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LLNL-TR-820977

NOx Sensor for Monitoring Emissions, CRADA TC02179.0

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Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

NO_X Sensor for Monitoring Emissions

Final Report
CRADA No. TC02179.0
Date Technical Work Ended: September 6, 2014

Date: March 6, 2017 Revision: 0

A. Parties

This project was a relationship between Lawrence Livermore National Security (LLNS) and EmiSense Technologies, LLC.

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EmiSense Technologies, LLC
4205 West 1980 South
Salt Lake City, UT 84104

Technical Contact: Jim Steppan
Tel: (801) 204-9506, ext. 444
Email: jsteppan@emisense.com

B. Project Scope

This was a collaborative effort between Lawrence Livermore National Security, LLC as manager and operator of Lawrence Livermore National Laboratory (LLNL) and EmiSense Technologies, LLC, to develop a commercial NO_x sensor and suitable electronics.

For over ten years, LLNL has been involved with developing solid-state electrochemical gas sensors for monitoring emissions with EmiSense. This collaboration has also included a strong research interaction with Ford Motor Company. LLNL has focused on materials structure-properties relationships and electrochemical evaluation to understand sensing mechanisms and guide sensor development. In 2005, LLNL began pursuing a unique alternating current (ac) impedance-based (i.e., impedancemetric) sensor with potential advantages over more traditional direct current (dc) methods of operation.

In 2009, EmiSense was formed via a merger of assets, intellectual property, product lines, trade secrets, and capital from CoorsTek, Inc. and Innovate! Technology, Inc. Prior to this merger, the EmiSense research team developed advanced emissions sensor technology as a part of Ceramatec, a CoorsTek research and development subsidiary. EmiSense integrates CoorsTek intellectual property and high-volume global manufacturing capacity with Innovate's sensor technology and signal-processing patents. EmiSense is focused on converting breakthrough science into tangible smart sensors products with capabilities that include thermal and mechanical element modeling, advanced electronic test and characterization, tape casting, printing, via filling, high-temperature sintering, laminating, laser cutting, thermal imaging, prototyping, durability analytics, and high-resolution microscopy. EmiSense licensed the LLNL NO_x sensor technology in 2011.

This CRADA was originally designated as a thirty (30) month project, and consisted of four (4) major tasks with subtasks, and the following deliverables:

Task 1:	Develop Laboratory prototype with optimized geometry/processing using information from electrochemical evaluation (LLNL) Month 10
Task 2:	Develop pre-commercial prototype design with temperature control solution (EmiSense) Month 18
Task 3:	Develop pre-commercial prototype circuit design (EmiSense) Month 24
Task 4:	Develop pre-commercial prototype sensor combining temperature control solution and circuit design appropriate for vehicle/engine testing at Ford Motor Company (EmiSense) Month 28
Tasks 4.1-4.2:	Draft Final Report and Abstract due within thirty (30) days of completion or termination of the project, as required under Article XI of the CRADA. (LLNL/EmiSense) Month 30

C. Technical Accomplishments

The specific technical accomplishments were to design, fabricate, and demonstrate a commercial NO_x sensor, develop electronics that are suitable for a feed gas NO_x sensor, and perform sensor validation testing with Ford Motor Company.

Automotive exhaust sensor development has typically focused on solid-state electrochemical technology, which has proven to be robust for in-situ operation in harsh, high-temperature

environments (e.g., the oxygen stoichiometric sensor). Electrochemical sensors can be operated in various modes, including amperometric and potentiometric, both of which are more common methods that employ direct current (dc) measurements. This CRADA used a unique approach developed by LLNL that operates the sensor in a different mode, impedancemetric, which involved alternating current (ac) measurements at a specified frequency. This approach has shown the potential to overcome the drawbacks of other dc methods using similar or related materials, resulting in higher sensitivity towards NO_x, better long-term stability, ability to subtract out background interferences, total NO_x measurement, and lower cost materials and operation.

D. Expected Economic Impact

The global market for NOx sensors is estimated to be $2.5B by 2020, with growth driven by a combination of factors, including increasing use of diesel light vehicles to achieve efficiency goals, regulatory phase ins on all diesel combustion systems, and emerging market demand. This technology has the potential to create thousands of jobs in manufacturing, engineering and product management, and to bring the cost of emissions control down.

D.1 Specific Benefits

Benefits to DOE

This CRADA addresses the DOE goal of increasing energy security in the transportation sector by reducing oil consumption and emissions of CO2, both of which are supported with NOx sensor technology.

Benefits to Industry

The new sensor has the potential to overcome the drawbacks of existing sensors, resulting in higher sensitivity towards NO_x, better long-term stability, less cross-sensitivity to other exhaust-gas constituents, and lower cost materials and operation. EmiSense licensed the technology and plans to make it commercially available in 2018.

E. Participant Contribution

Late 2012: Started work under the CRADA, including tasks in materials, processing, electronics, and testing. No tasks completed or milestones achieved.

Early 2013: Continued work under the CRADA, including tasks in materials, processing, electronics, and testing. "Voltage-Current Time Differential Method for Operating Electrochemical Sensors" (LLNL disclosure IL12816)

Late 2013: Continued work under the CRADA, including tasks in temperature control, processing methods, multiple-frequency and multiple-waveform electronics, and testing.

Early 2014: Continued work under the CRADA, including tasks in temperature control, processing methods, multiple-frequency and multiple-waveform electronics, and testing.

Late 2014: Completed work under the CRADA, and executed first round of characterization of cross sensitivities to oxygen, water, and ammonia.

F. Documents/Reference List

None

Reports

None

Copyright Activity

None

Subject Inventions

U.S. Patent Application No. 14/055562 [US Published Patent Application No. 20150101937], *Electrochemical Sensing Using Voltage-Current Time Differential;* LLNS Inventors: Leta Yar-Li Woo, Robert S. Glass / EmiSense Inventors: Joseph Fitzpatrick, Ganggiang Wang, Brett Henderson, Anthoniraj Loudhusman, Jim Steppan, Klaus Allmendinger; Filing Date: 10/16/13 (IL12816)

EmiSense licensed the above subject invention through a license amendment executed on September 22, 2015, which added this patent to EmiSense's existing Limited Exclusive Patent License Agreement with LLNL (TL02521), effective June 17, 2011.

Background Intellectual Property

LLNL disclosed following Background Intellectual Property for this project:

U.S. Patent Applications:

U.S. Patent Application No. 12/427,194 [US Published Application No. 20090223836], *Frequency Technique for Electrochemical Sensors*, Inventors: Jacobus H. Visser; Robert F. Novak; Erica Perry Murray; Leta Yar-Li Woo; Robert S. Glass; Louis P. Martin; Filing Date: 4/21/09 (IL12048A)

U.S. Patents:

U.S. Patent No. 7,153,401, *Current-Biased Potentiometric NOx Sensor for Vehicle Emissions*; Inventors: Louis P Martin, Ai Quoc Pham; Filing Date: 2/27/03; Issue Date: 12/26/06 (IL11022A)

U.S. Patent No. 8,177,957, *A Multiple Frequency Method for Operating Electrochemical Sensors*; Inventor: Peter Martin; Filing Date: 8/16/07 / Issue Date: 5/15/12 (IL11679A)

EmiSense executed a Limited Exclusive Patent License Agreement for the background intellectual property, effective June 17, 2011.

EmiSense Technologies, LLC:

EmiSense disclosed the following Background Intellectual Property:

U.S. Patent Application No. 12/134,832, *Pulse Width Modulation Wideband Ion Sensor*

U.S. Patent No. 6,978,655, *System, Apparatus, and Method for Measuring an Oxygen Concentration of a Gas*

U.S. Patent No. 7,089,811, *System, Apparatus, & Method for Guiding and Exhaust Gas*

U.S. Patent No. 7,249,489 (Divisional), *System, Apparatus, and Method for Measuring an Oxygen Concentration of a Gas*

Brazilian Patent Application No. 0810966-4, *System, Apparatus, and Method for Measuring an Ion Concentration of a Measured Fluid*

Chinese Patent Application No. 200880018785.8, *System, Apparatus, and Method for Measuring an Ion Concentration of a Measured Fluid*

German Patent Application No. 11 2008 001 147.8, *System, Apparatus, and Method for Measuring an Ion Concentration of a Measured Fluid*

Indian Patent Application No. 5389/DELNP/2009, *System, Apparatus, and Method for Measuring an Ion Concentration of a Measured Fluid*

Japanese Patent Application No. 2010-511358, *System, Apparatus, and Method for Measuring an Ion Concentration of a Measured Fluid*

Korean Patent Application No. 10-2009-7023261, *System, Apparatus, and Method for Measuring an Ion Concentration of a Measured Fluid*

G. Acknowledgement

Industrial Participant's signature of 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 generated by his/her respective company and attributable to the project have been disclosed and included in Section E or are included on a list attached to this report.
4) The Participant certifies that if tangible personal property was exchanged during the agreement, all has either been returned to the initial custodian or transferred permanently.
5) The Participant certifies that proprietary information has been returned or destroyed by LLNL.

4-11-17

Patrick Thompson, Chief Executive Officer — Date
EmiSense Technologies, LLC

4/12/17

Roger Aines, LLNL Program Leader — Date
Lawrence Livermore National Security

4/13/17

Michael S. Sharer, Manager, Technology Commercialization — Date
Lawrence Livermore National Security

Attachment I – Final Abstract

NO_X Sensor for Monitoring Emissions

Final Abstract (Attachment I)
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C. Benefit to Industry

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D. Benefit to DOE/LLNL

This CRADA addresses the DOE goal of increasing energy security in the transportation sector by reducing oil consumption and emissions of CO2, both of which are supported with NOx sensor technology.

E. Project Dates

March 6, 2012 to September 6, 2014