



Project Accomplishment Summary

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Sandia National Laboratories

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Sandia Corporation
Albuquerque, New Mexico

PROJECT ACCOMPLISHMENTS SUMMARY

Cooperative Research and Development Agreement (#SC13/01800.01)

between **Sandia National Laboratories** and **International Electronic Machines Corporation**

Note: This Project Accomplishments Summary will serve to meet the requirements for a final abstract and final report as specified in Article XI of the CRADA. Additionally, a final report was written and submitted to IEM and is available through SNL (SNL report tracking number 308290).

Title: Wireless Chemical Sensor Systems (Optimization of Field-Structured Chemiresistors for *in situ* Quantification of Propellant Stabilizer Concentration)

Final Abstract:

This project is a Cooperative Research and Development Agreement (CRADA) with International Electronic Machines Corp. (IEM, Troy, NY), who is contracted through the U.S. Naval Air Systems Command (NAVAIR) (under SBIR N111-010) to develop an *in situ* wireless chemical sensor system called the Stabilizer Level Accurate Measurement System (SLAMS). The SLAMS device is specified to include a miniature, very thin, self-contained chemical-sensor node to detect and track the level of stabilizer present in various PADs and CADs. IEM is focused on the wireless sensor platform, node communication, and electronics; whereas Sandia National Laboratories' (SNL's) efforts are focused on the chemical sensor development and integration. The sensor technology being employed is known as field-structured chemiresistors (FSCRs), which was invented by James Martin, et al. (SNL) and refined by Martin and Read. These sensors are small, require very little power, and have tunable sensitivity and selectivity. In the following, we discuss SNL's efforts to optimize the FSCRs for the demanding chemical and environmental conditions that will be encountered in this application.

FSCRs are, in essence, strain sensors, wherein—in the case of chemical detection—the strain is induced by chemical vapors swelling the sensor composite. Therefore, sensor sensitivity can be increased by maximizing the affinity for a chemical to absorb into and swell the composite. We have conducted research to determine the sorption affinities of diphenylamine (DPA), 2-Nitrodiphenylamine (2-NDPA), and 2,4-dinitrodiphenylamine (2,4-DNDPA) with the polymers polydimethylsiloxane (PDMS), trifluoropropyltrimethoxysilane (TFPMS), diphenyl- polymethylsiloxane (DP-PMS), and polyethylene glycol (PEG). Based on these sorption measurements it is determined that the diphenyl-PMS is the best candidate polymer for a DPA-selective chemiresistor. We have successfully detected saturated DPA with PDMS based FSCRs at 40 and 55°C (16.5 and 37ppm DPA, respectively) with an array of chemiresistors—although the response time to DPA is found to be exceptionally long (on the order of hours). To explore this concerning observation, we have modeled the response time of the sensors as a function of DPA saturation vapor-pressure/concentration, which we have in turn modeled as a function of temperature and altitude. The data we have collected and calculated give rise to a serious concern that the extremely low vapor pressures of the stabilizers may inhibit the practical, vapor-phase monitoring of these compounds *in general*. This is due not only due to the retardation of the polymer sorption kinetics, but also—and more generally— due to the slow kinetics of the transient vapor-liquid phase equilibrium, which would be subject to a convoluted time lag when subjected to relatively fast changes in the environment; namely temperature and altitude (atmospheric pressure).

Based on the sorption measurements, we have formulated a polymer to have both the material/mechanical properties necessary for chemiresistor use, as well as increased selectivity to the propellant stabilizers. This polymer is a PDMS elastomer backbone with appended diphenyl functional groups, which are designed to interact with the phenyl groups constituting the stabilizers. Several FSCR sensors employing this novel polymer were fabricated and a subset of these was tested simultaneously with traditional PDMS sensors to varying concentrations of DPA vapor. The DP-PMS sensors showed over a 2.6-fold increase in sensitivity to DPA. In addition, DPA vapor absorption into PDMS and DP-PMS polymer samples was measured gravimetrically. These data show a 3.4-fold increase in swelling at identical DPA vapor concentrations.

In light of the extraordinarily long FSCR response times to DPA, FSCR sensors were specially fabricated with thinner composite films. The thinnest, and fastest sensor, yielded a 15.4-fold decrease in response time to DPA at 80°C compared to a control sensor with similar sensitivity. Although these experiments show that response time can be dramatically improved, we discuss the additional complexities arising from the highly variable stabilizer vapor pressures due to temperature fluctuation. It is shown that the response time of an FSCR is *super*-exponentially dependent on temperature, which results in a 47-fold span in response time between 0–40°C. This dependence is inherent to any such polymer-sorption-based, vapor-detection sensor.

Subsequently, several experiments were performed in an effort to decrease the chemiresistor composite thickness while maintaining the properties necessary for sensor performance. It is, however, found to be very difficult to control the polymer-composite thickness in practice—especially in the regime of extremely thin films. The experimental fabrication methods we have investigated include: aerosol spray coating, solvent-cast drop coating, and ultra-fine paint coating. Another complexity that arises when attempting to deposit thin composite layers is the relative size of the particle to the thickness of the composite. It is necessary to decrease the particle size to well below the desired composite thickness to ensure mobility of the particle phase during field-structuring, as well as ensuring an appreciable number of conductive network chains exist throughout the thickness of the composite (i.e. sufficient polymer encapsulation). In an effort to decrease the particle size, we experimented with nanoparticles as the composite particle phase. However, gold-plated nickel nanoparticles are not currently commercially available, and in-house gold-coating methods to produce conductive, magnetic particles in the nanoscale have not yielded sufficiently conductive sensors. However, with the successful implementation of nanoparticles, we anticipate a composite thickness that is 500 nm to 1µm (for current FSCR composites, 100µm would be considered very thin). Since analyte-absorption time, and therefore sensor response time, increases proportionately with the square of the polymer thickness, this would lead to a 10,000-fold reduction in response time for the case of going from a 100µm thick composite to 1µm.

Sensors were fabricated with traditional gold-plated nickel microparticles using the above-mentioned experimental composite deposition methods. Composite-thickness measurements were obtained for these various deposition methods with a very precise micrometer. The lower limit of mean film thicknesses measured 20 ± 10 , 26 ± 9 , and $30 \pm 10 \mu\text{m}$ for the nanoparticle, airbrushed, and paint-brushed sensors, respectively; whereas, control FSCR composite thickness was measured at $183 \pm 45 \mu\text{m}$. This translates to a 9.5–7 -fold decrease in thickness for the new coating methods. Response times to DPA were measured for sensors of each type resulting in decreases in response time by a factor of seven for the thinnest sensors over previously fabricated solvent-cast, “thin” sensors. Thinner coatings did decrease the reproducibility of the sensor-to-sensor conductivity, and a significant portion of the sensors (~23%) were non-conductive. This is explained by the observation that it is very difficult to control the particle loading when applying thin, decreased viscosity, composite precursor films.

As an addendum (after this report was initially written) efforts were continued for the development of fabrication methods for ever-thinner chemiresistor composites. One such vein is research to employ non-agglomerated magnetic, conductive nanoparticles as the particle phase to allow for extremely thin composite films. The nanoparticle synthesis was subcontracted to NanoComposix Inc. (San Diego, CA) who provided 165mg of 300nm nanoparticles in silicone resin. The particles are comprised of a magnetite (Fe_3O_4) core, coated with a silica shell for stability, and finally capped by a gold shell for electrical conductivity. These nanoparticles formed thin composites with evident chain structures, but were found to not have sufficient conductivity to render conductive composites.

NanoComposix determined during their experiments that a ligand or capping agent must be used to maintain nanoparticle morphology and prevent agglomeration (the latter being necessary to maintain thin composites). It is hypothesized that the conductivity was hampered by a lipoic acid capping agent that NanoComposix chose under the assumption that it would give the best reasonable chance of being conductive. Several experiments were undertaken at both NanoComposix and SNL to remove the lipoic acid from the surface of the nanoparticles while in the uncured polymer suspension. However, none of these methods yielded adequately conductive composites.

Despite the lack of success in fabricating a *conductive*, field-structured-nanoparticle composite, significant progress was made toward thinner composite films with traditional gold-plated nickel microparticles. The fabrication of these sensors involves a *stamp* method for depositing the thinnest microparticle films yet. The stamp procedure entails brushing a thin layer of uncured, solvent -cast silicone onto a small cured silicone stamp. The uncured silicone is then stamped onto the sensor substrate, which leaves a very thin and uniform film. Dry microparticles are then added on top of this film and the excess/non-adhered particle powder is then blown off with compressed nitrogen. The composite is then cured as it normally would in a magnetic field at temperature. Using this method, we have demonstrated the fastest characteristic response times to date with $\tau = 62\text{s}$ for DPA at 80°C , whereas the control sensors had $\tau = 740\text{s}$. Previous thinning methods had yielded sensors with typical characteristic response times between 160s and 250s. At 25°C the 99% equilibrium response of these new stamped sensors is ~ 1 hour to DPA. Conversely, the control sensors would take 6.3 days to reach this point at the same conditions. This is a 13-fold decrease in response time and enables this sensor technology to succeed in detecting these extremely low-volatility propellant stabilizers in a real-world environment. 50 sensors were fabricated using the stamp method and Sulzer-Metco particles and checked for conductivity and are being shipped to IEM.

A simulation was written in MATLAB to model the depletion of propellant stabilizers as a function of time and variable temperature supplied by the user. This particular simulation modeled the depletion of DPA from 2 to 0.2 wt% DPA in the single-base propellant systems, NC-27 and GP A5020. Results showed that for the average temperatures in Riyadh, Saudi Arabia that DPA reached 0.2% wt. in ~ 80 years. This simulation code is supplied in Appendix C for use for any propellant system for which temperature data is provided and reaction rate constants for stabilizer depletion is known.

Investigation into sensors for NO_x detection in a SLAMS sensor platform reveals that it may be *possible* to develop such a sensor; however, there are fundamental operating limitations to the current NO_x sensor technologies that may be incompatible with the constraints inherent to a SLAMS device. Generally, NO_x detectors are operated at relatively high temperatures ($200\text{--}400^\circ\text{C}$) to achieve adequate sensitivity. Operation in air (or any oxygen containing environment) can lead to sensor degradation and a loss of sensitivity. Operating at lower temperatures can severely decrease sensitivity and increase response time to the order of hours. In addition, many types of NO_x sensors tend to be non-reversible *in situ*, i.e. they accumulate NO_x (and other) compounds until they are regenerated at high temperatures in an inert gas environment. It is our opinion that, NO_x sensor technology is not readily compatible with the SLAMS application. Although NO_x detection for SLAMS may be possible with a large research and development effort. Additional literature reviews have also not revealed any other promising sensor candidates—vapor-phase detectors or otherwise. Most applicable bench-scale techniques simply are not amenable to the SLAMS application due to prohibitive size, weight, power, and procedural complexity.

It is our concluding recommendation that future chemiresistor research for the SLAMS application be focused on further thinning the sensor composite for decreased response time to the stabilizers. In addition, it is necessary to characterize the effect of native PAD/CAD interferents (such as waxes and propellant constituents) on FSCR response to the stabilizers and daughter products. Further development and engineering would entail the fabrication of heteropolymer chemiresistor arrays for increased selectivity and wheat-stone bridge type configurations for temperature-effect mitigation.

Benefits to DOE that will result from this CRADA are two-fold; (1) SNL's Defense-Systems mission statement reads, "Defense Systems and Assessments supports the warfighter by accelerating the development of innovative systems, sensors, and technologies for the national security community." The goal for this specific application of this chemical sensor platform for this NAVAIR SBIR would ensure the safe and dependable operation of aircraft ejection seats and is directly in line with this mission. Although this sensor will not be fielded at the conclusion of this project, the progress made has yielded important strides toward solving this complex sensing (2) SNL has invested well over \$1M in the basic development of this sensor technology. However, funds have not been available to take this technology to the next level, which is an engineered system that is deployed in the field. This successful demonstration for a real-world application would attract future industry and government funding opportunities for continued research as well as patent licensing opportunities.

IEM has the benefit of expanding their wireless sensor technologies as well as the ability to license SNL intellectual property for commercialization of this system. Taxpayers will benefit from dollars saved from having to currently pull and test (or replace) aircraft ejection seats on a shorter time scale than if there was an easy in situ test for the efficacy of the ejector seat. Field-structured chemiresistors are a relatively new technology and very little has yet been done to engineer and optimize these sensors for real-world applications. SNL stands to learn a great deal about the implementation of these sensors in engineered devices. The safety of the pilots who stand to use aircraft ejection seats is first and foremost the primary reason to develop this sensor for determining/monitoring the efficacy ejection-seat propellant. Enhancing military equipment and safety for our armed-service personnel directly benefits national security.

Background:

Currently there is no way of quantifying the stabilizer levels in PADs/CADs used for military aircraft ejection seats. This results in PADs and CADs having to be replaced on short, conservative timescales. This project serves to meet this need using the integration of an appropriate *in situ* chemical sensor technology with wireless communication for real time communication of the propellant's state. SNL has unique expertise in conducting field-structured chemiresistor (FSCR) research and development (FSCRs are an SNL-developed technology), which is necessary to optimize these sensors for this demanding application. IEM has expertise in electronics, wireless node communication, and sensor platforms making this relationship highly synergetic.

Description:

The overarching objective of this project is to develop a fully operational prototype of a wireless chemical sensor system called the Stabilizer Level Accurate Measurement System (SLAMS). The SLAMS device design constitutes a miniature, very thin, self-contained chemical-sensor node to quantify and monitor the concentration of propellant stabilizers present in Propellant and Cartridge Actuated Devices (PADs and CADs), such as those present in aircraft ejection seats.

IEM is focused on the wireless sensor platform, node communication, and electronics; whereas SNL's efforts are focused on the chemical sensor development and integration. The sensor technology being employed is known as field-structured chemiresistors (FSCRs), which was invented by James Martin, et al. (SNL) and refined by Martin and Read.

IEM produced the wireless sensor platform for integration of the sensors with the cartridge actuated devices. In addition, IEM tested the sensors with the wireless platforms against the analytes of interest. Although these sensors are not directly slated to be used for this application, there were many accomplishments and much was learned and reported to the customer about this sensing application in general. Please see the abstract for accomplishment details. Both the IEM representative, Ryk Spoor, and the NAVAIR manager, Madgy Bichay were pleased with the performance of SNL in conducting this research (please contact SNL Senior Manager Steven Casalnuovo for additional details).

Benefits to the Department of Energy:

SNL's Defense-Systems mission statement reads, "Defense Systems and Assessments supports the warfighter by accelerating the development of innovative systems, sensors, and technologies for the national security community." The development of this specific application of this chemical sensor platform for this NAVAIR SBIR would ensure the safe and dependable operation of aircraft ejection seats and is directly in line with this mission. In addition, SNL/DOE has invested well over \$1M in the basic development of this sensor technology. However, funds have not been available to take this technology to the next level, which is an engineered system that is deployed in the field. This successful demonstration for a real-world application would attract future industry and government funding opportunities for continued research as well as patent licensing opportunities.

Economic Impact:

Taxpayers will benefit from dollars saved from having to currently pull and test (or replace) aircraft ejection seats on a shorter time scale than if there was an easy in situ test for the efficacy of the ejector seat. The safety of the pilots who stand to use aircraft ejection seats is first and foremost the primary reason to develop this sensor for determining/monitoring the efficacy ejection-seat propellant. Enhancing military equipment and safety for our armed-service personnel directly benefits national security.

In addition, this sensor has been marketed as an inexpensive technology to implement for volatile organic compound monitoring and detection, even in the event of maritime oil spills. The maturation of this sensor platform for future use in this application—an implementation which would have significant environmental, safety, health and economic benefits.

Project Status:

The project has been completed.

ADDITIONAL INFORMATION

Laboratory/Department of Energy Facility Point of Contact for Information on Project

Douglas Read
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Company Size and Points of Contact

The size of IEM is not published (in terms of annual sales and number of employees).

IEM collaborates on virtually all projects with experts in relevant areas. Over the years IEM has established a large number of strategic alliances with universities, federal research laboratories, federal and state government agencies, and both small and large corporations. More on IEM can be found at: <http://www.iem.net/about-iem>.

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CRADA Intellectual Property

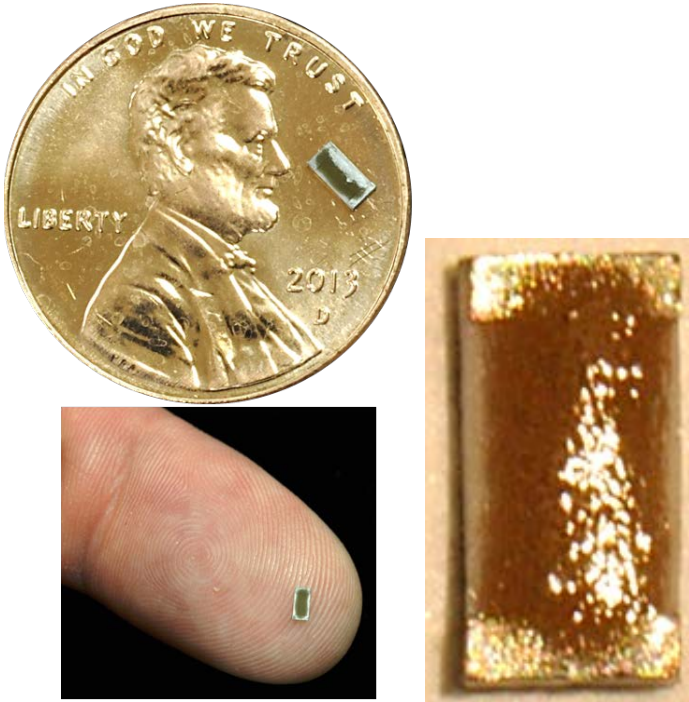
None

Technology Commercialization

N/A

Project Examples

There is a 94-page SNL report internally-published (due to OUO data) SNL report tracking number 308290. In addition the sensors from this research (still at SNL) are stored and preserved.

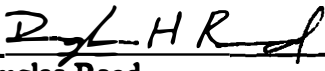


The figures are three views of single field-structured chemiresistor. This extremely small version of an FSCR was the latest generation of its kind developed during this CRADA project.

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This summary has been approved for public release by Sandia and International Electronic Machines Corporation.

Sandia National Laboratories

By 
Douglas Read
Principal Investigator

10/18/2017
Date

Sandia National Laboratories

By 
Manager
WFO/CRADA Agreements

10/16/17
Date

International Electronic Machines Corporation

By _____
Title:

Date

In order to expedite the process, if we do not receive your signed reply by 10/26/17 we will assume your concurrence for the release of this document to the public.