PERFORMANCE EVALUATION OF THE MINIATRIZED CATALYTIC COMBUSTION TYPE HYDROGEN SENSOR

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ABSTRACT

Fast response and high durability hydrogen sensor is required in the safety management of hydrogen station and fuel cell vehicle. We had developed the catalytic combustion type hydrogen sensor in the shape of the miniature beads. It is using the optimized Pd-Pt/Al_2O_3 catalyst and the Pt micro-heater coil. Both warm-up time and response time of this sensor achieved less than 1 second by downsizing the element to 200μm diameter. Furthermore, we improved the resistance of sensor poisoning to silicone vapor and confirmed long term stability within +/-10% of output error up to 8 years. Therefore, we assume that our sensor technology contribute to hydrogen safety.

1. Introduction

For realization of the future hydrogen energy society, the establishment of the hydrogen safety use technologies viewed as important in every situation such as production, transportation, storage, filling and consumption. Accordingly, the various safety measures are taken in the hydrogen facilities. In this field, the hydrogen alarm systems have the role to early detection of the hydrogen leak accident emergency. For example, the installation of the hydrogen alarm system is made mandatory by the high pressure gas safety act on the Japanese hydrogen station. In here 5 to 10 points of hydrogen sensors per one facility are installed. The alarm concentration is fixed between 500ppm and 2% depending on an install location. And either the semiconductor type gas sensor or the catalytic combustion type gas sensor is chosen according to an alarm concentration. By the way, our gas alarm system is being adopted in 22 Japanese hydrogen stations as of March, 2015. Besides, it adapts to an international standard. The current hydrogen alarm system has already been able to implement a reliable system by annual periodical maintenance. However, with the expansion of the field of the hydrogen energy applications, it is predicted in future when higher performance hydrogen sensor is required in detection range and response time, accuracy, life, disabilities. For example, as for the hydrogen detector for FCV (Fuel Cell Vehicle), maintenance free, and the durability more than 15 years and a fast response are demanded, and it is not easy to satisfy this demand performance with an existing sensor. In addition, the hydrogen detection range and the accuracy are required 0-4%vol and +/-10% respectively. We consider that the catalytic combustion type gas sensor is suitable for this application. Therefore we solved this subject by improvement of catalyst material and miniaturized the element size of the catalytic combustion-type gas sensor named on μ-CS sensor. In this paper, we report the advantages and the performances of the μ-CS sensor. Furthermore, we consider requirements necessary for the early detection of the hydrogen leak from the result of the hydrogen diffusion experiment and report the usefulness of a fast response sensor.

2. μ-CS sensor structure

The catalytic combustion type gas sensor detects oxidation heat of the flammable gas on the noble metal catalyst as a temperature change of the detector elements. Thus, it is capable of being obtained the fast response sensor if it is improved the thermal response of the detector element. Regarding this, it is effective to miniaturize an element. Fig.1 shows the overview SEM photograph of the Pt micro heater coil and the detector element. Characteristic of the μ-CS sensor are miniaturized an element by using the micro heater coil of the φ 10μm Pt wire. The detector element spherically sinters Pd-Pt supported alumina (Pd-Pt/Al_2O_3) to a Pt micro heater coil. The element diameter is φ 200μm. On the other hand, the temperature compensation element spherically sinters a simply alumina (Al_2O_3). These

two elements incorporated in a bridge circuit and become the sensor. Incidentally, element diameter of the conventional sensor is φ 700μm. A volume of the μ-CS sensor elements are 1/40 than this, and electric consumption is reduced with about 1/5. It must improve sintering strength of Pd-Pt/Al_2O_3 and Al_2O_3 to miniaturize an element. So we solved this problem by adding a sintering assistant to Pd-Pt/Al_2O_3 and Al_2O_3. In the other developments about the miniaturizing sensor, the planer type sensors using the MEMS (Micro Electronic Mechanical Systems) technology are reported. The MEMS is the technique that can manufacture micro fine Pt thin film heater less than 100μm square on SiO_2 membrane. However, the MEMS type micro heater occur the radiation loss by the thermal conduction through the SiO_2 membrane supporter. This radiation loss of the element neighborhood is a factor to influence hydrogen detection accuracy. In contrast, the beads type element can minimize thermal conduction loss because a Pt wire serves as a support and an electric conductor.
Furthermore, heat by the catalytic combustion of hydrogen efficiently reaches the resistance (Pt wire coil) because a catalyst covers up the Pt wire coil. We think that beads element type gas sensor is more dominant as for the hydrogen detection performance.

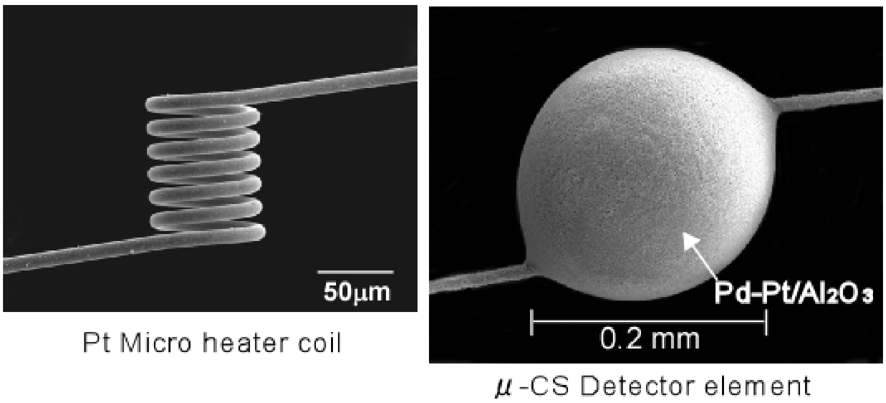

Figure 1. The overview SEM photograph of the Pt micro heater coil and the detector element.

3. Evaluation of the response properties

3.1 Testing condition

The responses profiles of the μ-CS sensor was evaluated that air and 500ppm hydrogen exchange by turns, using the equipment as shown in Fig.2. It was compared with the period of the exchange with 10sec. cycle in 2sec. cycle and 1sec. cycle. Then, the conventional catalytic combustion sensor was evaluated on the same condition and compared with the μ-CS sensor. By the way, a capacity of the sensor flow cells was 2mL, and the flow rate was 5L/min to shorten substituted time of the test gas.

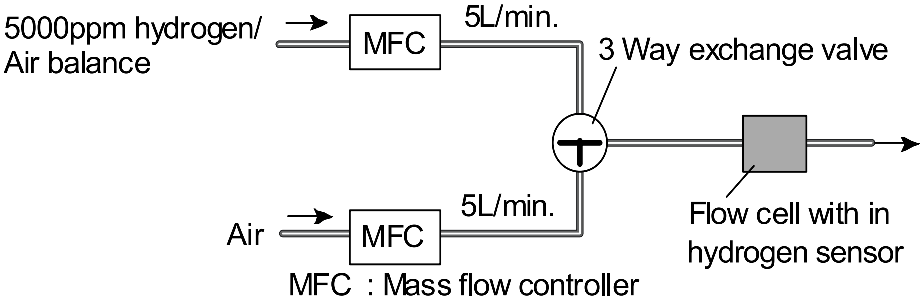

Figure 2. Constitution outline of the response evaluation equipment

3.2 Evaluation results of the response properties.

Fig.3 shows compared results of the response profiles of the conventional sensor with the μ-CS sensor. T_{90} response time (90% arrival time to saturated output) of the μ-CS sensor was 0.7 seconds. In contrast, the T_{90} response time of the conventional sensor was 3.5 seconds. As a result, it was known that the miniaturizing of the sensor element is effective in fast response. When it exchanged test gases in a short time, the superiority of the fast response sensor appeared conspicuously. When the test gases exchanged in 1second cycle and 2seconds cycle, the sensor output was shown in Fig.3 (B) and Fig.3 (C), respectively. It was confirmed that the μ-CS sensor can track the hydrogen concentration changes of 1 second. On the other hand, the conventional sensor's output lower than true concentration because a response have time delay.

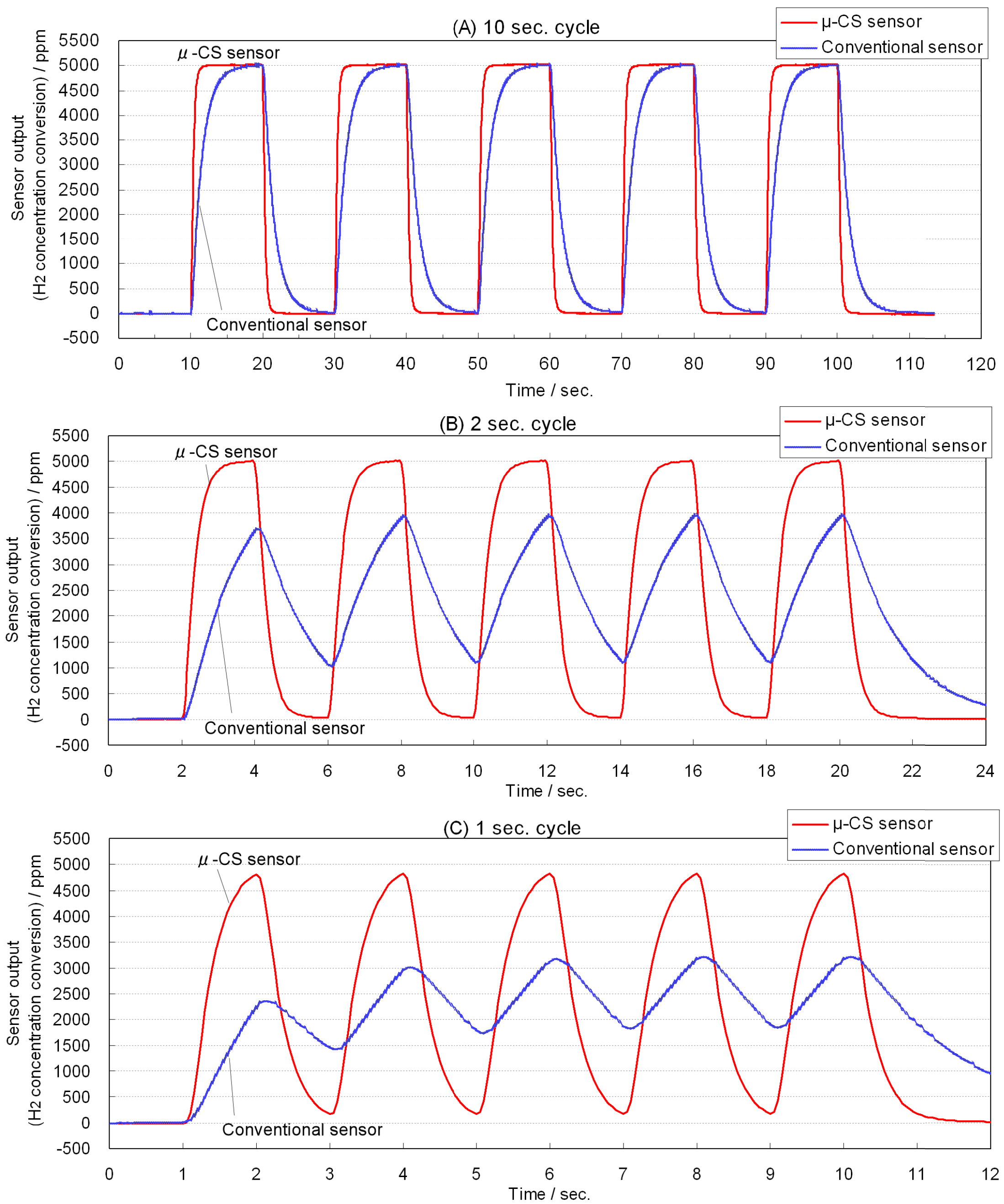

Figure 3. The response properties to 5000ppm hydrogen comparison between the μ-CS sensor and the conventional sensor.

4. The evaluation of response property by the hydrogen diffusion experiment.

4.1 Experiment method

The response profiles of the conventional sensor and the μ-CS sensor were compared using the equipment which simulated a sensor setting location as shown in Fig.4. Each sensor fixed it to the ceiling side of the equipment. And it was experimented on hydrogen leakage and ventilation flow rate were constant conditions. The constitution of this equipment referred to the hydrogen diffusion experimental equipment of H. Tsukikawa et al [4]. The capacity of container was 58L. The area of the air inlet was 72cm^2. The ventilation speed of the fan was 65L/min. The ventilation rate on this condition is approximately 1.1time/min., in other words, an air in the container is substituted at the rate of 1.1 times for 1min. In this experiment, the each sensor's outputs were compared with hydrogen leakage 2L/min., 1L/min. and 0.1L/min. In here, hydrogen leakage 0.1L/min. assumes a slow leak mode.

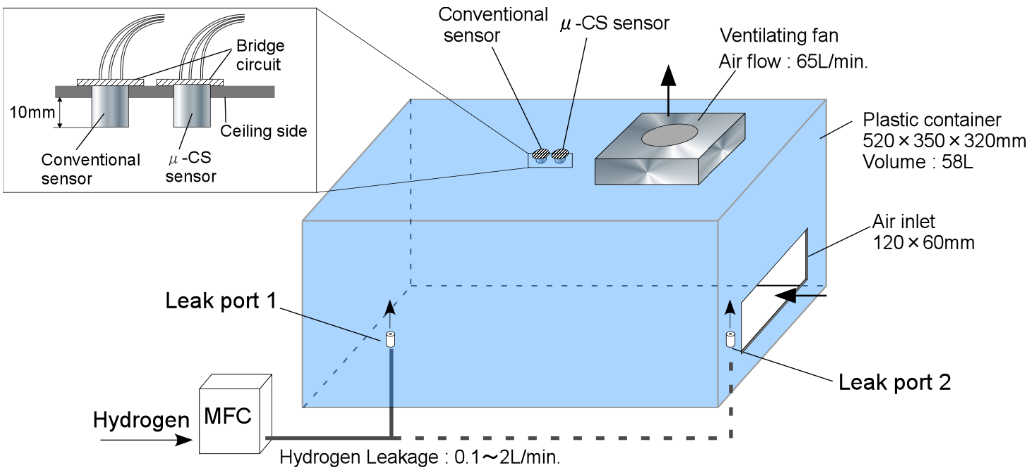

Figure 4. Equipment outline of hydrogen diffusion experiment.

4.2 Diffusion experiment results

Fig.5 shows the each sensor output when hydrogen leaked from port1. In hydrogen leakage 2L/min., the sensor output has begun to change from an inflow start after about 3sec. It was observed that the μ-CS sensor's output sharply fluctuate between 4500ppm to 10760ppm with a hydrogen concentration conversion value after start 35sec.. On the other hand, fluctuation of the conventional sensor's outputs was smaller than μ-CS sensor. H. Tsukikawa et al. report the following results by a hydrogen diffusion experiment [5]. Leaked hydrogen reaches the ceiling immediately and spreads along a ceiling side. The local hydrogen concentrations greatly fluctuate under the influence of the complicated air flow. It is thought that hydrogen migrate to the ventilation fan side without being diluted uniformly, even our experiment is the same. Therefore, judging from the response properties of Fig3, it is thought that the μ-CS sensor can measure hydrogen concentration in real time. In the case of hydrogen leakage 1L/min., this sensor output fluctuation was observed. The μ-CS sensor's output change after hydrogen inflow start 40sec. was approximately 1500-3000ppm by hydrogen concentration conversion. In addition, in the case of hydrogen leakage 0.1L/min. which assumed the slow leak mode, the μ-CS sensor's output fluctuation was observed. Then, Fig.6 shows a result of the each sensor's outputs in case of hydrogen leak port2 (air inlet side) and hydrogen leakage 2L/min. On this condition, hydrogen is diluted more and arrives at the sensors. Although each sensor's output was smaller than a case of Fig.5 (A), a fluctuation was observed in the μ-CS sensor's output. These diffusion experiments results suggest, even if hydrogen leaks out on the high ventilation rate condition, the hydrogen safety is secured because the hydrogen concentration kept low. On the other hand, it suggest too that the phenomenon recognition of the hydrogen leak may be late by the existing hydrogen alarm systems which warn only when it detect hydrogen more than alarm concentration. By the hydrogen safety management, early detection of the hydrogen energy system trouble is demanded. If the hydrogen alarm system detect a short term fluctuation of the μ-CS sensor's output, it is possible for a pre-warning before than hydrogen concentration in environment reaches the alarm concentration. Therefore, it is thought that the fast response hydrogen sensor is useful for the construction of a safer hydrogen alarm system.

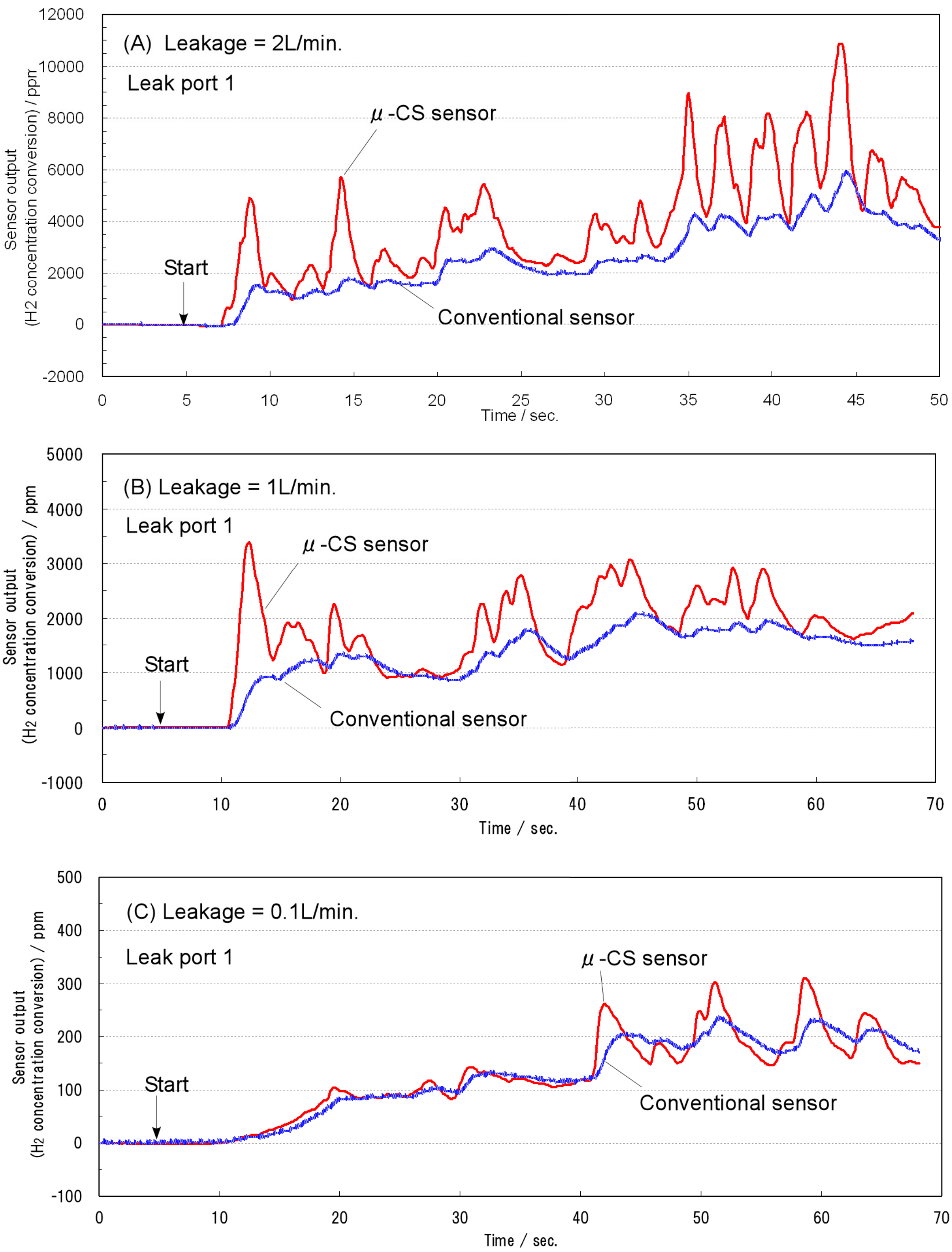

Figure 5. The hydrogen diffusion experiment results on hydrogen inflow from leak port1(comparison between the μ-CS sensor and the conventional sensor.) Fig. 5. (A) Hydrogen Leakage = 2L/min., Fig. 5. (B) Hydrogen Leakage = 1L/min., Fig. 5. (C) Hydrogen Leakage = 0.1L/min.

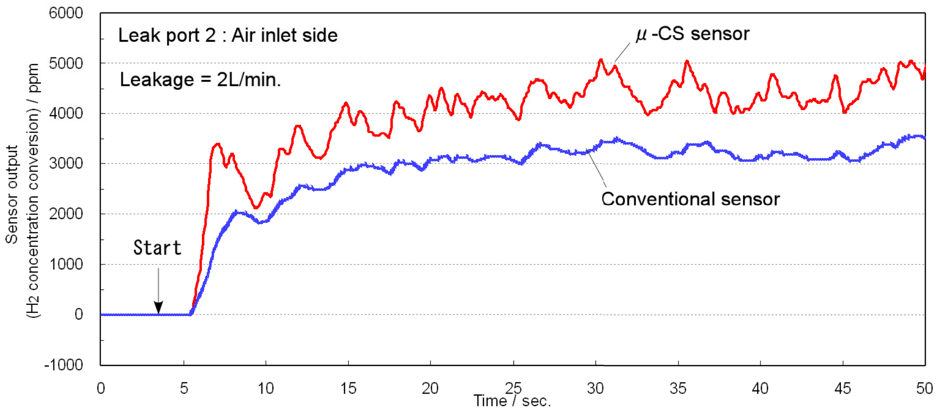

Figure 6. Hydrogen diffusion experiment results on hydrogen inflow from leak port 2 (comparison between the μ-CS sensor and the conventional sensor.) Hydrogen Leakage = 2L/min.

5. Durability evaluation

The chemical components such as H_2S or SO_2 or silicone (siloxane) adversely affecting sensitivity in the setting place of the hydrogen sensors may coexist. It is known that a siloxane in particular deposit silicide on the catalyst surface and inhibit a reaction with hydrogen. To maintenance free hydrogen sensor, it is required that the performance of sensitivity decrease less under the siloxane coexistence environment either. The hydrogen sensitivity of the μ-CS sensor and SEM photograph of this detector element surface before and after the 1% HMDSO (hexamethyl disiloxane) at 20 hours exposure test was shown in Fig.7. It was confirmed that the μ-CS sensor have stability to even high-concentration siloxane vapor. And, hexagonal crystals like SiO_2 were deposited it on the detector element surface after exposure. As a result, it is thought that the deposition of the silicide to the active site is restrained because the siloxane is completely oxidized on the detection element surface, and growth of the SiO_2 nucleus is promotes.

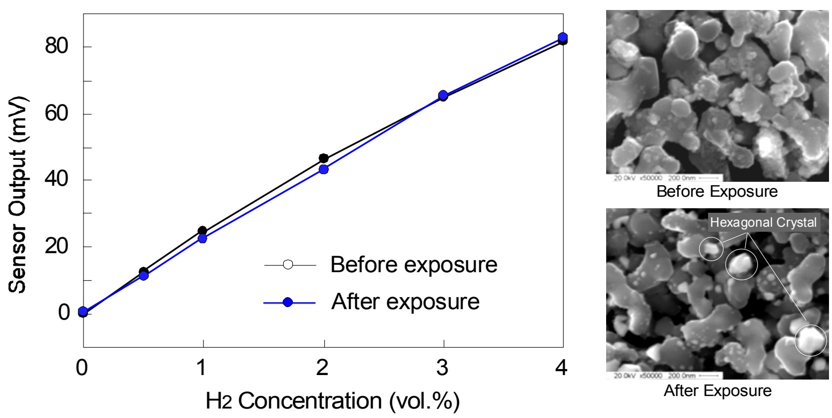

Figure 7. Test result of resistance to Silicone Poisoning

6. Life time of the μ-CS sensor

We estimated the sensitivity decrease rate for 15 years of use based on the monitoring data (sensor output recorded while the sensor was energized for 3010 days in a row indoors). The sensitivity decrease rate for 15 years continuous use estimated based on $Y=a\cdot e^{-bX}$ (Arrhenius' equation) is 10% or less. The sensitivity of the catalytic combustion sensor will not deteriorate under a normal environment if not energized. Given that the sensor is used for 8 hours per day in an FCV, longer life sensor can be expected.

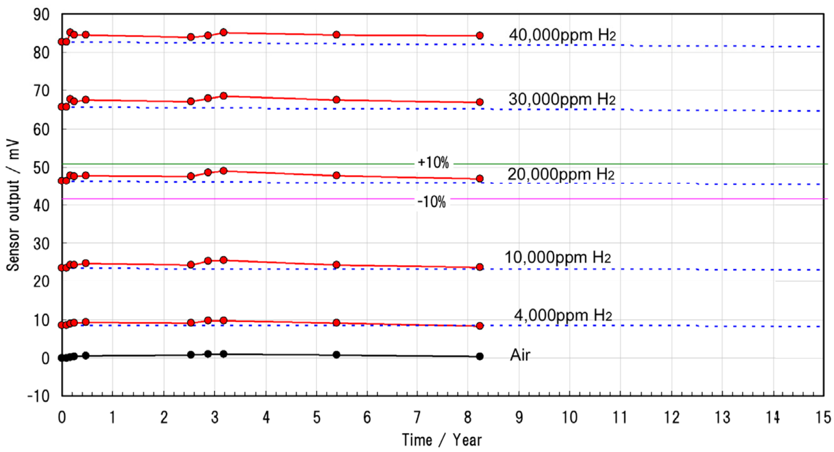

Figure 8. Evaluation result of long-term stability indoors

7. Other evaluation results of the μ-CS sensor

The influence of the temperature / humidity had evaluated that the precision errors were +/-10% or less at any conditions (-35 to 100 degree C / 0 to 95%RH). Furthermore, we had confirmed that hydrogen sensitivity of the μ-CS sensor is stable to various severe tests such as high concentration hydrogen exposure, a high temperature leaving test, a low temperature leaving test, a vibration tolerance, an impact tolerance and so on. These results mean that the life of the μ-CS sensor is equal to the conventional sensor. Generally on catalytic combustion sensor, it is known the more downsizing sensor's life shorten because deterioration of the catalytic activity is reflected conspicuously to sensitivity. In contrast, it is realizing longer life on the μ-CS sensor. This result suggests that the catalytic activity of the μ-CS sensor is stable, and it have been successful to the overcome defects with the sensor downsizing.

8. Conclusions

The new catalytic combustion type hydrogen sensor (μ-CS) which miniaturized elements using a Pt micro heater coils was developed. It was confirmed by a hydrogen diffusion experiment, because it can detect a change of local hydrogen concentration at the real time, the fast response sensor is useful to shortening an alarm delay time. The μ-CS sensor's life is estimated more than 10 years. Furthermore, μ-CS sensor has the high durability to the siloxane vapor mixture conditions. Besides, it had confirmed that the μ-CS sensor endure other various severe environment. Therefore, we conclude that the μ-CS sensor is useful to the future hydrogen safety managements. The μ-CS sensor has been already put to practical use to the pocket size gas detector (XA-380). We would apply the μ-CS sensor to a hydrogen alarm system and a hydrogen detector for the FCV in future.

References

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