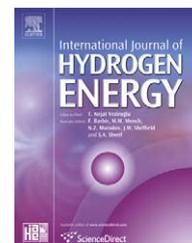


Available at [www.sciencedirect.com](http://www.sciencedirect.com)journal homepage: [www.elsevier.com/locate/he](http://www.elsevier.com/locate/he)

# Robust hydrogen detection system with a thermoelectric hydrogen sensor for hydrogen station application

M. Nishibori<sup>a,\*</sup>, W. Shin<sup>a</sup>, N. Izu<sup>a</sup>, T. Itoh<sup>a</sup>, I. Matsubara<sup>a</sup>, S. Yasuda<sup>b</sup>, S. Ohtani<sup>b</sup>

<sup>a</sup>National Institute of Advanced Industrial Science and Technology (AIST), Shimo-Shidami, Moriyama-ku, 463-8560 Nagoya, Japan

<sup>b</sup>Riken Keiki Co., Ltd, 2-7-6 Azusawa, Itabashi-ku, 174-8744 Tokyo, Japan

## ARTICLE INFO

### Article history:

Received 30 October 2008

Received in revised form

8 January 2009

Accepted 8 January 2009

Available online 12 February 2009

### Keywords:

Prototype system

Hydrogen station

Thermoelectric hydrogen sensor

Field test

## ABSTRACT

A prototype hydrogen detection system using the micro-thermoelectric hydrogen sensor (micro-THS) was developed for the safety of hydrogen infrastructure systems, such as hydrogen stations. We have designed a detection part with a pressure proof enclosure adoptable for the international standard of Exd II CT3, and carried out an explosion strength test, explosion and fire hazard tests, and an impact test. The hydrogen sensing performance of the detection part of this prototype system showed a good linear relationship between the sensing signal and hydrogen concentrations in air, for a wide range of hydrogen concentrations from 10 ppm to 40,000 ppm (4 vol.%). This prototype detection system was installed in the outdoor field of the hydrogen station and the response for H<sub>2</sub> gas in air of 100 ppm, 1000 ppm, and 10000 ppm was tested monthly for 1 year.

© 2009 International Association for Hydrogen Energy. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

To prevent the real and perceived hazards of hydrogen fuel use, extensive safety precautions must be put in place before any serious movement can be made towards a hydrogen base energy in the future. The current strict regulation for a hydrogen station needs the installation of suitable safety systems including hydrogen detectors. Therefore, the need for highly sensitive, selective, stable, and robust gas sensors is growing, and much research and development has been conducted in the field of hydrogen sensors for hydrogen leakage detection [1–4]. However, hydrogen gas sensors that can quickly, reliably, and durably detect hydrogen over a wide range of hydrogen and moisture concentrations are not currently available. Therefore the development of a hydrogen sensor which can detect from low (ppm level) to high concentrations (% level) in air with high precision and endurance is important.

The catalytic combustion-type sensor is widely used as a leak detection alarm because it provides good performance in durability and stability. This sensor can detect hydrogen concentrations from 1000 ppm to several %. Leakage detection in the lower concentration range is also important for the safety of hydrogen facilities, and the semiconductor-type SnO<sub>2</sub> sensor is used for this lower concentration range from several ppm to 2000 ppm. Currently, most hydrogen stations operating in Japan have adopted an alarm system that combines a semiconductor-type sensor [5] and a catalytic combustion-type sensor [6]. Fig. 1 compares the gas detection principles of the catalytic combustion-type gas sensor [7] and the thermoelectric gas sensor [8]. The catalytic combustion-type sensor detects hydrogen by the increase in the temperature of the sensor element generated by the heat of catalytic combustion of hydrogen (= resistance change in a platinum coil heater). This sensor becomes insensitive for low gas concentrations,

\* Corresponding author. Tel.: +81 52 736 7121; fax: +81 52 736 7244.

E-mail address: [m-nishibori@aist.go.jp](mailto:m-nishibori@aist.go.jp) (M. Nishibori).

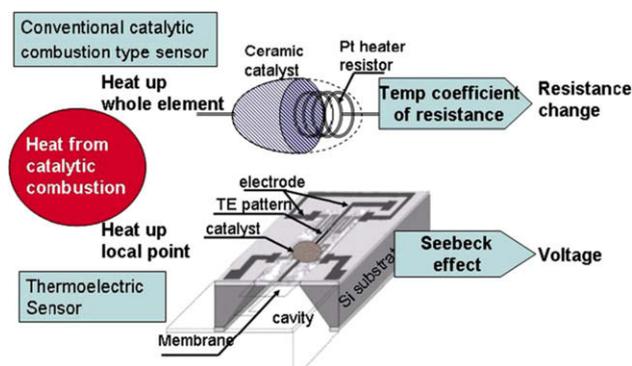


Fig. 1 – Gas detection principle of the micro-THS.

therefore it is used for a hydrogen concentration range of 1000 ppm to several %.

A micro-thermoelectric hydrogen sensor (micro-THS) operates on the basis of the oxidation of hydrogen by a Pt/alumina catalyst combustor, similar to the catalytic combustion-type sensor. The micro-THS consists of a thermoelectric film, a symmetrical micro-heater, and a Pt/alumina catalyst integrated on its surface. When the Pt/alumina catalyst oxidizes hydrogen gas and releases the combustion heat, a local temperature gradient occurs between a hot point and a cold point on the device. This temperature gradient is converted into voltage by the Seebeck effect of a thermoelectric SiGe thin film. This structure was developed several years ago to improve the sensitivity [9–11], and this sensor can detect a very wide range of hydrogen concentrations from 0.5 ppm to 50,000 ppm (5 vol.%) in air [12]. We have also found that a ceramic catalyst enhances the long-term stability of the hydrogen detection performance [13].

We have prepared a prototype hydrogen detection system with a micro-THS integrated in a flameproof sintered metal cap and pressure proof enclosure and have evaluated its hydrogen sensing performance. Moreover, we have performed a field test on this prototype hydrogen detection system (hereinafter referred to as the prototype system) installed in a hydrogen station to measure the response to hydrogen of 100, 1000, 10,000 ppm in air, for 1 year.

## 2. Fabrication of the micro-sensor device

To enhance the output signal of the micro-THS, it is necessary to lower the thermal capacity of the device. The three components, a thermoelectric converter, a catalyst, and the micro heaters, are integrated in the thin dielectric membrane, which can reduce the total heat capacity and heat transfer. Fig. 2 shows the fabrication process of the micro-THS device developed for these requirements.

Micro-THS devices with a chip size of  $4 \times 4 \text{ mm}^2$  were fabricated using an SiGe thermoelectric thin film and Pt heater patterns including a hot-plate type membrane releasing wafer process. The details of the micro-fabrication process have been reported previously [9,10]. The Pt/alumina catalyst was prepared by the impregnation of an alumina powder ( $\alpha$ -alumina, 100 nm, Taimicron, Taimei Chemicals Co., Ltd.)

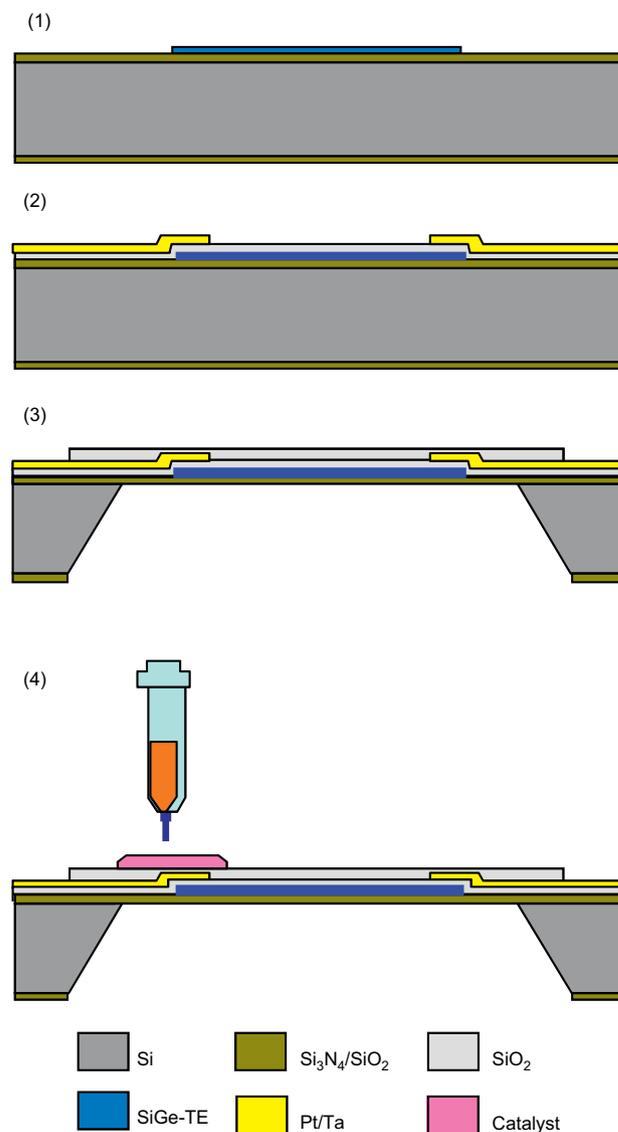


Fig. 2 – Fabrication processes of the micro-THS. (1) Thermoelectric SiGe pattern processed by sputter deposition photolithography and RIE etching, (2) SiO<sub>2</sub> passivation by PECVD window etching by RIE and Pt heater lift off, (3) passivation and window opening, (4) ceramic catalyst deposition by dispenser.

with an aqueous solution of platinum(IV) chloride pentahydrate. The powder of the catalyst was mixed with an organic vehicle (a blend of terpineol and ethyl cellulose) to make a ceramic paste. A drop of the ceramic paste was dispensed on the micro-heater meander using the dispenser technique [9]. The size of the catalyst was controlled to keep it constant at 0.6 mm in diameter by controlling the dispensing time and the air pressure. After the deposition, the ceramic paste was baked in air at 300 °C for 2 h.

The Pt content of the Pt/alumina catalyst in this study was fixed at 40 wt.%, which was found to be optimum by the previous study [11]. The grain size of the Pt metal was estimated to be 3 nm by transmission electron microscopy (TEM, JEOL, JEM2010) observation after baking.

The driving temperature of the micro-THS is controlled at 100 °C on the catalyst surface for hydrogen-selective detection. It has already been reported that high selectivity for hydrogen is achieved because only hydrogen gas burns on the catalyst at lower than 100 °C [8].

Fig. 3 shows the package of the micro-THS with the flameproof sintered metal cap. The chip was mounted on the plastic base and the electrode of the chip was connected to the terminal of the base with Au wires. The micro-THS uses the local temperature gradient generated by the combustion heat of the catalyst, and the thermoelectric device acts as a micro-calorimeter. The signal of this micro-calorimeter device can be easily affected by the air flow, like the flow sensor. The flameproof sintered metal cap not only prevents adhesion of dust but also influences the air flow. If the metal cap is too porous, the effect of dust and wind becomes serious. But if it is too compact, the response for the hydrogen gas becomes worse. We investigated the influence of the package structure on the gas detection characteristics and applied the package that was most suitable for the micro-THS.

### 3. Prototype system

#### 3.1. Design of the detection part

In order to install the micro-THS at the hydrogen station, which is a hazardous area, safety technologies such as the explosion-proof structure of the flameproof sintered metal cap and a pressure proof enclosure are necessary. We have designed a detection part with the structure of the pressure

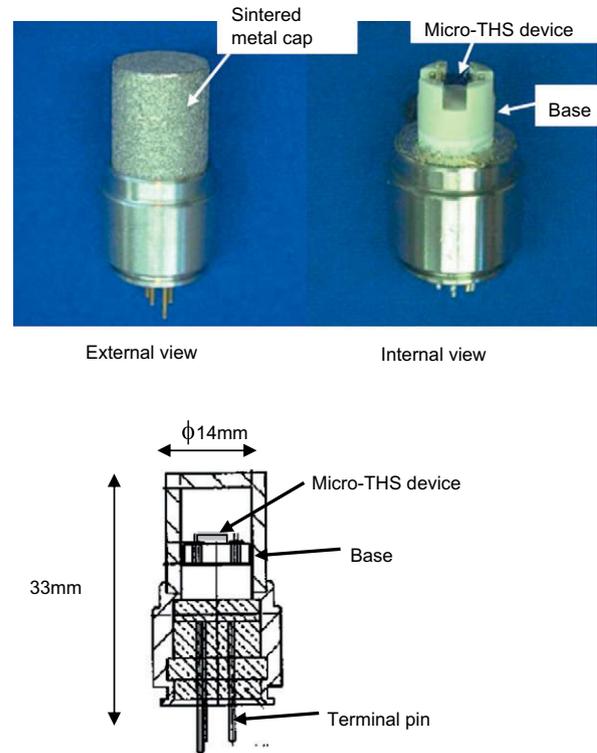


Fig. 3 – Sensor package with sintered metal cap.

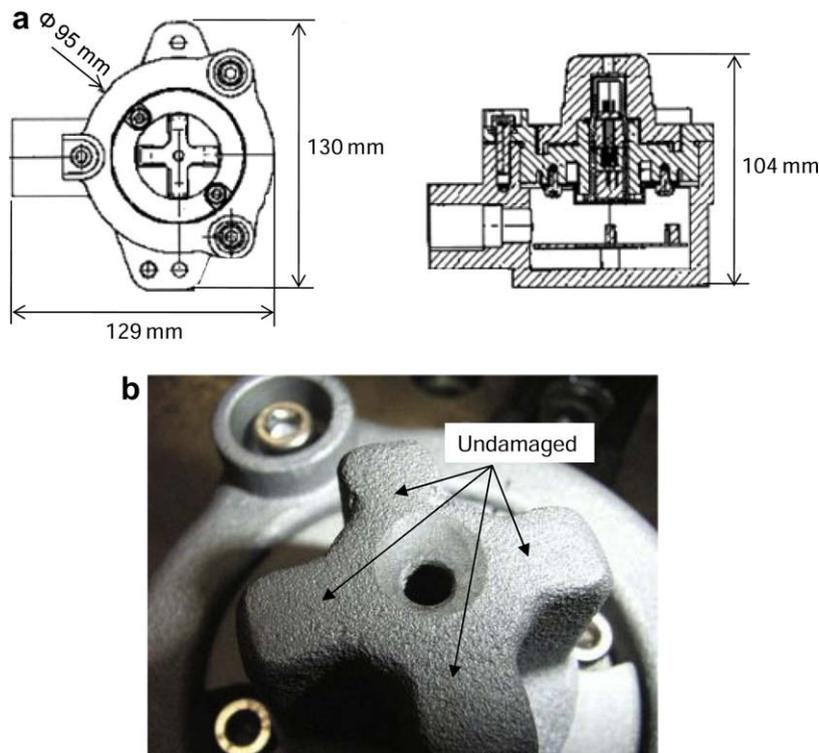
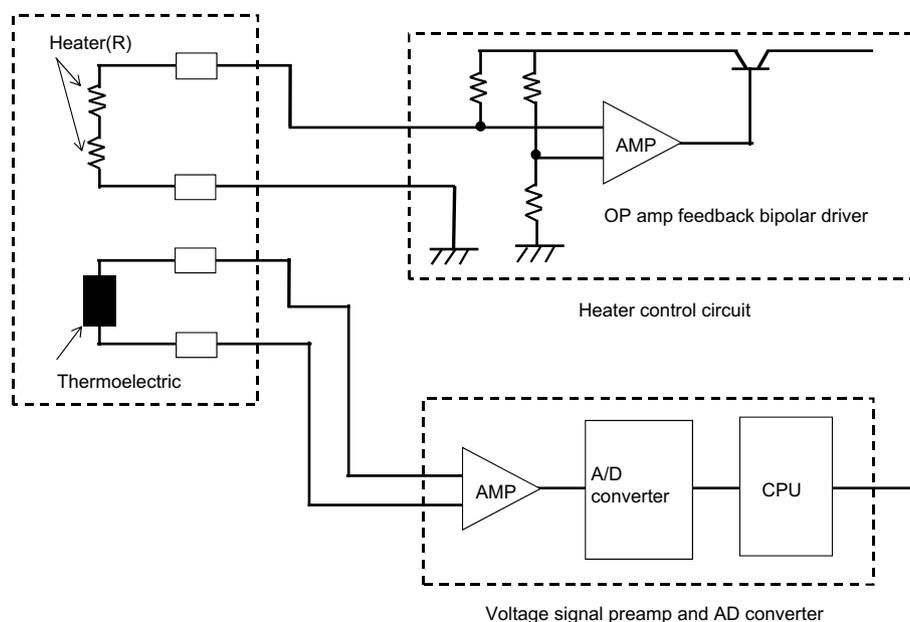


Fig. 4 – (a) Structure of the pressure proof enclosure designed in this study. (b) Photo of the structure of the pressure proof enclosure after impact test.



**Fig. 5 – Schematic circuit diagram of the detection part of the prototype system with the micro-THS. The Pt heater (R) increases with temperature by 0.35%/K approximately.**

proof enclosure adoptable for the international Exd II CT3 standard [14–16], and carried out explosion-proof tests and impact tests. Fig. 4(a) shows the schematic of the detection part of the structure with the pressure proof enclosure designed in this study.

The explosion-proof test includes an explosion strength test and explosion and fire hazard tests. For the explosion strength test, a test gas is injected into the explosion-proof structure placed inside the flameproof electric equipment, and forced ignition is induced to confirm the tolerance of the enclosure against explosive pressure. For the explosion and fire hazard tests, a test gas is injected both inside and outside the explosion-proof structure, and forced ignition is induced inside

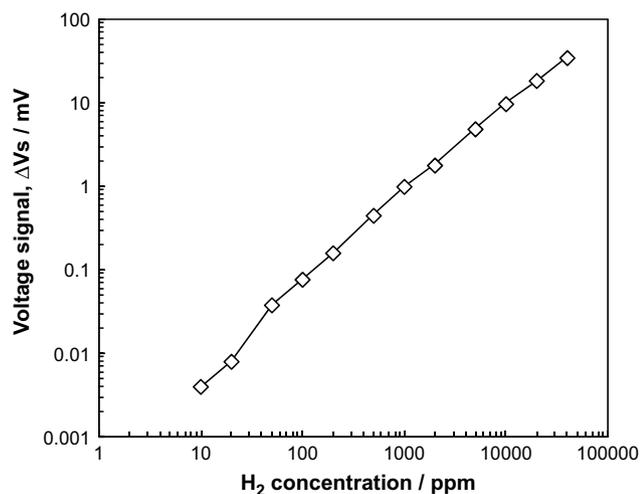
to confirm that the flame induced inside the flameproof sintered metal cap does not ignite the test gas outside. For these tests, hydrogen and acetylene were used as the test gases.

An impact test is carried out to confirm the impact strength of the pressure-proof enclosure of the flameproof electric equipment against the impact induced by dropping a plumb bob (impact strength). For this test, a plumb bob of 1 kg was dropped on the pressure proof enclosure from a height of 0.7 m which is comparable to impact energy of 7 J.

For the explosion strength test, it was confirmed that there was no damage or deformation of the pressure proof enclosure by the explosion. For the explosion and fire hazard tests, it was confirmed that the flame which occurred inside the flameproof sintered metal cap did not diffuse outside the detection part. For the impact test, it was confirmed that the pressure-proof enclosure was not damaged by the impact, as shown in Fig. 4(b).

### 3.2. Signal processing of indicator

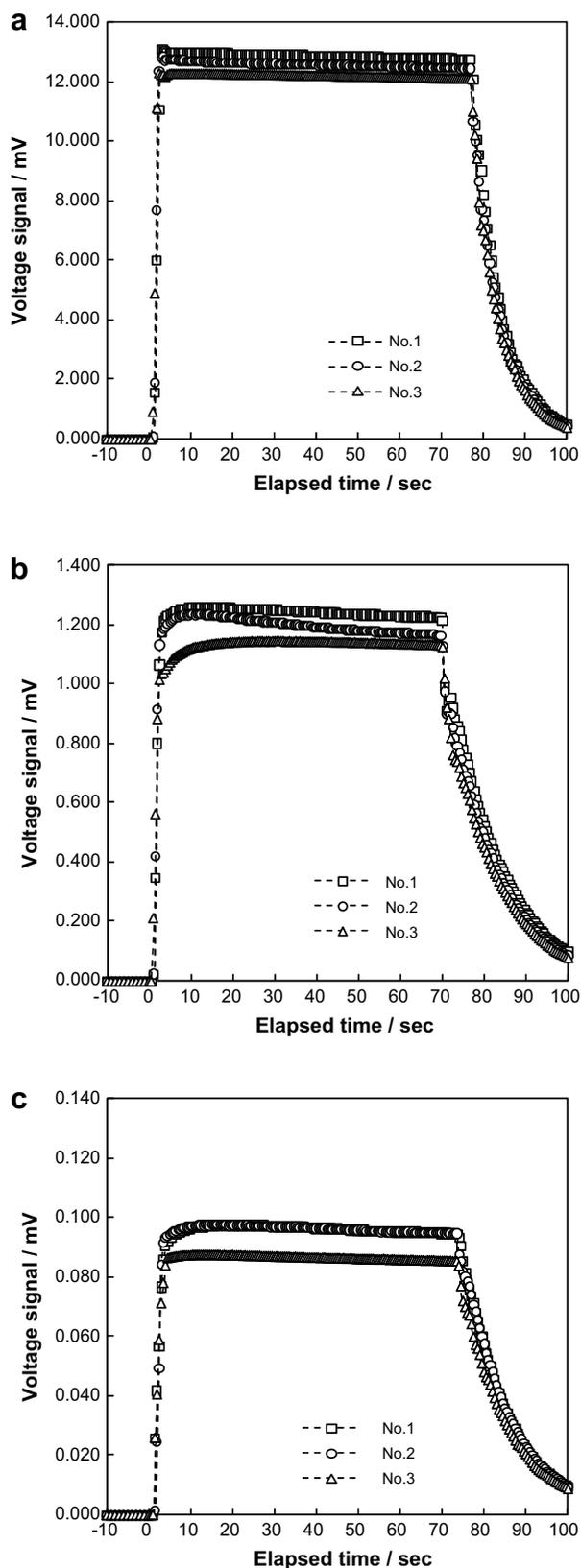
Analog data transfer of 4–20 mA as in a conventional gas alarm system has not enough resolution to take advantage of the wide range of gas concentration detection of the micro-THS, 0.5–50,000 ppm hydrogen in air. For the development of the measurement part, the signal transfer system was



**Fig. 6 – Hydrogen sensing performance of the micro-THS with the flameproof sintered metal cap for a wide range of hydrogen concentrations in air.**

**Table 1 – Indication performance of the sensor indication module for a wide range of hydrogen concentrations in air (at 1 L/min).**

H <sub>2</sub> concentration in air (ppm)	0	10	100	1000	10000	40000
Indication of sensor module (ppm)	0	10	90	980	10000	39800



**Fig. 7** – Sensing performances of the 3 micro-THSs for (a) 10,000 ppm, (b) 1000 ppm and (c) 100 ppm hydrogen in air using the 100-L volume gas diffusion-type test chamber.

**Table 2** – Response time ( $T_{90}$ ) of the micro-THS.

Device no.	1	2	3
10,000 ppm H <sub>2</sub> in air	3.0	2.5	2.0
1000 ppm H <sub>2</sub> in air	3.0	2.5	3.0
100 ppm H <sub>2</sub> in air	3.5	3.5	3.5

changed to digital RS485 communication from the analog data transfer rule of the 4–20 mA output as shown in Fig. 5. With this improvement, the 12 bit indication of the hydrogen concentration, 0–40,000 ppm, with a digit of 10 ppm becomes possible.

The micro-THS has a problem in that the sensing performance can be reduced in a chilly atmosphere. For a catalyst temperature of 100 °C, the sensing performance of an atmosphere of –20 °C decreases by 20% compared with that of the ambient atmosphere of 20 °C. In the chilly conditions, the catalyst temperature cannot be kept at 100 °C if the heater driving voltage is fixed to be constant. To keep the temperature of the catalyst integrated on the micro-THS constant is important for the precise detection of the hydrogen concentration.

To overcome this problem, the detection part has been modified to control the power of the micro-heater against the environmental temperature. Fig. 5 shows a schematic circuit diagram of the detection part of the prototype system which consists of an output signal processing block and a heater driving circuit. The resistance of the micro-heater Pt line changes with the environmental temperature. The heater current is fed back by this OP amp feedback bipolar driver.

#### 4. Sensing performance of the prototype system

##### 4.1. Detection range and response time

Fig. 6 shows the hydrogen sensing performance of the micro-THS with the flameproof sintered metal cap for a wide range of hydrogen concentrations in air. The sensing performance of this sensor showed a good linear relationship between the voltage signal and hydrogen concentrations in air, for a wide range of hydrogen concentrations from 10 ppm to 40,000 ppm in air. Therefore, the sensor indication module has to be prepared for a wide range of hydrogen concentrations in air. Table 1 shows the indication performance of the sensor indication module of the prototype system with the pressure-proof enclosure for a wide range of hydrogen concentrations in air. We confirmed that the sensor indication module can respond for a wide range of hydrogen concentrations from 10 ppm to 40,000 ppm in air.

Fig. 7 shows the sensing performance of the three micro-THSs for 10,000 ppm, 1000 ppm and 100 ppm hydrogen in air. These performance tests were carried out using the pressure proof enclosure in the 100-L volume gas diffusion-type test chamber. For the gas response measurement, an appropriate amount of pure hydrogen gas was injected into the 100-L chamber. The sensing signal increased fast as the ambient atmosphere in the test chamber turned from air into hydrogen

**Table 3 – Alarm output time of the prototype system.**

Alarm level (ppm)	100	500	1000	5000	10000
Test H <sub>2</sub> gas concentration (ppm) at 1 L/min	160	800	1600	8000	16000
Alarm output time (s)	4.7	4.6	4.4	4.1	4.0

mixed gas, and the signal decreased fast as the ambient atmosphere in the test chamber turned into air. Table 2 shows the response time which is calculated from Fig. 7. The average response time ( $T_{90}$ ) is 2.5 s for 10,000 ppm hydrogen in air, 2.8 s for 1000 ppm hydrogen in air, and 3.5 s for 100 ppm hydrogen in air. We have confirmed that the response time of the micro-THS is fast, not only for a high hydrogen concentration of 10,000 ppm in air but also for a low hydrogen concentration of 100 ppm in air.

Table 3 shows the alarm output time of the prototype system for a wide range of hydrogen concentrations from 100 ppm to 10,000 ppm. In this test, the alarm output time was measured using test hydrogen gas concentrations of 1.6 times the alarm level and the hydrogen response performance was investigated using an applicator as shown in Fig. 8. The test gas supply was applied to the sensor device installed in the pressure proof enclosure via the applicator at the rate of 1 L/min by a diaphragm pump. The prototype system demonstrated a fast response within 5 s at the alarm level of 100 ppm to 10,000 ppm. Although the prototype system reads out the output sensing signal without delay, the alarm output time is intentionally delayed for 2.0 s by the delay function of the prototype system after reaching the alarm level. This is the reason that the alarm output time of the prototype system is delayed for 1.0–2.0 s compared with the response time of the micro-THS which is shown in Fig. 7.

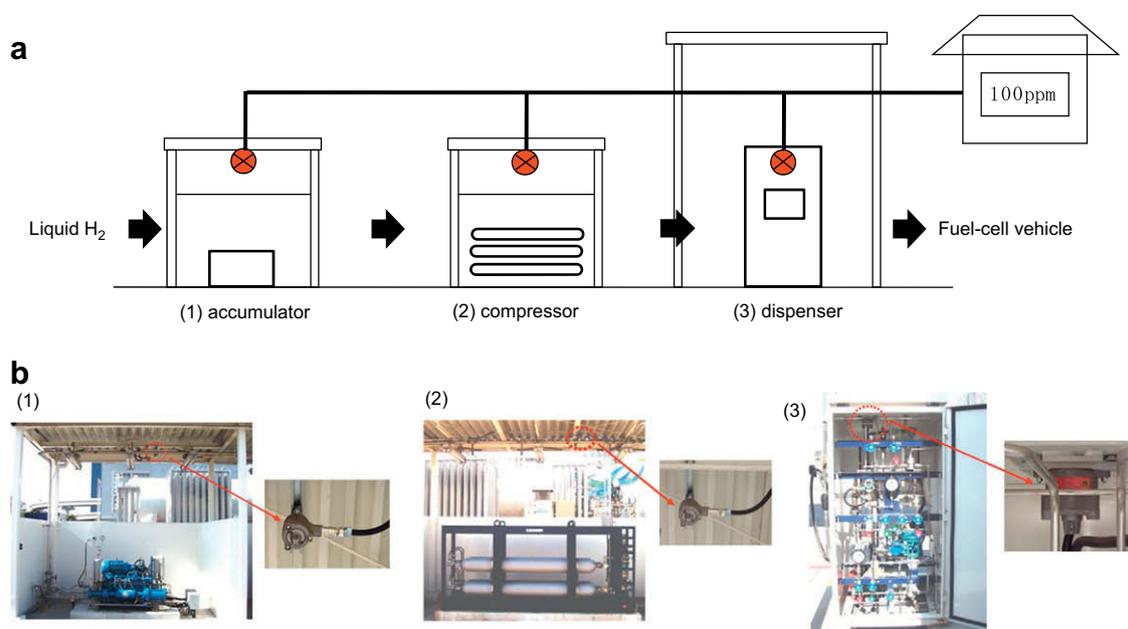


**Fig. 8 – Photo of the sensing performance test using the pressure proof enclosure with gas flow of 1 L/min.**

#### 4.2. One-year field test of the prototype system at a hydrogen station

For real application, it is important to evaluate the reliability of the prototype system under an actual environment, in order to demonstrate whether the performance of this system is good enough for practical use or not, and to figure out any problems in long-term operation. In this study, the prototype system with the micro-THS was installed in the outdoor field of Ariake hydrogen station [17] in Tokyo, Japan, as shown in Fig. 9(a), and the performance tests were carried out monthly for 1 year.

Fig. 9(b) shows the detection parts of the prototype system installed in the hydrogen station. The detection parts of the



**Fig. 9 – (a) Schematic of the location of the detector in the hydrogen station. (b) Photos of the installed sensors, (1) accumulator, (2) compressor, (3) dispenser.**

prototype system are installed in the upper part of the accumulator (1), the upper part of the compressor (2) and inside the dispenser box (3), and the variation in the value of the hydrogen concentration of each module for 10,000 ppm, 1000 ppm and 100 ppm hydrogen in air was monitored monthly.

Fig. 10 shows the change of the hydrogen sensing performance for each prototype system for 1 year and the change in the absolute humidity at the Ariake hydrogen station for this field test period. For 100 ppm hydrogen in air, the indication of the sensor module changed in the range of 10–80 ppm and decreased in the summer season. For 1000 ppm hydrogen in air, the indication of the sensor module changed in the range of 350 ppm to 980 ppm and also decreased in summer for 100 ppm hydrogen in air. For 10,000 ppm hydrogen in air, although the indication of the sensor module changed in the range of 9560 ppm to 10,180 ppm, there was almost no decrease in the indicated value in the summer season. The indication of the sensor module at 100 ppm and 1000 ppm in air recovered in winter.

We monitored the resistance of the Pt heater remained constant as a temperature sensor to confirm the catalyst temperature was also kept constant. As the catalyst temperature remained constant throughout the year, it seems that the decrease in sensing performance of the prototype system is the effect of humidity. The absolute humidity was calculated to be  $19.98 \text{ g/m}^3$  (28,500 ppm) and  $1.77 \text{ g/m}^3$  (2280 ppm) for relative humidity of 59% at  $32^\circ\text{C}$  and 20% at  $9^\circ\text{C}$ , respectively. In the summer season, the concentration of water vapor is about 30 times the hydrogen test gas concentration of 1000 ppm. The micro-THS with a catalyst temperature of  $100^\circ\text{C}$  cannot oxidize the hydrogen effectively against this high water vapor concentration. The influence of humidity can be disregarded at a catalyst temperature above  $125^\circ\text{C}$  [18]. With a catalyst temperature of  $125^\circ\text{C}$ , it suggests that the indication of the sensor indication module becomes constant in the summer season and stable even at low hydrogen concentrations of 1000 ppm and 100 ppm.

Fig. 11 shows the sensing performance of the prototype system for a low hydrogen concentration of 100 ppm in air

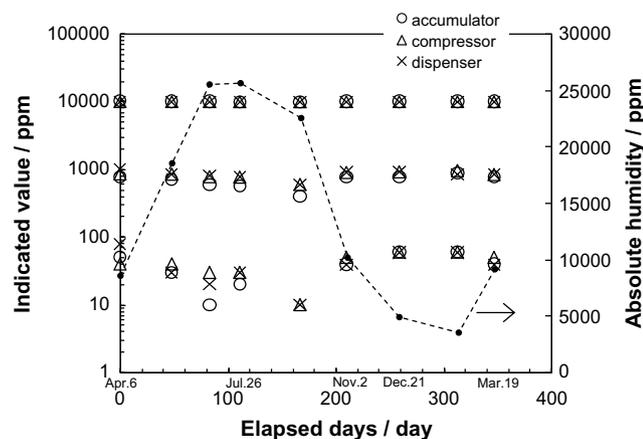


Fig. 10 – Difference in the hydrogen sensing performance of each module for 1 year and the change in absolute humidity at the Ariake hydrogen station.

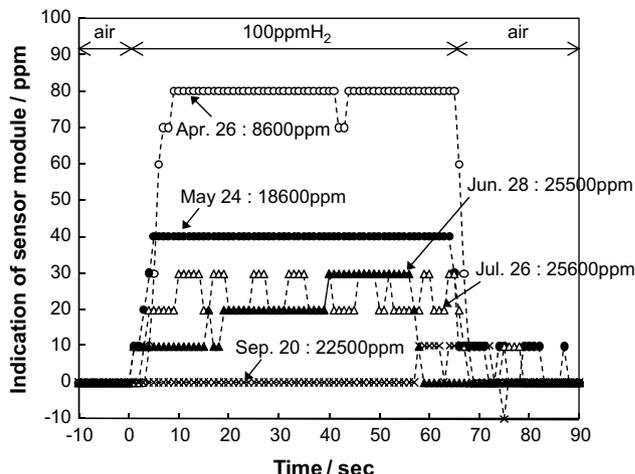


Fig. 11 – Sensing performance of the prototype system installed at the inside of the dispenser box for a low hydrogen concentration of 100 ppm in air through 1 year. Absolute humidity values are shown with the measurement dates.

through 1 year. The response time of the low concentration becomes slow in the summer season and recovers in the winter season. The delay of the response is a typical phenomenon of degraded catalyst performance in the catalytic combustion detection of a low gas concentration, and becomes prominent in humid conditions, as the amount of combustion heat is small and the temperature increase of the catalyst is extremely small. Moreover, this typical phenomenon is reversible, so-called falling asleep of the sensor, and can be recovered from the low sensitivity state of the sensor by the exposure of hydrogen gas. To avoid this falling asleep, one should increase the temperature of the catalyst, but at the same time, lose the gas selectivity of the catalytic combustion. The sensor in this test has low catalyst temperature to realize hydrogen selectivity, which induces easily the falling asleep, shown as the data for June 28 in Fig. 11.

Further investigations to solve this problem, for example, a short-pulse heating of the catalyst between the detection is now being tested to see if this improves the sensor performance or not.

## 5. Conclusion

The micro-THS is an innovative sensor element. The characteristics of low power consumption and a response time of several seconds of this sensor are not seen in the existing hydrogen sensors. This micro-THS satisfies the initial performance demanded of a hydrogen leak sensor for hydrogen stations. Durability improvement of the sensor device and the development of a reliable module will be necessary in the future to accomplish practical use of the micro-THS.

This new hydrogen sensor is a most important beginning for hydrogen infrastructure. We expect that this sensor technology will contribute to early realization of a hydrogen energy society in the future.

## Acknowledgments

This work was supported by the New Energy and Industrial Technology Development Organization (NEDO), Japan. The field test was done by the Ariake hydrogen station (Ariake station) operated by Showa Shell Sekiyu K.K. and Iwatani International Corporation. The Ariake station is a hydrogen station installed by Japan Hydrogen & Fuel Cell Demonstration Project (JHFC), Ministry of Economy, Trade and Industry, Japan.

## Appendix A Supplemental material

Supplementary information for this manuscript can be downloaded at doi:10.1016/j.ijhydene.2009.01.027.

## REFERENCES

- [1] Adamyan AZ, Adamyan ZN, Aroutiounian VM, Arakelyan AH, Touryan KJ, Turner JA. Sol-gel derived thin-film semiconductor hydrogen gas sensor. *Int J Hydrogen Energy* 2007;32:4101–8.
- [2] Kumar MK, Ramaprabhu S. Palladium dispersed multiwalled carbon nanotube based hydrogen sensor for fuel cell applications. *Int J Hydrogen Energy* 2007;32:2518–26.
- [3] Shukla S, Zhang P, Cho HJ, Ludwig L, Seal S. Significance of electrode-spacing in hydrogen detection for tin oxide-based MEMS sensor. *Int J Hydrogen Energy* 2008;33:470–5.
- [4] Tsai TH, Chen HI, Lin KW, Hung CW, Hsu CH, Chen LY, et al. Comprehensive study on hydrogen sensing properties of a Pd-AlGaN-based Schottky diode. *Int J Hydrogen Energy* 2008;33:2986–92.
- [5] Aroutiounian V. Metal oxide hydrogen, oxygen, and carbon monoxide sensors for hydrogen setups and cell. *Int J Hydrogen Energy* 2007;32:1145–58.
- [6] IEC 60079-29-1. Explosive atmospheres – Part 29-1: Gas detectors – Performance requirements of detectors for flammable gases.
- [7] JIS M 7626. Stational type combustible gas alarm, Japanese Standards Association, 1994.
- [8] Tajima K, Shin W, Izu N, Matsubara I, Murayama N. Micromechanical fabrication of low-power thermoelectric hydrogen sensor. *Sens Actuators B* 2005;108:973–8.
- [9] Shin W, Choi Y, Tajima K, Izu N, Matsubara I, Murayama N. Planar catalytic combustor film for thermoelectric hydrogen sensor. *Sens Actuators B* 2005;108:455–60.
- [10] Shin W, Nishibori M, Choi Y, Tajima K, Izu N, Matsubara I, et al. Integration of ceramic catalyst on micro-thermoelectric gas sensor. *Sens Actuators B* 2006;118:283–91.
- [11] Choi Y, Tajima K, Shin W, Izu N, Matsubara I, Murayama N. Integration of microcatalysts on thin membrane for thermoelectric gas sensor devices. *J Mater Sci* 2006;41:2333–8.
- [12] Nishibori M, Shin W, Houlet LF, Tajima K, Izu N, Itoh T, et al. New structural design of micro-thermoelectric sensor for wide range hydrogen detection. *J Ceram Soc Jpn* 2006;114:853–6.
- [13] Nishibori M, Tajima K, Houlet LF, Shin W, Izu N, Itoh T, et al. Long-term stability of Pt/alumina catalyst combustors for micro gas sensor application. *J Eur Ceram Soc* 2008;28:2183–90.
- [14] IEC 60079-1. Explosive atmospheres – Part 1: Equipment protection by flameproof enclosures “d”.
- [15] Guide for official assay of explosion-protected electrical apparatus. Technology Institution of Industrial Safety, 1996.
- [16] Shimada Electric Co., Ltd. [http://www.shimada-elec.co.jp/english/index\\_e.htm](http://www.shimada-elec.co.jp/english/index_e.htm).
- [17] Ariake Hydrogen Station. Operated by Showa Shell Sekiyu K. K. and Iwatani International Corporation, Japan Hydrogen & Fuel Cell Demonstration Project (JHFC), <http://www.jhfc.jp/e/station/kanto/ariake/index.html>.
- [18] Nishibori M, Shin W, Izu N, Itoh T, Matsubara I. Monitoring hydrogen in human breath with thermoelectric hydrogen sensor for the evaluation of colonic flora. *Proceedings of the 12th International Meeting on Chemical Sensors*, 2008.