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Title: EERE-SBIR TECHNOLOGY TRANSFER OPPORTUNITY: H2 Safety Sensors for H2

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Technology Opportunities Page

EERE-SBIR TECHNOLOGY TRANSFER OPPORTUNITY: H_2 Safety Sensors for H_2 Infrastructure Applications

The Office of Energy Efficiency and Renewable Energy's Fuel Cell Technologies Office (FCTO) works in partnership with industry (including small businesses), academia, and DOE's national laboratories to establish fuel cell and hydrogen energy technologies as economically competitive contributors to U.S. transportation needs.

The work that is envisioned between the SBIR/STTR grantee and Los Alamos National Laboratory would involve Technical Transfer of Los Alamos Intellectual Property (IP) on Thin-film Mixed Potential Sensor (U.S. Patent 7,264,700) and associated know-how for H2 sensor manufacturing and packaging.

In Phase-I, DOE EERE expects the grantee to focus on the following:

- Develop low cost electronics packaging manufacturable at high volume; and
- Integrate LANL sensor into a commercial package that can meet the codes and standards for being deployed at a H2 fueling station.

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[link to full solicitation]
[link to Summary of Technology and FAQs]

Summary of Technology:
Los Alamos National Laboratory with funding from the U.S. Department of Energy's Fuel Cell Technologies Office (FCTO), has developed and tested inexpensive, zirconia-based, electrochemical (mixed-potential) sensors for H_2 detection in air. Mixed potential sensors are a class of electrochemical devices that develop a voltage in response to differences in the electrode properties and the different redox reaction rates of various gases at each electrode / electrolyte /gas interface. Although zirconia-based mixed potential sensors have been investigated for other applications for several decades, issues with signal stability and device-to-device reproducibility have kept them out of the commercial mainstream. Work in the fundamental understanding of the mixed potential phenomena at Los Alamos has led to new materials, methods, and designs for this important class of sensor. Unique Los Alamos patented sensor designs facilitate a reproducible device response resulting from stable electrochemical interfaces. In addition, mixed potential signals with high signal-to-noise result because gas diffusion is through the less catalytically active electrolyte than the electrode. The sensors show a desirable response time, stability, and resistance to aging and degradation from thermal cycling. Los Alamos and its prototyping partners have developed these sensors and associated electronics and LANL is currently field testing the technology at a California Hydrogen filling station to demonstrate the technology in real-world H_2 applications. Currently, Los Alamos is looking for commercialization partners to license this technology and develop it into a certified commercial H_2 sensor for infrastructure applications.

Los Alamos has built a database consisting of laboratory and field trials testing results as well as independent validation and verification testing feedback from the DOE's Hydrogen Sensor Testing Laboratory and will offer specific answers to frequently asked questions (FAQs) regarding this new technology.

Frequently Asked Questions (FAQs) [dropdown menu]:

TECHNOLOGY OVERVIEW & TECHNICAL QUESTIONS

Is there cross sensitivity to oxygen and humidity?
No. Both testing at LANL and the DOE H_2 Sensor Testing Lab at NREL have showed minimum cross sensitivity to oxygen and water vapor. In fact, we have tested it for a specialized application as a safety sensor for H_2 production Electrolyzers where there is a need to measure H_2 crossover into the anode stream (conditions of 100% O_2 and condensing water). The PEM electrolyzer industry has exhausted their efforts to find a H_2 safety sensor technology that would work in this environment to no avail. We have data that show excellent performance whether at 20% O_2 or 100% O_2 and at high RH (including condensing conditions.) Some oxygen must be present for our sensors to function.

What is the heated element temperature?
The sensor element (approx. 3mm x 3mm) is heated to between 450°C and 500°C using a screen printed, Pt thin film resistive heater, based on the required sensitivity and response time needs because, like the automotive O_2 sensor, it uses YSZ as a solid electrolyte and the device must be heated to elevated T in order to function. While this seems contradictory to the intended application, our device is similar in this regard to commercial combustible gas detectors that use a pellistor type sensor.

These sensors use a heated pellet (200-400°C) of catalytic material and are called Explosimeters and are used in mine safety applications and are not an ignition source because they use a flame arrestor. The flamer arrestor technology ameliorates the concerns that it will ignite the very combustible gas one is trying to detect. It is the same for our H_2 sensor.

Do you have data on the sensor response time?

The sensor element is quite fast like the automotive O_2 sensor. Under flow conditions in the lab, we typically see response times on the order of under 1 sec. Experimental data, evolving from our automotive exhaust gas sensor R&D, indicate our mixed potential sensors respond on the order of 600 msec.

What is the ignition time?

See above. Our sensors do not ignite flammable mixtures of H_2 and air. As part of our lead-up to field trials testing, we tested our H_2 sensor in mixtures up to 20vol% H_2 in air. While this is less than MIE (minimum ignition energy: 22 to 26%H_2), our sensor did not ignite the flammable mixtures either when the flame arrestor was present or without the presence of the flame arrestor. It made no difference. Our sensor element is small and possesses a sufficiently small surface area that we were unable to ignite flammable hydrogen/air mixtures in testing even when we exceeded the normal operating T of the device to the point that the sensor element was glowing orange in color.

Can you comment on response linearity and hysteresis?

These devices are electrochemical in nature and as such, produce a logarithmic voltage output with H_2 concentration. The log-linear conversion can be easily accommodated by electronics or software depending on application. Hysteresis, while present for a short period of time after returning from an exposure to high H_2 concentrations, well above LFL, is minimal and not pronounced.

Is water protection needed? If YES: implementation?

No. While the sensor cannot be immersed or come into contact with liquid water while it is at operating T, (although it would most likely survive, it is not recommended), protecting the sensor element from direct impingement of water is sufficient during normal operation. For electrolyzer safety applications, the sensor was tested in the presence of blowing droplets of water. The water droplets hit an internal metal shield that was developed to deflect the water droplets away from the sensor element. In 24 hours of testing, over 300ml of liquid water passed by the shielded sensor with no effect. Our field trials testing of our H_2 safety sensors at commercial hydrogen fuel cell vehicle filling stations was conducted in 2014 and 2015 in outdoor locations. Our enclosures easily protected the sensor element despite exposure to downpours, blowing rains, standing water, etc.

Can you explain more about the sensitive layer production process?

Our sensors are made for us by our commercial partner using LANL patented designs and commercially available ceramic tapes and screen printed inks, etc. and can be researched by using the general description of "High Temperature Ceramic Co-Fire" process or HTCC. It is the same commercial method used to make ceramic automotive gas sensors, capacitor and surface mount resistors, etc. It is readily scalable and inexpensive.

Understanding that the technology is still in development, is it possible to estimate the hydrogen measurement range for the device?

The hydrogen safety sensor is based on a mixed potential electrochemical sensor technology and as such, the response characteristics - including detection limits and usable sensing range - are a strong function of temperature. Two electrode materials are presently under consideration. Indium Tin Oxide - the original working electrode developed in collaboration with Lawrence Livermore National Laboratory - and a more robust oxide material, Sr-doped Lanthanum Chromite. Sensors fabricated using ITO are more selective to H_2 and we have tested sensors over a range from ppm levels up to 5%. Above 5%, the sensor typically saturates as these devices respond logarithmically to $[H_2]$. Sensitivity and range of response is intimately tied to operating temperature and sensitivity may be increased at the expense of usable dynamic range. The Chromite electrode, while more robust for operating in harsh environments is not as sensitive as ITO and devices prepared so far and saturate at lower $[H_2]$ in the range of 2-3 vol% in air.

Can you describe any other known performance characteristics, such as chemical cross-sensitivities (carbon monoxide) and operating temperature ranges?

The sensor has been independently tested by the DOE's hydrogen sensor testing laboratory at NREL to principal interferences of concern by DOE including CO. The results of NREL's independent testing were published by P. Sekhar et al. in J. Hydrogen Energy 39 (2014) 4657 and CO exhibited minimal cross interference (as was the case with NH_3 and CO_2). The largest cross interference among the gases tested by NREL was methane. However, when methane and H_2 were tested simultaneously, the sensor responded preferentially to H_2.

What is the extent of the development, or Technology Readiness Level (TRL)?

The technology has been part of a DOE funded (EERE, Safety Codes and Standards sub-program) project since 2008 although the core sensor R&D that the H_2 sensor is based on extends further back to the 1990's. The sensor technology has been recently deployed in real-world, field trials testing at a commercial hydrogen filling station in Burbank CA in FY15. Links to DOE Annual Merit Review presentations on record have been provided as well as the publications list. Moreover, the sensor element, the prototype sensor element packaging including flame arrestor, the sensor power supplies, and the control electronics have been designed and manufactured by commercial manufacturers and integrated into the examples of NEMA-8 type commercial enclosures.

What is the desirable temperature range?

The sensor element itself normally operates at between 400-500°C. There are understandably upper limits for the electronics and enclosure. DOE testing protocols used by the DOE H_2 Safety Sensor Testing Laboratory, stipulate testing units between -30°C and 80°C. During LANL-conducted field trials testing at a commercial H_2 filling station, normal working temperatures for the unit at the Burbank location were identified to be less than 50°C.

How far has the development been demonstrated and at what point will the lab consider a hand-off to a commercial partner?

Sensor packaging, heater control electronics, and a prototype field trials unit (deployed) have all been demonstrated. LANL has received 1st batch of sensors manufactured using standard, commercial High Temperature Ceramic Co-fire (HTCC) methods by LANL partner ESL ElectroScience (King of Prussia, PA). Field trials testing has identified areas of improvement to the sensor control unit and attention must be allocated to ensure existing electronics design and packaging conform to applicable CLASS 1, DIV 1-2 standards. LANL plans to provide a fully functional sensor unit to the selected commercial partner at the onset of the work and will work closely with the commercial partner to address any issues with packaging and certification of the sensor.

Material compatibility, longevity and sensor response factor issues?

The sensors are a derivative of automotive O_2 sensor technology and as such have been designed with robustness and potential to operate in an automobile exhaust for extended periods of time. Materials longevity in the intended operating environment as well as materials compatibility within the device construct itself have been a prime driver of the sensor R&D at LANL. The sensors being manufactured by ESL ElectroScience appear to break-in initially but after an initial break-in period, are stable. Sensors made in-house (LANL) do not typically exhibit this break-in behavior. LANL NO_x, NH_3, and HC sensors (related to the H_2 sensor in design and construct) under development and subject to dynamometer testing in engine exhaust have proven to be robust and exhibit long operational lifetime and no evidence of drift or aging within the levels of testing conducted so far.

What are the selectivity challenges and operational environment considerations?

Information regarding the selection of electrode materials and sensor design as pertaining to selectivity has been extensively published in the peer-reviewed open literature and in the DOE Annual Merit Review (AMR) presentations, which have been provided. Field trials testing of the LANL H_2 safety sensor in a heavily populated, outdoor urban environment have also produced data that indicate that cross-sensitivity to common pollutants has not been a problem. The high temperature, mixed potential electrochemical sensor approach exhibits no, or minimum cross sensitivity to physical influences such as relative humidity and barometric pressure that have been shown to affect other sensor technologies. A charcoal filter is used to eliminate interferences from common reducing gases.

What are the start-up issues?

The sensors have been tested based on the user activating a single on/off power switch. The sensor power supply/control module applies voltage-limited DC power and heats the sensor element to the preset operating point and that's all that is required of the operator.

What have been the electrode lamination/delamination observations etc?

There are several manufacturing approaches in addition to two different working electrode materials that have been investigated and delamination, unwanted electrode interaction/reaction with the sensor platform or substrate, etc. have not been observed. Early electrode development work with ESL ElectroScience for LANL's automotive sensor research addressed undesirable electrode issues.

What are the pin-hole free material fabrications considerations?

The electrodes or the electrolyte do not have to be absolutely defect free, such as pinholes, to operate reliably. The devices do require stable electrode/electrolyte interface morphology by design however. In fact, the design is based on patented IP that stipulate that the most stable and reproducible device design is one based on using dense electrodes and a porous YSZ solid electrolyte. Some level of pinholes in both electrode and solid electrolyte are perfectly tolerable.

Can you explain what the technology does in water presence vs dry conditions?

The elevated operating temperature required by the mixed potential, electrochemical sensor imparts these devices with minimal sensitivity to changes in relative humidity (R.H.). It was observed that changing testing conditions from no water vapor to humidified conditions will change the hydrogen response but once water is present in the testing environment, changes in R.H. have little effect on the device response. Response of the LANL sensor under varying RH conditions has been independently validated by testing at the H_2 Safety Sensor Testing Laboratory at NREL (data are available by request). Moreover, the results of humidity testing of mixed potential electrochemical hydrogen sensors have been presented at the Electrochemical Society meetings and published in the open literature. Moreover, several severe weather events and large amounts of precipitation were encountered in outdoor field trials testing with no problem. Lastly, for other applications, this technology was successfully tested in condensing conditions.

What is the current state of the manufacturing process?

We have demonstrated two types of working electrodes that, in-part comprise the H_2 sensor element. The present sensors are designed using an indium tin oxide-working electrode identified by LLNL early in the joint LANL-LLNL EERE SCS project. Since this material is not compatible with ESL's manufacturing process, the working electrode and solid electrolyte must be deposited at LANL subsequent to receiving substrates/sensor platforms from ESL. As discussed in a variety of forums over the past years, these steps increase cost and complexity of making the H_2 safety sensors, but the ITO serves to create a high performance device (e.g fast and selective). A new La-Sr-Cr-O working electrode identified by LANL as an outcome of ultra-harsh durability testing by NREL, was substituted for the LLNL ITO electrode in the last year of the EERE-funded work at LANL. This material is compatible with commercial high temperature ceramic co-fire processes and as a consequence, ESL has successfully manufactured this form of the H_2 sensor in batches of 10 and 20 sensors. The trade off between ease of manufacturing, sensitivity, and durability must be evaluated as part of the commercialization process.

Is it entirely thin film at this point?

A combination of commercial ceramic tapes (for the sensor platform) and screen-printed electrodes and resistive heater are used to fabricate the device. A thin YSZ tape (<100µm) is applied to complete the sensor. Typical thicknesses of the electrodes are in the 40 - 60 µm range. The sensors have been thoroughly tested using in-house approaches such as sputter depositing or electron beam evaporating the electrodes and YSZ electrolyte on a prefabricated sensor platform with integrated Pt resistive heater. For the ITO based sensor, the platform, heater and Pt counter electrode are manufactured by the HTCC process while the ITO electrode and YSZ electrolyte are prepared by sputtering and e-beam evaporation respectively. For the LSCO based sensor, all the elements of the sensor are prepared by the HTCC process.

Did it go through an evolution from thick film to thin film?

Yes. Early approaches may be found in the links to the AMR progress reports submitted to the DOE. The proof of concept and evaluation of ITO as a desirable working electrode material was first established using LANL patented thick tape casting methods whereby dense electrodes were sandwiched between think YSZ tapes and co-fired.

Will devices be available for evaluation during Phase I of the Award?

LANL will provide sensors and their current packaging in the same format as what was field tested in Burbank, CA without the wireless transmitting capability. Additional sensors may be made available if stocks of materials and supplies permit.

Is it acceptable to contact the fueling station where LANL conducted its field tests?

We will ask the owner of Hydrogen Frontier if direct contact is okay and will provide answer in an up date to the FAQ.

Will the LANL Team be able to answer questions once the DOE Call has issued?

Yes, we anticipate that we may update the list of Frequently Asked Questions periodically as new questions are raised. To the extent that a company has a question that it considers proprietary, it is incumbent upon the company to let LANL know that their specific question is of a proprietary nature and therefore, request that it not be included in the list of FAQs.

COMMERCIALIZATION OVERVIEW & LICENSING QUESTIONS

What is the licensing strategy for this technology?

Los Alamos currently has existing Background Intellectual Property (BIP) that will be available for licensing through a No-Cost, Nonexclusive License Option Agreement that will be applicable during the for the SBIR TTO Phase 1 Award. Such Nonexclusive License Option Agreement will grant the Awardee the necessary rights to perform research and development pertaining to the Los Alamos technology during their Phase I Award. If the Awardee receives a Phase II Award, the Awardee may elect to exercise their option to negotiate a Nonexclusive License for consideration. Alternatively, the Awardee may request to extend their option period.

Please note that the License Option Agreement is NOT a grant of commercial license rights which allows your company to license, manufacture and, or sell the Los Alamos technology. Rather, such License Option Agreement is strictly for the purpose of providing rights to perform research and development during the course of the SBIR TTO Award.

What is a CRADA and how does it work?

The contractual mechanism under which LANL is authorized to collaborate with industry is called a Cooperative Research and Development Agreement, or CRADA. The CRADA provides for a CRADA Option Agreement that gives the commercial partner an option for an exclusive license (within a defined field of use – in this case H_2 Safety Sensors for Hydrogen Infrastructure applications) to any IP conceived or first reduced to practice in the performance of work under the CRADA.