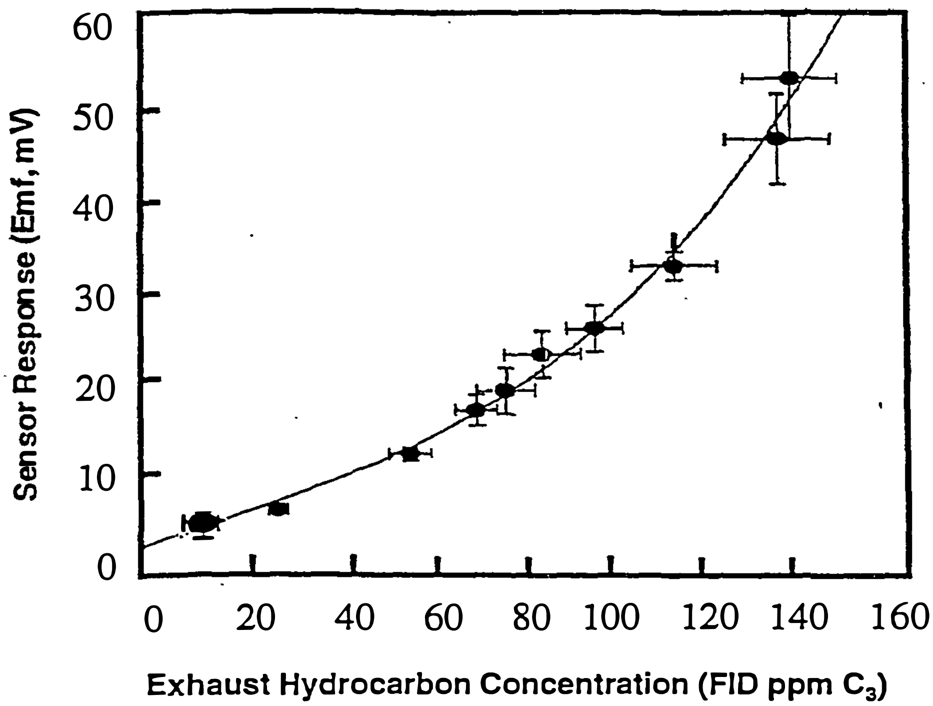

Figure 3. Engine dynamomter testing (4.6L V8) of LLNL NMHC sensor.

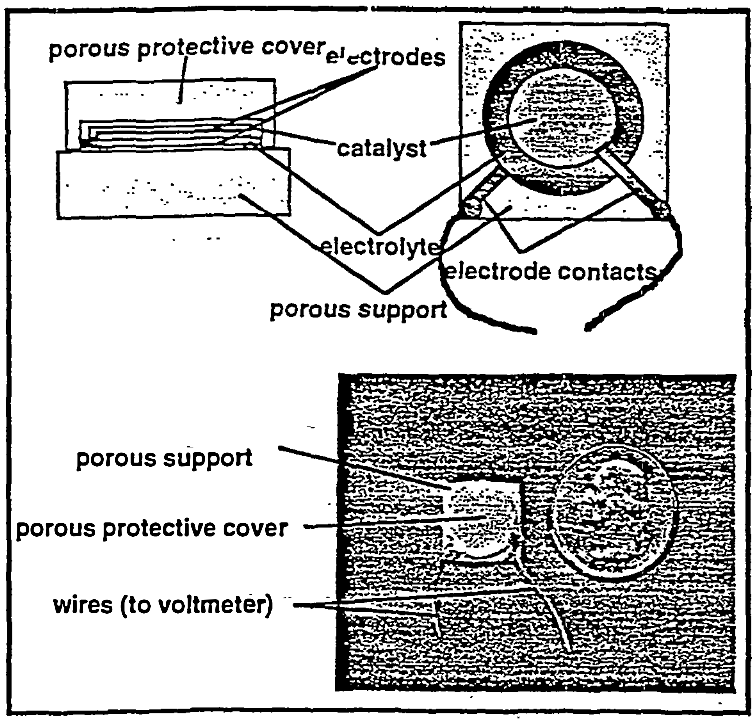

Figure 4. LLNL thin film hydrocarbon sensor

D. Expected Economic Impact

At the time the CRADA was established, U. S. automobile manufacturers were being challenged by increasingly stringent exhaust emissions regulations and the need to increase fuel economy. "Lean burn" engines were under development. Sensors, placed in the exhaust stream would aid in engine management and reduce emissions. Such sensors would, in fact, be crucial to the future survival of the U. S. automobile industry. The Japanese appeared to be ahead in the development both of "lean burn" engines as well as sensors for exhaust control and engine management. The DOE/DP Laboratories had developed several technologies for environmental sensing. This technology, and the extensive materials fabrication and characterization facilities available in the DOE/DP laboratories, was expected to significantly aid the U. S. automobile industry in the development of exhaust gas sensors.

Relation to PNGV Goals:
PNGV is committed to the development of automobiles having reduced emissions and better fuel economy. This work will help develop sensor diagnostics which will allow automobile manufacturers to meet EPA and California emission laws.

E. Benefits to DOE

The DOE laboratories and plants were facing increasing governmental and public scrutiny with regard to compliance with environmental regulations. Environmentally-conscious manufacturing and R&D operations, which involved environment, safety, and health issues, and the reduction of waste, were receiving much attention. There was a clear need for sensor technology both for environmental monitoring and for process control. Senses were needed for gaseous emissions.

As for the automobile industry, electrochemical sensors were one of the sensor technologies of choice because of the high sensitivity and low cost. Sensors would be used in the remediation of DOE sites which had become contaminated with radioactive or toxic waste. Finally, the development of generic sensor technology which could be useful in treaty verification, both for nuclear as well as chemical weapons, would also be of obvious benefit.

This project enhanced DP Laboratory competencies in materials science and microfabrication. The type of materials to be deposited, and the sensors to be developed were unusual and the experience gained would be beneficial. It was an ideal type of project for LLNL. It required multidisciplinary expertise found at The Laboratory.

The DOE committed itself to the development of fuel efficient, "clean" transportation. This project clearly contributed to that goal. Finally, industry in California was particularly regulated with regard to stack emissions.

Another benefit of this work was that it would allow LLNL to develop a technology base in the development of gas-phase electrochemical sensors. In fact, there was a direct overlap between what was needed for industry and what was mandated for automobiles. LLNL was able to act as a resource for California, and the nation, for gas sensor technology. Contributions to enhanced industrial economic competitiveness, other than automotive, and the ability to comply with clean air legislation, were additional benefits of this research.

Relation to DOE's mission:
The DOE needs gas phase sensors for a variety of applications. In particular, they are needed for weapons manufacturing activities, specifically in high explosive and tritium processing. The hydrocarbon sensor we are developing for automotive applications could also be used for monitoring tritium release and could be used in a tritium capture system. Sensors are also needed in enhanced surveillance and in monitoring emissions produced in demilitarization facilities (burns and detonations) to ensure environmental and worker safety. The rugged sensors we are developing for exhaust gas monitoring could also be useful in demilitarization. Finally, this project enhances Laboratory core competency in applied materials science which is relevant to weapons production.

F. Industry Area
Automotive, electronics

G. Project Status

This project is ongoing. The expected date of completion is September 31, 2000.

H. LLNL Point of Contact for Project Information

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I. Company Size and Point(s) of Contact

General Motors' annual sales are $177 billion, and the company employs 680,000 people.

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Ford Motor Company's annual sales are $122 billion, and the company employs 363,892 people.

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Chrysler Corporation's annual sales are $61 billion, and the company employs 121,000 people.

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J. Project Examples

There are dime-size and smaller working sensors that have been used for exhaust gas monitoring in full-up dynamometer tests.

Background Intellectual Property

No Background Intellectual Property was disclosed by any of the participants.

Publications from CRADA:

1. R. S. Glass and A. Q. Pham, "Challenges in the Development of Sensors for Monitoring Automobile Emissions," in Proceedings International Symposium on Automotive Technology and Automation, Florence, It., June 16-19, 1997.

2. A. Q. Pham and R. S. Glass, "A Novel Sensor for Hydrocarbons Based Upon Proton Conductors," in preparation.

3. D. Thompson, J. H. Visser, A. Q. Pham, R. S. Glass, and E. M. Logothetis, "Results of Dynamometer Testing of a Novel Hydrocarbon Sensor Based Upon Proton Conductors," in preparation.

Subject Invention:

A. Q. Pham and R. S. Glass, "Hydrocarbon Sensor," LLNL ROI No. CIL-10130 (February, 1997).

K. Release of Information

I certify that all information contained in this report is accurate and releasable to the best of my knowledge.

____

Karena McKinley, Director
Industrial Partnerships
and Commercialization

Date

RELEASE OF INFORMATION

I have reviewed the attached Project Accomplishment Summary prepared by Lawrence Livermore National Laboratory and agree that the information about our CRADA may be released for external distribution.

* Galen B. Fisher 7/26/2000

Galen Fisher, Principal Research Scientist
General Motors Corporation (now Delphi Research Labs, Delphi Automotive Systems)

Date

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Theros Logothetis, Corporate Technical Specialist
Ford Scientific Research Laboratory

Date

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Anson Lee, Engineering Manager
Daimler Chrysler AG

Date

Robert S. Glass 8-23-00

Robert Glass, Principal Investigator
Lawrence Livermore National Laboratory

Date

* I am signing this as the technical person who was most familiar with the work at the time much of it was done, even though I am no longer a General Motors employee.

K. Release of Information

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Karena McKinley, Director
Industrial Partnerships
and Commercialization

Date

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Galen Fisher, Principal Research Scientist
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Theros Logothetis, Corporate Technical Specialist
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Date

3/28/2000

Anson Lee, Engineering Manager
Daimler Chrysler AG

Date

Robert Glass, Principal Investigator
Lawrence Livermore National Laboratory

Date

K. **Release of Information**

I certify that all information contained in this report is accurate and releasable to the best of my knowledge.

____

Karena McKinley, Director — Date
Industrial Partnerships
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RELEASE OF INFORMATION

I have reviewed the attached Project Accomplishment Summary prepared by Lawrence Livermore National Laboratory and agree that the information about our CRADA may be released for external distribution.

____

Galen Fisher, Principal Research Scientist — Date
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retired → ~~Theros Logothetis, Corporate Technical Specialist~~ — Date
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Jacobus H. Visser, Senior Technical Specialist

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Anson Lee, Engineering Manager — Date
Daimler Chrysler AG

8-23-00

Robert Glass, Principal Investigator — Date
Lawrence Livermore National Laboratory

K. Release of Information

I certify that all information contained in this report is accurate and releasable to the best of my knowledge.

Karena McKinley — 8/23/00

Karena McKinley, Director
Industrial Partnerships
and Commercialization — Date

RELEASE OF INFORMATION

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* Galen B. Fisher — 7/26/2000

Galen Fisher, Principal Research Scientist — Date
General Motors Corporation (now Delphi Research Labs, Delphi Automotive Systems)

Theros Logothetis, Corporate Technical Specialist — Date
Ford Scientific Research Laboratory

Anson Lee, Engineering Manager — Date
Daimler Chrysler AG

Robert Glass, Principal Investigator — Date
Lawrence Livermore National Laboratory

* I am signing this as the technical person who was most familiar with the work at the time much of it was done, even though I am no longer a General Motors employee.