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LIVERMORE  
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LLNL-TR-820977

# NOx Sensor for Monitoring Emissions, CRADA TC02179.0

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March 30, 2021

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# NO<sub>x</sub> Sensor for Monitoring Emissions

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## Final Report

CRADA No. TC02179.0

Date Technical Work Ended: September 6, 2014

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Date: March 6, 2017

Revision: 0

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### A. Parties

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

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### 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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> sensor, develop electronics that are suitable for a feed gas NO<sub>x</sub> 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<sub>x</sub>, better long-term stability, ability to subtract out background interferences, total NO<sub>x</sub> measurement, and lower cost materials and operation.

## **D. Expected Economic Impact**

The global market for NO<sub>x</sub> 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 CO<sub>2</sub>, both of which are supported with NO<sub>x</sub> sensor technology.

#### Benefits to Industry

The new sensor has the potential to overcome the drawbacks of existing sensors, resulting in higher sensitivity towards NO<sub>x</sub>, 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, Ganggang Wang, Brett Henderson, Anthoniraj Loudhusman, Jim Stepan, 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 NO<sub>x</sub> 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*

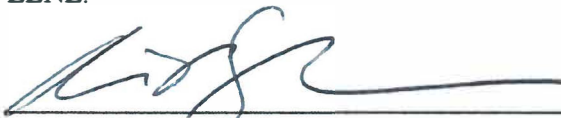
Japanese Patent Application No. 2010-511358, *System, Apparatus, and Method for Measuring an Ion Concentration of a Measured Fluid*

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:

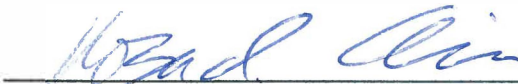
- 1) The Participant has reviewed the final report and concurs with the statements made therein.
- 2) The Participant agrees that any modifications or changes from the initial proposal were discussed and agreed to during the term of the project.
- 3) The Participant certifies that all reports either 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.



Patrick Thompson, Chief Executive Officer  
EmiSense Technologies, LLC

4-11-17

Date



Roger Aines, LLNL Program Leader  
Lawrence Livermore National Security

4/12/17

Date



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

4/13/17

Date

Attachment I – Final Abstract



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## **NO<sub>x</sub> Sensor for Monitoring Emissions**

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**Final Abstract (Attachment I)**

**CRADA No. TC02179.0**

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## **B. Purpose and Description**

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<sub>x</sub> sensor and suitable electronics.

## **C. Benefit to Industry**

The new sensor has the potential to overcome the drawbacks of existing sensors, resulting in higher sensitivity towards NO<sub>x</sub>, 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.

## **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 CO<sub>2</sub>, both of which are supported with NO<sub>x</sub> sensor technology.

## **E. Project Dates**

March 6, 2012 to September 6, 2014