

Achievements and Challenges in Catalytic Combustion Hydrogen Sensors: Commercial Use in Fuel Cell Vehicles and Miniaturization using MEMS Technology

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Abstract

Safe use of hydrogen in future low-carbon society requires hydrogen sensors that detect hydrogen leakage with high sensitivity and selectivity. For this purpose, we developed bead-shaped catalytic combustion sensors for hydrogen detection. The sensors consist of an alumina bead loaded with precious metal and a platinum heater coil. Developing the proprietary catalysts and downsizing the sensor elements led to very fast startup, extremely quick response to hydrogen, and long-term stability of the sensors. These features make the sensors very suitable for detecting hydrogen leakage in fuel cell vehicles (FCVs). Indeed, the sensor modules equipped with the sensor elements fulfilled strict demands such as high detection accuracy and durability against various harsh environments possible in FCVs. Consequently, the sensor modules have been installed in a commercial FCV (MIRAI, Toyota Motor Co., Ltd.) since 2020.

An important challenge in catalytic combustion sensors is miniaturizing the sensors using micro electro-mechanical systems (MEMS) technology. Miniaturized sensors exhibit reduced power consumption and thus can be operated with a battery. Indeed, we have already launched battery-operated city gas alarms equipped with MEMS chemo-resistive sensors in Japan and the USA. In this paper, we present various properties of MEMS catalytic combustion sensors together with bead-shaped ones.

Key words: hydrogen, hydrogen sensor, catalytic combustion, FCV, MEMS

1. Introduction

The safe use of hydrogen as a sustainable energy source is necessary to realize a low-carbon society in the future. To deal with the explosion danger of hydrogen in a wide concentration range (4~75 volume% in air), affordable, robust, and reliable hydrogen sensors capable of detecting leakage are essential. To address this assignment, New Cosmos Electric, which specializes in gas alarms and detectors, developed various hydrogen gas sensors fulfilling the requirements in emerging hydrogen use. For example, the installation of hydrogen alarm systems has become mandatory under the High-Pressure Gas Safety Act at Japanese hydrogen stations for automobiles. Presently, our gas detection and alarm systems are installed in approximately 80% of the hydrogen stations Japan, illustrating our contribution to realizing a low-carbon society.

Another example is the use of our hydrogen sensors in commercial fuel cell vehicles (FCVs).

Sensor modules equipped with hydrogen sensor elements have been installed in commercial FCVs as crucial components for hydrogen fuel sources. These sensor modules must ensure the detection of hydrogen leaks just in case of an accident, and high-performance hydrogen sensors capable of enduring various harsh environments possible in FCVs are required. We developed hydrogen sensors suitable for such uses by developing proprietary catalysts and downsizing the sensor elements. Furthermore, we have ensured a stable supply of gas sensors based on mass-production technology built on household gas alarms. As shown in Fig. 1, these sensors have been adopted in a commercial FCV (MIRAI, Toyota Motor Co., Ltd.) since 2020 [1].

This paper is organized as follows. We first briefly review the requirement for hydrogen sensors in FCVs and discuss the selection of hydrogen sensors suitable for the use. We then explain the working principle of the selected sensor for this purpose: catalytic combustion

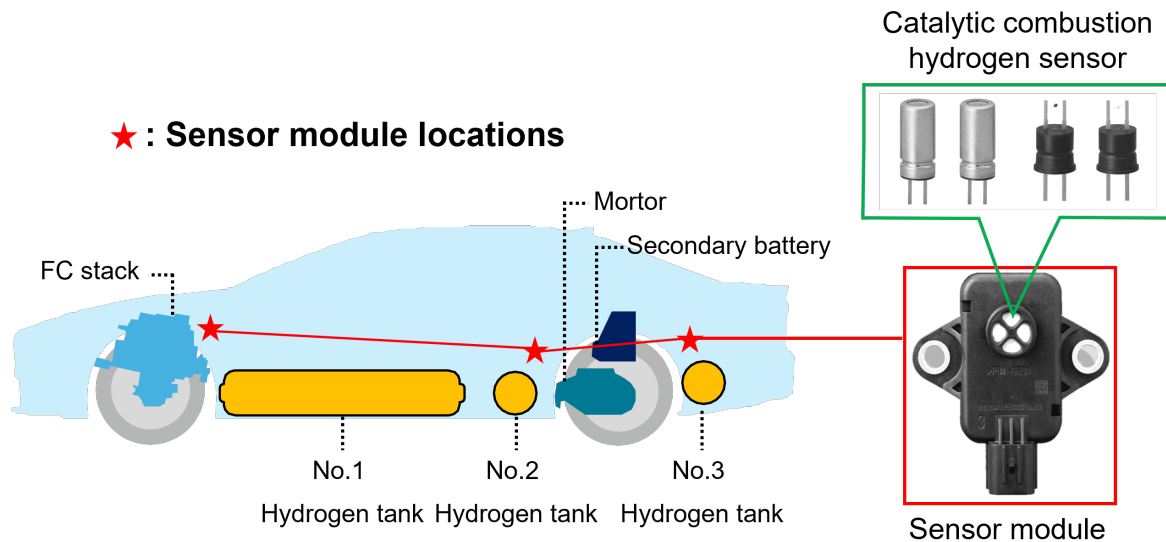


Fig. 1 Commercial FCV and the sensor module equipped with a catalytic combustion hydrogen sensor.

sensors [2]. We in detail present two important technical advances required for hydrogen sensors for FCVs: miniaturization of sensor elements and developing the proprietary catalysts. Before conclusion, we show a more advanced miniaturization using micro electro-mechanical systems (MEMS) technology for future emerging hydrogen use.

2. Requirement for hydrogen sensor in FCVs

Hydrogen sensors are important devices that detect and quantify hydrogen by its reaction with hydrogen present in the atmosphere and convert the change into an electrical signal or change in resistance. Given that gas sensors must be continuously exposed to their surrounding environment, the required specifications vary significantly based on factors such as environmental temperature, humidity changes, durability against toxic gases that degrade catalytic activity and gas selectivity. Furthermore, hydrogen exhibits numerous physical properties distinct from other gases, including its low mass density, combustibility, and high diffusion velocity. To date, hydrogen sensors with various detection principles have been extensively studied and developed. To name a few, these include thermoelectric, electrochemical, quartz crystal type, and hydrogen sensors that utilize the hydrogen absorption reaction in Pd alloys.

Presently, hydrogen sensors employed for leak detection in hydrogen stations and production facilities are mainly based on semiconductor and catalytic combustion detection principles. In addition, gas thermal conduction type is used in special applications such as hydrogen

concentration measurement in inert gas. Each sensor type has a different hydrogen detection range and is suitable for specific applications.

FCVs represent a sustainable alternative to traditional internal combustion engine vehicles, offering zero-emission transportation powered by hydrogen fuel cells. However, the safe handling and use of hydrogen in FCVs require robust sensing technologies to detect hydrogen leaks and ensure driving safety. Therefore, hydrogen sensors to be installed in FCVs satisfy the following important requirements:

- (1) a wide detection range (0-40,000 ppm)
- (2) detection accuracy ($\pm 10\%$ above 10,000 ppm)
- (3) fast startup (< 2 seconds) and 90% response speed (< 3 seconds)
- (4) durability against harsh environments
- (5) long life (> 10 years) and Driving time ($> 10,000$ hours)
- (6) operating temperature (-35 to 85°C)
- (7) low power consumption
- (8) low cost (mass producibility).

To fulfill these strict demands, we selected a catalytic combustion gas sensor, which has a track record the service for many years. However, objectively demonstrating the maintenance of hydrogen detection accuracy was a major challenge, especially over a service life of 10 years or more and under the harsh environmental conditions typical of vehicles. For this purpose, we developed an improved catalytic combustion hydrogen sensor.

3. Catalytic Combustion gas sensor

The catalytic combustion gas sensor has two key elements: a detector element reactive to combustible gases and a compensator element that remains inert. The detector element consists of an alumina bead loaded with precious metal such as Pd or Pt (Pd-Pt/Al₂O₃ catalyst), in which a Pt heater coil is embedded. On the other hand, the compensator element consists of an alumina bead without a precious metal and a Pt heater coil.

To detect a target gas, the Pt heater coil is heated to an appropriate temperature, e.g., 350°C by self-heating due to voltage application. In the presence of combustible gas, combustion occurs on the detector element, raising the temperature of the sensor and increasing its resistance. On the other hand, the compensator element, unaffected by combustion, maintains a constant temperature and resistance. By incorporating these elements in a bridge circuit (Fig. 2), the difference in sensor resistance causes an imbalance in the bridge circuit, and this change can be detected as a sensor output (ΔV), which is proportional to the concentration of combustible gas.

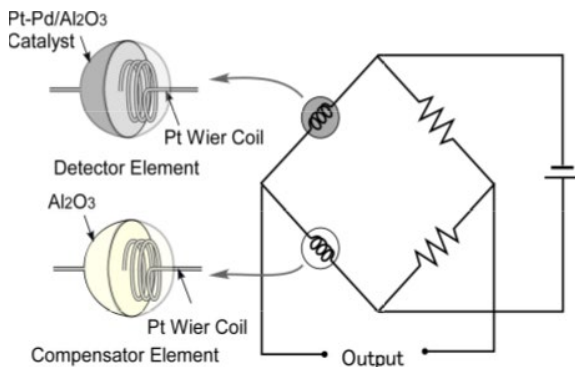


Fig. 2 Basic measuring circuit of the sensors.

4. Miniaturization of sensor elements

Hydrogen sensors for FCVs have strict requirements for fast startup and quick response to hydrogen within a few seconds. Thus, we attempted to downsize the sensor elements to improve thermal response and reduce response time to hydrogen. Figure 3 shows scanning electron microscope (SEM) images of the conventional and the improved sensors. The diameter of the bead-shaped element for the improved sensor was approximately 0.5 mm, which was half of that for the conventional sensor, 1.0 mm. That is because we used a smaller Pt coil heater for the improved sensor than that for the conventional sensor. The volume of the

improved sensor elements is thus approximately 1/8 of that of the conventional sensor. This miniaturization first of all reduced power consumption. The improved sensor required 125 mW for operation, which was one-third of that for the conventional sensor, 400 mW.

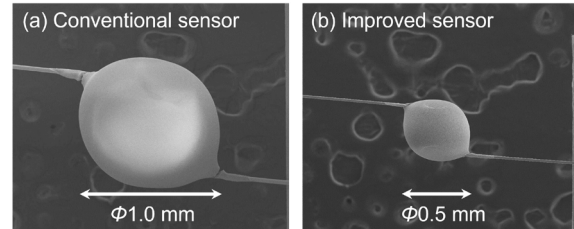


Fig. 3 SEM images of (a) the conventional and (b) the improved sensors.

Figure 4 shows a comparison of the thermal response characteristics of the conventional sensor and the improved sensor in air. The startup time, which can be evaluated by the return of a stable baseline after energization, of the conventional sensor was 10 seconds. In contrast, the improved sensor required only 1 second for startup. Such a quick startup of the hydrogen sensor can reduce explosion risk at system startup if a hydrogen leak occurs during system shutdown.

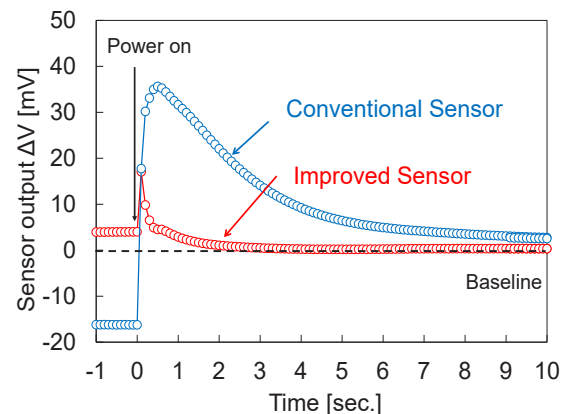


Fig. 4 Thermal response characteristics of the conventional and the improved sensors in air.

Figure 5 shows the hydrogen response characteristics of the improved sensor and conventional sensor to 10,000 ppm hydrogen in air. T_{90} response time, which is the arrival time to 90% of saturated output, of the conventional sensor was 5.8 seconds. On the other hand, T_{90} of the improved sensor was as short as 2.1 seconds. These results (Figs. 4 and 5)

demonstrate that miniaturization effectively improves startup and response time. Both values satisfied the requirement (3) in section 2.

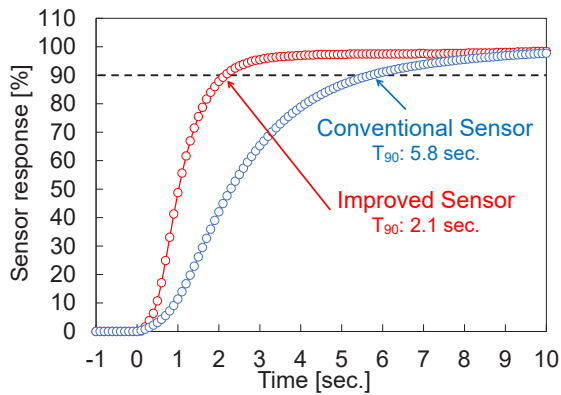


Fig. 5 Hydrogen response characteristics of the conventional and the improved sensors to 10,000 ppm hydrogen in air.

5. Developing proprietary catalysts

Catalytic combustion gas sensors commonly decreased sensitivity due to catalyst poisoning on the catalyst surface [3], particularly in the presence of siloxane vapor coexisting in the environment of FCVs. To enhance the durability of the active catalyst for the detector element [4], we fabricated highly dispersed Pd-Pt nanoparticles on alumina supports. Figure 6 shows transmission electron microscope (TEM) images of the Pd-Pt/Al₂O₃ catalyst. These images visualized highly populated and yet well-dispersed Pd-Pt nanoparticles on the surface of Al₂O₃ support. The improved sensors were fabricated with this proprietary catalyst.

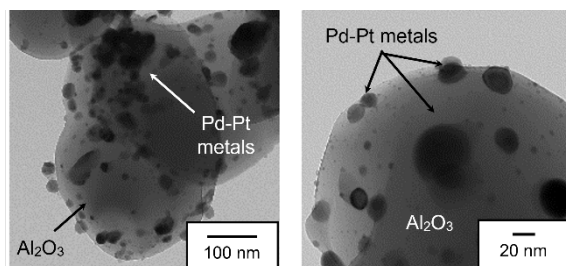


Fig. 6 TEM images of Pd-Pt/Al₂O₃ catalyst.

Figure 7 shows the hydrogen sensitivity of the sensor before and after exposure to 1vol.% hexamethyldisiloxane for 20 hours. Surprisingly, the sensitivity of the sensor remained almost unchanged even after exposure to such a high concentration of siloxane vapor. Interestingly, SiO₂ precipitations were observed on the

surface of the detector element after exposure to siloxane. Such SiO₂ particles at the surface are supposed to adsorb siloxane vapor preferentially and keep the sensor inside free from siloxane. Thus, we consider SiO₂ particles as the origin of the excellent siloxane durability, at least after their formation.

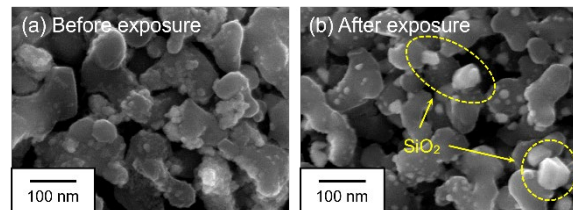
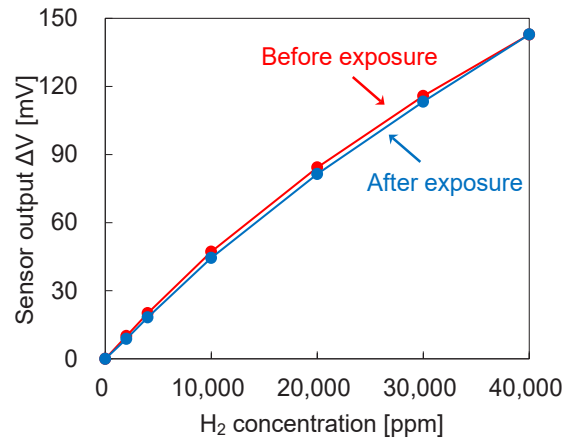


Fig. 7 Hydrogen sensitivity and SEM images of before and after exposure 1vol.% hexamethyldisiloxane at 20 hours.

Another degradation mechanism affecting catalytic activity is the sintering of the catalyst particles due to long-term heating. We solved this problem by alloying Pd with Pt. Figure 8 shows the long-term stability of the improved sensor continuously energized in air. The change of hydrogen sensitivity for 16 years was less than 10% at hydrogen concentrations of interest ((2) in section 2), demonstrating excellent long-term stability of the sensor. In actual use, no sensors are continuously energized; sensors are heated only when in use and unheated when not in use. Because empirically catalytic combustion gas sensors show no sensitivity deterioration during no heating, a longer sensor life than that in Fig. 8 can be expected.

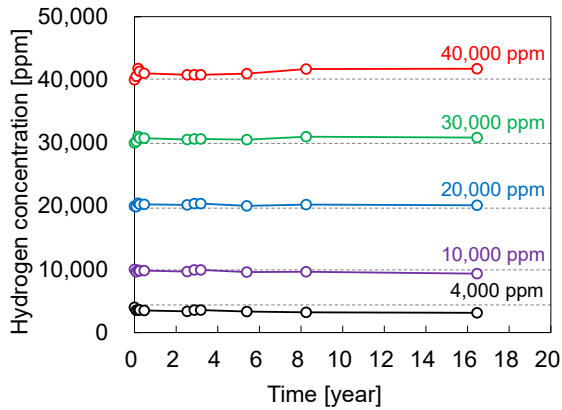


Fig. 8 Long term stability of the improved sensor in air.

6. MEMS catalytic combustion sensor

As shown in section 4, miniaturization of sensor elements is very effective for improving response time and power consumption. Thus, we are currently endeavoring to further miniaturize catalytic combustion gas sensors using MEMS technology [5], which fabricates microstructures on a Si substrate. This technology enables miniaturization of a Pt heater coil into a micro-heater as shown in Fig. 9, allowing for the fabrication of two micro-heaters on a single chip. Furthermore, MEMS technology enables the mass production of gas sensors at a reduced cost, facilitating its commercialization and widespread deployment. By depositing the sensor material on the micro-heater, we succeeded in miniaturizing the sensor elements to only 0.15 mm. The volume of the MEMS catalytic combustion gas sensor element is approximately 1/60 of that of the improved sensor for FCVs. Consequently, the miniaturized sensors exhibit dramatically reduced power consumption, enabling operation with a battery. Indeed, we have already launched battery-operated household city gas alarms equipped with MEMS chemoresistive sensors in Japan and the USA [6].

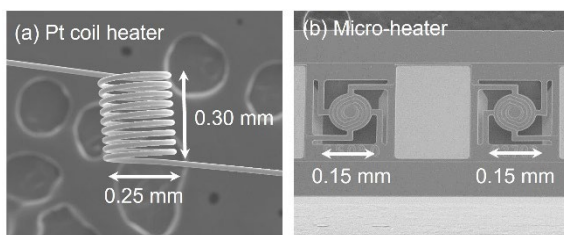


Fig. 9 SEM images of (a) a Pt heater coil of the improved sensor and (b) micro-heaters of the MEMS catalytic sensor.

The thermal response characteristics of the MEMS catalytic sensor are shown in Fig. 10. The heating time required to reach a prescribed temperature for hydrogen detection was only 100 milliseconds, for both the detector and the compensator elements. This represents an extremely fast startup time, as compared with the bead-shaped sensors (Fig. 5). Furthermore, the power consumption of the MEMS catalytic sensor is only 0.8 mW owing to its operation by pulsed voltage drive. The pulsed voltage operation is preferable for reducing power consumption, as compared with continuous operation in the bead-shaped sensors. This means that the MEMS catalytic sensor has ultra-low power consumption, which is sufficient for battery operation.

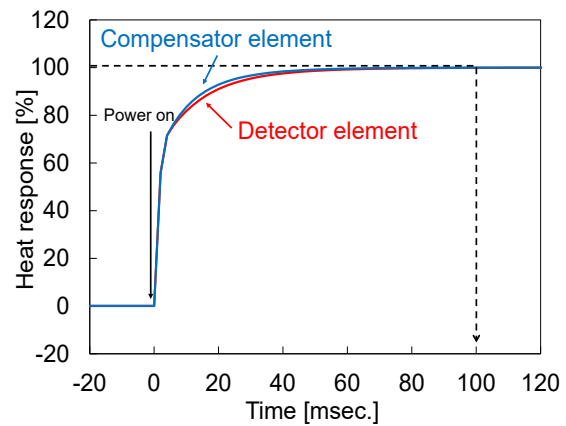


Fig. 10 Thermal response characteristics of the detector and the compensator elements of the MEMS catalytic sensor.

Figure 11 shows the gas sensitivity characteristics for hydrogen, methane, and isobutene operated with a pulsed voltage drive (100 milliseconds on and 7 seconds off). The MEMS catalytic sensor was designed to detect various combustible gases. The sensor output was proportional to the gas concentration and particularly linear to lower explosive limit (LEL) concentration for all combustible gases, indicating similar high accuracy performance to the conventional bead-shaped sensor.

Finally, the long-term stability of the MEMS catalytic sensor to hydrogen was tested, as shown in Fig. 12. The MEMS catalytic sensor was very stable with no significant sensitivity change for 540 days (approximately 1.5 years) in a laboratory environment (20°C and 60%RH), similar to that for the improved sensor. The test is still ongoing and we will carefully investigate the durability of the MEMS sensor.

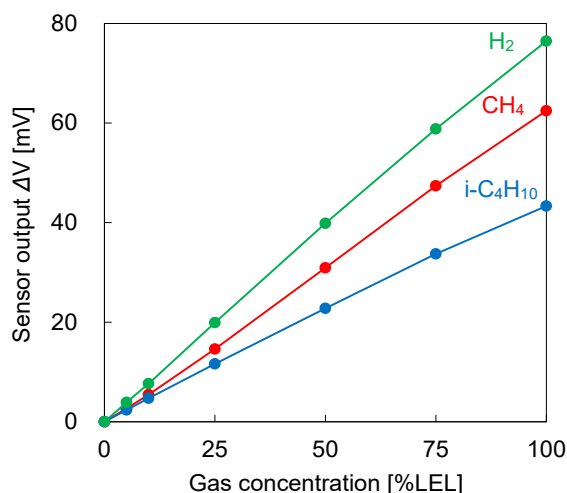


Fig. 11 Gas sensitivity characteristics of the MEMS catalytic sensor to hydrogen, methane, and isobutane.

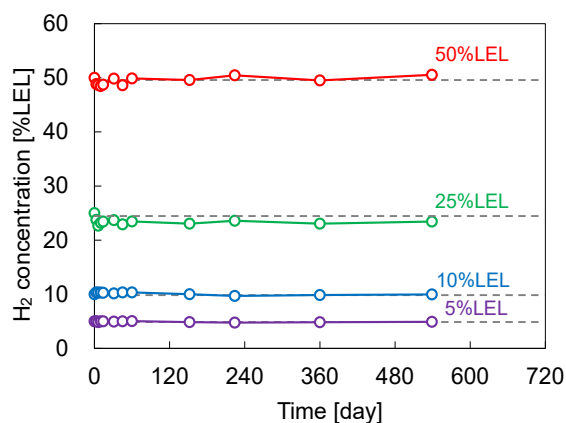


Fig. 12 Long term stability of the MEMS catalytic sensor in air.

7. Conclusion

We have successfully developed a catalytic combustion hydrogen sensor for FCVs. The improved sensor with the development of proprietary catalysts and miniaturization of sensor elements offers the following features compared to the conventional sensor.

- (1) Very fast startup (< 2 seconds)
- (2) Extremely quick response to hydrogen (< 3 seconds)
- (3) High durability against siloxane vapor
- (4) High accuracy with a hydrogen sensitivity change rate within $\pm 10\%$ even after 15 years

As a result of these achievements, our improved sensor has been adopted and installed in a commercial FCV (MIRAI, Toyota Motor Co., Ltd.).

Furthermore, we are currently challenging to develop MEMS catalytic sensors using MEMS technology, which enables further sensor miniaturization and extremely fast startup (only 100 milliseconds). In addition, this development enables low power consumption because the MEMS catalytic sensor operates by pulse voltage drive.

In the future, MEMS catalytic sensors will be applied to battery-powered hydrogen alarms and portable detectors. With our life-saving sensor technology, we aim to contribute to the prevention of gas accidents all over the world toward hydrogen energy society.

8. Acknowledgement

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