DEVELOPMENT OF LOW COST SENSORS FOR HYDROGEN SAFETY APPLICATIONS

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Abstract

We are developing rugged and reliable hydrogen safety sensors that can be easily manufactured. Potential applications also require an inexpensive sensor that can be easily deployed. Automotive applications demand low cost, while personnel safety applications emphasize light-weight, battery-operated, and wearable sensors. Our current efforts involve developing and optimizing sensor materials for stability and compatibility with typical thick-film manufacturing processes. We are also tailoring the sensor design and size along with various packaging and communication schemes for optimal acceptance by end users.

Introduction

Under a Cooperative Research and Development Agreement (CRADA) and license agreement, Oak Ridge National Laboratory (ORNL) and DCH Technology, Inc. are teaming to develop the Thick Film Hydrogen Sensor (TFHS) for specific market applications related to the hydrogen economy. The development of efficient hydrogen production, storage, and utilization technologies brings with it the need to detect and pinpoint hydrogen leaks to protect people and equipment. The TFHS, developed at ORNL, is potentially well suited to meet cost and performance objectives for many of these applications.

Workers at ORNL demonstrated monolithic, resistive sensors that are inherently robust, selective to hydrogen, and easy to manufacture (Lauf 1994, Hoffheins 1995). A thick-film sensor was designed that, to the largest extent possible, used traditional materials and fabrication methods, which have obvious cost advantages. The response to hydrogen is reversible, so the sensor can be used over and over.

The sensing mechanism of the sensor relies upon the absorption of atomic hydrogen into palladium metal. Changes in hydrogen concentration in the palladium matrix are reflected by changes in its electrical resistivity and can be easily measured.

The TFHS design is a Wheatstone bridge circuit based principally upon three thick film components, Figure 1. Each layer is separately printed and fired onto a ceramic substrate. The layers are: 1) conductor, which joins the palladium segments and provides connection points for power and signal circuitry, 2) palladium resistor, composed of the four serpentine palladium segments, and 3) passivation, which forms a hydrogen-impermeable barrier over two of the palladium resistors. These two passivated legs serve as reference resistors and thus compensate for changes in the resistance of the palladium due to temperature variation.

We use traditional thick-film techniques to fabricate the sensor. It is highly automated and it is economical for small or large batch production. With the development of the palladium resistor composition by DuPont Electronics (Felten 1994), all of the sensor materials are now off-the-shelf components.

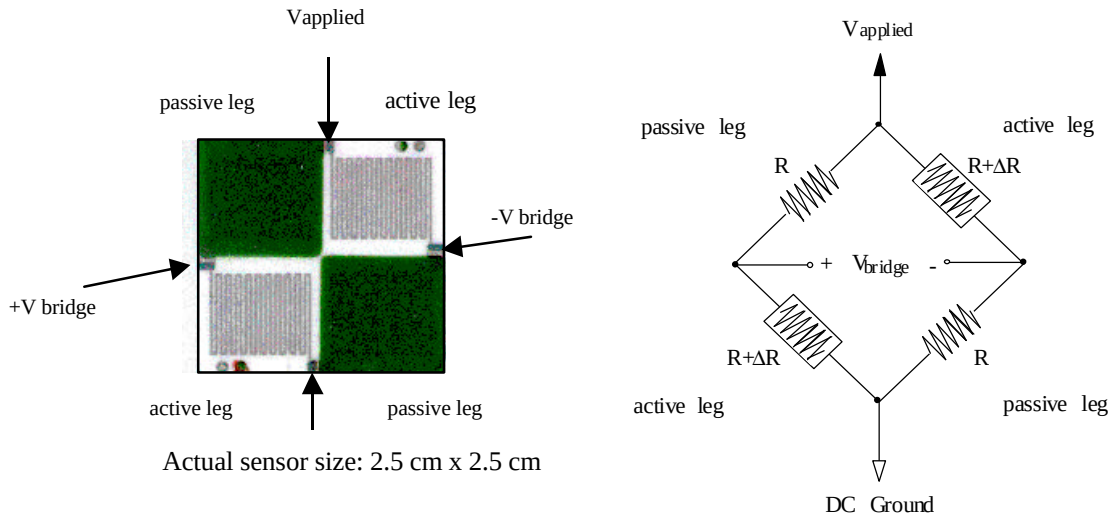

Figure 1. Sensor design and schematic representation

The TFHS has been tested under a wide variety of conditions (Hoffheins 1998, Hoffheins 1997). It has shown good response to a range of hydrogen concentrations (0.5 to 30%) at temperatures between 0 and 200°C, and in dry and humid environments. Preliminary results indicate little or no cross interference by hydrocarbons. We are continuing sensor materials studies to optimize sensor stability, sensitivity and durability over a range of environmental conditions. One method of miniaturizing the sensor to reduce power consumption has been developed. DCH Technology has displayed and demonstrated the TFHS in their booths at the 1997, 1998, and 1999 National Hydrogen Association meetings.

Current Developments

Sensor Layout Improvements

Changes were made to the sensor patterns to improve operation and durability. The first modification was to rearrange the four serpentine resistors so that the loops of the pattern all lie in the same direction, Figure 2. In the previous design, the loop orientation of two resistors was perpendicular to that of the other two. The resistors are deposited by squeezing paste across a patterned wire mesh onto the alumina substrate. Because the patterns are all oriented in the same direction in the new design, there is an increased probability that they are more nearly identical in physical structure and electrical value. In fact, measured values of the printed and fired resistors are closer in value to each other than for those made with the previous design.

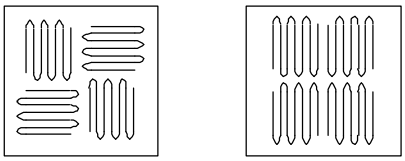

Figure 2. Schematic views of previous resistor pattern (left) and new resistor pattern (right).

The next modification to the sensor design extended the passivation layer to completely cover the terminations of the palladium resistors designated as reference legs. In the original design, a small portion of the reference resistor was exposed where it contacted the conductor layer. The exposed surface could be an entry point for hydrogen gas into the reference legs, which would ultimately compromise effectiveness of the passivation.

A new batch of sensors, incorporating the design modifications, was manufactured. Figure 3 shows the response of one of these new sensors to increasing levels of hydrogen in air. The sensor is insensitive to the presence of hydrogen below the 0.2% level. From 0.2% up to 2% hydrogen, the response is linear. The time to reach the maximum output at each step is seven seconds. This time includes the time constant of the test chamber and associated tubing from the mass flow controller. The time constant of the test chamber is estimated at four seconds. Thus, the actual sensor time constant could be as little as three seconds to reach maximum output for the indicated increases in hydrogen concentration.

Sensor Materials Investigations

Soda-lime glass passivation

Current sensor prototypes use a borosilicate-based glass for the passivation layer. This has proven to be an effective barrier to hydrogen for lower concentrations (less than 4% in air). However, the composition is not resistant to acid. A test solution of 5% acetic acid in water dissolved the passivation to the point at which it could be completely wiped from the sensor surface. A more chemically inert passivation was sought to increase reliability of the sensor.

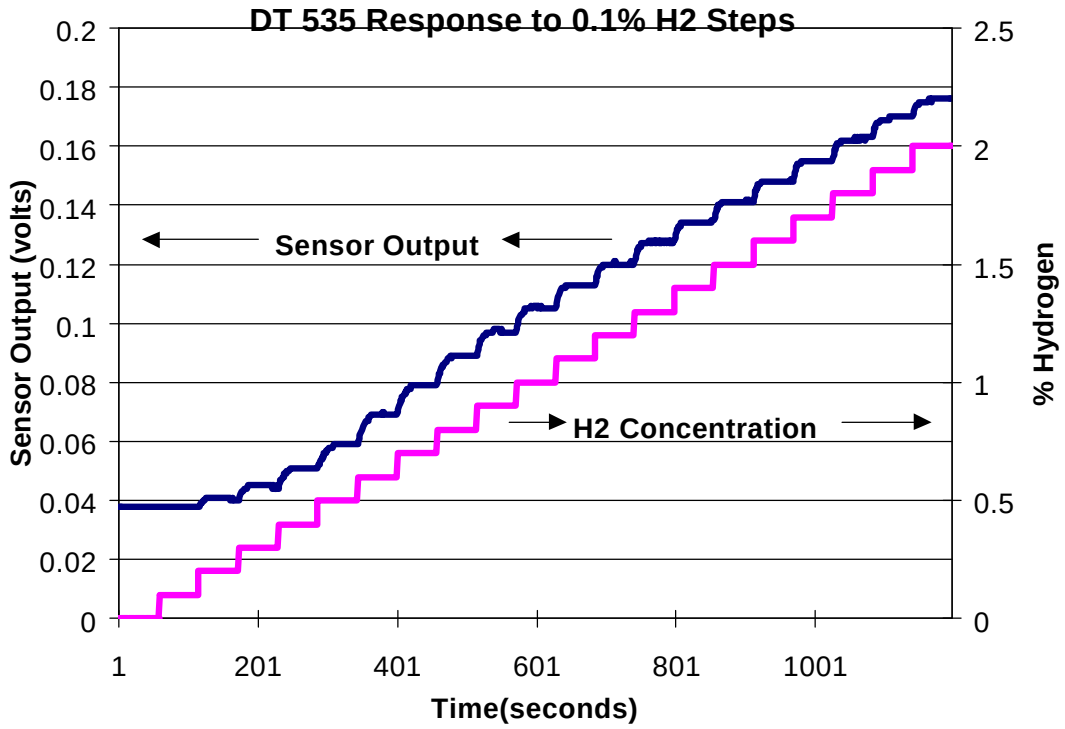

Figure 3. Sensor response to increasing levels of hydrogen in air.

We experimented with a paste consisting primarily of ground window glass (soda-lime glass) with organic vehicles added to facilitate screen printing. Soda-lime glass was considered because it is inexpensive, potentially more stable to shifts in the pH of an environment, and possibly a better barrier to hydrogen. Sample sensors were screen printed with this new composition and fired for one hour in a belt furnace at four temperatures ranging from 850ºC to 975ºC. The fired glass was clear and smooth. Samples fired at the higher end of the temperature range, 950ºC and 975ºC, had the smoothest surfaces indicating effective fusing of the glass particles. Yellowing of the glass occurred at all four conductor pads where the palladium resistors terminate, indicating some interdiffusion between the conductor material and the glass. Further studies are required to optimize material compatibility and to verify effective operation.

Sensor paste

During most of this reporting period, we were using a second version DuPont palladium formulation (Version 2). This paste was designed for greater durability at high concentrations of hydrogen (10 to 30% in air). Palladium particle sizes in this composition are roughly 1µm, a factor of 10 greater than that used in the original DuPont formulation (Version 1). However, the larger particles reduce the resistivity of the fired resistors, which in turn increases the power consumption of the sensor. Because the sensor is ultimately targeted for battery operation as well as low-concentration exposure, we returned to the Version 1 formulation to continue sensor

testing and development. Using the present sensor design, the resistivity of the fired paste is still too low for continuous battery operation. We are therefore evaluating control modes that power the sensor briefly to collect a reading, but are not energized most of the time.

Sensor Testing

Test Fixture

The sensor testbed consists of a sensor test chamber, gas handling equipment, and automated control provided by a personal computer (Pentium 200 MHz MMX computer with Windows 95 Operating System) with a customized LabView (Version 4) graphical user interface and National Instruments data acquisition interface (DAQPad 6020E).

The sensor test chamber is a plastic container with a sample volume of 65 cm^3. Clip leads connect the sensor to a 5 Vdc power supply and analog input of the data acquisition system. Gas mixtures are supplied to the chamber by two mass flow controllers, which are controlled by settings in the LabView program. Sensor and ambient temperatures are recorded automatically by resistance temperature detectors (RTDs). Test parameters such as hydrogen, concentration, gas flow rates, length of test, number of test cycles, and sampling rate can be input through the user interface and stored for future use. At the end of a test, data files are automatically stored on the test computer and with a backup copy stored on a server computer. Each test generates a file containing the following information: sensor power supply voltage, sensor and ambient temperatures, gas concentration profiles, sensor output, mass flow controller output, and time and date. The user interface displays sensor excitation voltage, output, sensor and ambient temperatures, gas on and off indications, and a real time graph of sensor output.

Improvements to the test stand for this reporting period included incorporation of computer-stored data sheets, automated file duplication and storage, and greater test configuration flexibility.

CRADA Partner Review

Team members from ORNL and DCH met to review CRADA progress and to align sensor performance objectives with DCH's marketing plans. We selected a sensor design, palladium resistor geometry, and palladium formulation as the basis for future testing and for comparing test results. Also, the following criteria, in line with potential sensor applications, were selected for subsequent sensor testing and development.

- Sensitivity and durability in the range of concentrations between 0 and 2% hydrogen in air.
- Temperature operation: -20°C to +40°C
- Response time: 3 seconds
- Insensitivity to CO, CO_2, CH_4, NH_3, Propane, Butane, Acetylene

Sensor Demonstration at NHA 1999

For demonstration and testing, a sensor package was designed and constructed, Figure 4. The package consists of two chambers mounted together. At one end of the module, a small chamber houses the sensor. Test gas is introduced to the chamber through external gas ports. The volume of the chamber was minimized for efficient gas exchange. The preamplifier, which amplifies the output of the sensor for input to the data acquisition system, is housed in the larger chamber. This portion of the package (and thus the overall sensor module) was oversized for fabrication, testing and modification of preamplifier designs. The completed prototype module provided an easily used sensor system with miniature pneumatic tubing connections and a three wire electrical interface (+5Vdc, common and analog output).

The initial preamplifier design was based on a single supply instrumentation amplifier (Analog Devices AMP-04) and incorporated an offset circuit using a low current, single supply op amp (National Instruments LMC6041). To avoid the need for dual voltage supplies (e.g. +/- 5 Vdc) the design carried the caveat that sensor elements would have to be selected to favor those with inherent positive offset voltages (in other words, the initial resistance of the active legs would be slightly higher than that of the passive legs). Subsequent sensor element modifications could ensure that this condition would be produced. The offset adjustment circuit was omitted in the initial demonstration unit.

This demonstration package was used to show TFHS operation at the 1999 National Hydrogen Association Meeting. It was connected to a National Instruments data acquisition PCMIA card (DAQCARD-700) housed in a laptop computer. The computer was loaded with a customized LabView user interface so that sensor excitation, temperature, and output could be displayed. The sensor output was converted to a %hydrogen reading and was displayed in real time by graphical and numerical displays. A series of red indicator lights on the display indicated whether sensor output was beyond designated threshold concentrations of 20%, 40% 120% and 160% of the lower explosive limit of hydrogen in air.

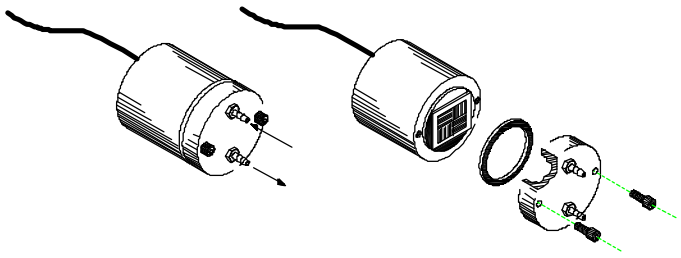

Figure 4. Sketch of housing used to demonstrate sensor operation.

Economic Evaluation

DCH Technology has continued its economic evaluation for the purpose of commercializing the Thick Film Hydrogen Sensor. This analysis identified three initial target markets in particular, and several others in general.

The automotive field of use is the first market of interest. Market surveys into this area yielded significant results. It is apparent that the manufacturing cost targets of the device meet the paradigm required for automotive applications, so DCH has been working to gain acceptance in the field. There is a demand in automotive for a rugged, low cost device for use in vehicles powered by fuel cell and hydrogen-fueled combustion engines. Beginning December 1998, DCH Technology started working with one of the "Big Three" US automotive companies to meet the design specifications for automotive sensors utilizing the Thick Film Hydrogen Sensor. In addition, the other automotive manufacturers have expressed interest in testing the sensor for their hydrogen vehicles as well.

The concept of a hydrogen safety badge is the second market area. Various government agencies have suggested that the thick film sensor, coupled with a small circuit board and battery could be worn as a badge in areas where a hydrogen hazard might exist. If hydrogen is detected in amounts over a predetermined alarm threshold, both audio and visual alarms are triggered on the badge. DCH designed the circuitry and produced a prototype board that was displayed at the 10th annual National Hydrogen Association Meeting April 7-9, 1999. The entire badge is about the size of a standard business card.

The third target application is the coupling of the sensor with a radio tag for wireless monitoring. This will be useful in such areas as refineries and utilities where the potential for hydrogen leaks exists, but existing technologies require thousands of feet of cabling to install. The dimensions and profile of the sensor and associated electronics allow for remote monitoring and transmission of signals over a long distance. DCH will be working with a utility later this year to test the concept and open the market.

Other market niches that are being developed include industrial safety monitoring, primarily in semiconductor plants, metals processing and hydrogen generation plants. A series of agreements for beta testing are in negotiation for these markets.

Future Work

For the rest of this funding period we will use the standard sensor configuration, defined by the CRADA partners, to continue to evaluate sensor performance for target hydrogen concentrations, temperatures, interference gases, and humidity. We will characterize response time, sensitivity, and drift.

Further plans include optimizing and finalizing sensor design, including sensor layout, materials formulation, and fabrication steps. We will test optimized designs for target applications. As the

sensor design is further matured, we will identify and work with a commercial thick-film circuit manufacturer to produce a pre-commercial version of the sensor.

Conclusions

We continue to mature the sensor design and narrow the focus of applicable niches for sensor deployment. The TFHS is inherently rugged and inexpensive, making it attractive as a wearable personnel safety device or for fuel cell powered automobiles. We are uncertain of the ultimate lifetime and usefulness of the palladium-based thick film material developed especially for the hydrogen sensor, so we are concentrating our efforts on understanding and maturing this product. The continued development of the sensor requires an iterative approach and close collaboration among team members at ORNL and DCH with continued helpful input from our thick film materials supplier.

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