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Title:	Development of a Reliable, Miniaturized Hydrogen Safety Sensor Prototype
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Development of a Reliable, Miniaturized Hydrogen Safety Sensor Prototype

In this article, the development and long-term testing of a hydrogen safety sensor for vehicle and infrastructure applications is presented. The working device is demonstrated through application of commercial and reproducible manufacturing methods and rigorous life testing results guided by materials selection, and sensor design. Fabricated using Indium Tin Oxide (ITO) as the sensing electrode, Yttria-Stabilized Zirconia (YSZ) as an oxygen ion conducting solid electrolyte and Platinum (Pt) as a pseudo-counter electrode, the device was subjected to interference studies, temperature cycling, and long-testing routine.

The sensor responded in real time to varying concentrations of H_2 (1000 to 20,000 ppm) monitored under a humidified condition. Among the interference gases tested such as nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), carbon monoxide (CO), and propylene (C_3H_6), the sensor showed cross-sensitivity to C_3H_6. Analyzing the overall device performance over 4000 hrs of testing for 5000 ppm of H_2, (a) the sensitivity varied ±21% compared to response recorded at 0 hrs, and (c) the response rise time fluctuated between 3 to 46 s.

The salient features of the H_2 sensor prototype designed and co-developed by Los Alamos National Laboratory (LANL) are (a) stable three phase interface (electrode\electrolyte\gas) leading to reliable sensor operation, (b) low power consumption, (b) compactness to fit into critical areas of application, (c) simple operation, (d) fast response, (e) a direct voltage read-out circumventing the need for any additional conditioning circuitry, and (f) conducive to commercialization.

Development of a Reliable, Miniaturized Hydrogen Safety Sensor Prototype

Recent developments in the search for renewable energy coupled with the advancements in fuel cell powered vehicles (FCVs) have augmented the demand for hydrogen safety sensors [1]. There are several sensor technologies that have been developed to detect hydrogen, including deployed systems to detect leaks in manned space systems and hydrogen safety sensors for laboratory and industrial usage. Among the several sensing methods electrochemical devices [2-8] that utilize high temperature-based ceramic electrolytes are largely unaffected by changes in humidity and are more resilient to electrode or electrolyte poisoning. The desired sensing technique should meet a detection threshold of 1% (10,000 ppm) H_2 and response time of ≤1 sec [9] targets for infrastructure and vehicular. Further, a review of electrochemical hydrogen sensors by Korotcenkov et.al [10] and the report by Glass et.al [11] suggest the need for inexpensive, low power, and compact sensors with long-term stability, minimal cross-sensitivity, and fast response. As part of the Hydrogen Codes and Standards program, Los Alamos National Laboratory (LANL) and Lawrence Livermore National Laboratory (LLNL) are working together to develop and test inexpensive, zirconia-based, electrochemical (mixed potential) sensors for H_2 detection in air. Previous work conducted at LLNL showed [8] that indium tin oxide (ITO) electrodes produced a stable mixed potential response in the presence of up to 5 % of H_2 in air with no response to CO_2 or water vapor. The sensor also showed desirable characteristics with respect to response time and resistance to aging, and degradation due to thermal cycling.

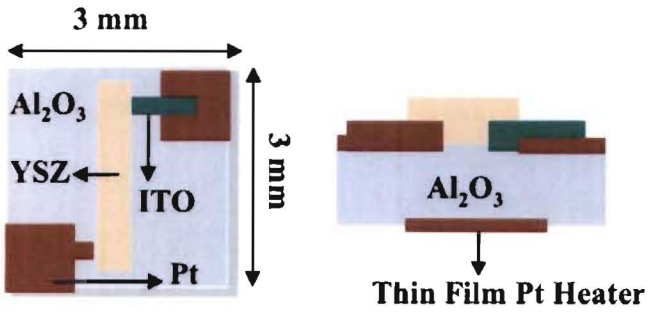

Figure 1. Schematic of the plan and cross-sectional view of the device
H_2 sensor prototype with integrated Pt heater

In this investigation, the development and testing of an electrochemical hydrogen (H_2) sensor prototype based on '(ITO)/ Yttria-Stabilized Zirconia (YSZ) / Platinum (Pt)' configuration is detailed. The device fabricated on an alumina substrate integrates a resistive Pt heater to achieve precise control of operating temperature while minimizing heterogeneous catalysis. Figure 1 shows the plan and cross-sectional view of the device prototype. The working device is demonstrated through application of commercial and reproducible manufacturing methods and rigorous life testing results guided by materials selection, and sensor design. Targeting fuel cell powered automotive applications, the safety sensor was subjected to interference studies, temperature cycling, operating temperature variations, and long-term testing over 4000 hrs.

Table 1. Summary of the Life Cycle Testing Experiments

Time (hrs)	Conditions
0 - 300	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
301 - 390	Temperature Cycling 6.5 V to 0 to 6.5 V, Three Cycles, Maintaining Humidity Level and Base Gas
391 - 822	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
823 - 894	Operating Temperature Variations – 6.5 to 5.75 V, Maintaining Humidity Level and Base Gas
895 - 1900	Static Conditions – No humidity, No Base Gas, Set Voltage – 6.5 V
1901 - 2296	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
2297 - 3249	Set Voltage – 6.5 V, Maintaining Humidity Level and Base Gas
3250 - 4000	Stress Testing – Temperature Cycling 6.5 V to 0: 100, 500, 1000, and 10000 Cycles, Sensor Response Measurement Before and After Each Cycle

The heater voltage was set to 6.5 V, which corresponded to an operating temperature of approximately 535^0 C following a polynomial trend, $Y = 4.941\ x^2 + 45.85\ x + 28.16$ (Y represents the operating temperature in degrees and x represents the heater voltage). The maximum power consumption of the device prototype was around 5 W (6.5 V, 0.78A). Various experiments were performed between 0 to 4000 hrs of testing (table 1). In the case of temperature cycling studies (301-390 hrs), the heater voltage was slowly ramped down from 6.5 to 0 V in 10 mins. After waiting for an hour, it was then ramped up to 6.5 V in 10 mins. The ramp rates and soak time were chosen arbitrarily. For operating temperature variations (823-894 hrs), the device was subjected to arbitrary heater voltages (temperatures): 6.5 V (535^0 C), 6.25 V (508^0 C), 6 V (481^0 C) and 5.75 V (455^0 C). From 3250-4000 hrs, accelerated stress testing was performed. The temperature was cycled between 6.5 V and 0 V in a short interval of time in a triangle waveform configuration. A cycle from 6.5 V to 0 and back to 6.5 V was completed in 2 secs. The sensor response before and after stress tests was recorded. Overall, the sensor was torture tested with 10,000 cycles of temperature ramp up and down.

The sensor responded in real time to varying concentrations of H_2 (1000 to 20,000 ppm). Among the interference gases tested such as nitric oxide (NO), nitrogen dioxide (NO_2), ammonia (NH_3), carbon monoxide (CO), and propylene (C_3H_6), the sensor showed cross-sensitivity to C_3H_6. The sensor response to H_2 was found to linearly vary with logarithmic concentrations of H_2.

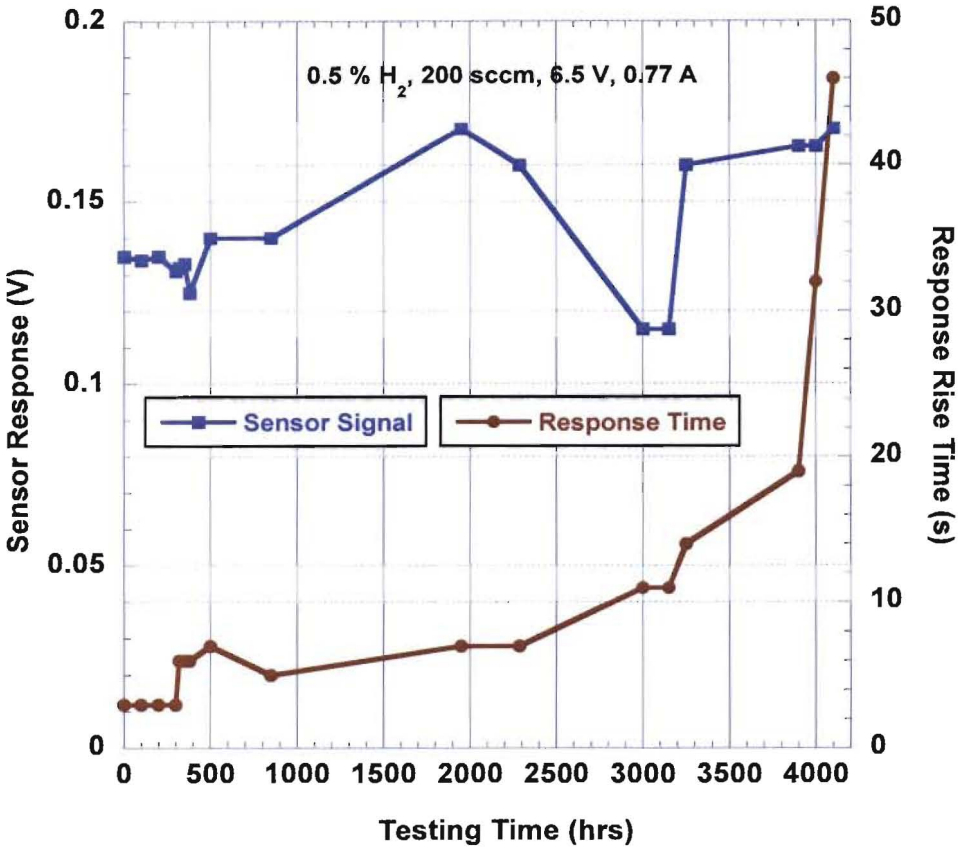

Figure 2. Sensor response and response rise time (0.5% H_2, 200 sccm, 6.5 V, 0.77 A) over 4000 hrs of testing (including 750 hrs of accelerated stress testing).

Figure 2 shows the sensor response and response time over 4000 hrs of testing. A detailed explanation of the observed results can be found in a recent article by the authors [12]. Analyzing the overall device performance over 4000 hrs of testing for 5000 ppm of H_2, (a) the sensitivity varied between 0.135 to 0.17 V with a minimum low of 0.12 V, (b) the baseline signal ranged from 0 to 0.04 V, and (c) the response rise time fluctuated between 3 to 47 s.

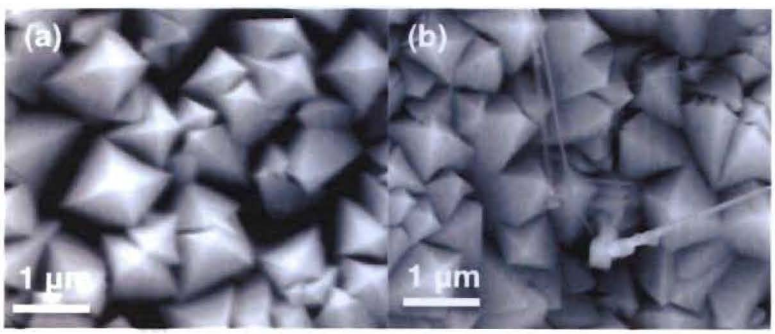

Figure 3. SEM micrograph of the ITO surface
(a) 0 hrs and (b) 4000 hrs

After 4000 hrs, the sensor response was seen to degrade. The sensor behavior shifted to negative y-axis around 5000 hrs with sluggish response (~1 min response time). Hence, the sensor was pronounced dead and inspected in a Scanning Electron Microscope (SEM).

Figure 3 show the SEM micrograph of the ITO surface before (0 hrs) and after (4000 hrs) testing. Nanostructures emanating from the grains along with surface pitting was observed on the ITO surface after 4000 hrs of testing. The composition of the nanostructures was not identified and the work is in progress to understand the formation of the nanostructures and their composition. It is anticipated that the three-phase interface (Electrode\Electrolyte\Gas) should have degraded when subjected to accelerated stress tests. A complete post-mortem analysis is required to better correlate the sensor behavior to the microstructural changes. Further, the search for a new sensing electrode material (replacing the ITO) for stable and selective detection of H_2 is in progress.

The authors believe that the stable response of the prototype device over 4000 hrs is a significant achievement and in the right direction for developing commercial and low cost H_2 safety sensors. Such a stable behavior of the device may be attributed to a stable, engineered three-phase interface. Though there is a huge room for improvement in terms of sensor performance, the salient features of the investigated H_2 sensor prototype include (a) conducive to commercialization, (b) low power consumption, (c) compactness to fit into critical areas, (d) simple transduction mechanism, and (e) fast response.

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