Practical Test Methods for Hydrogen Gas Sensor Response Characterization

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Response test methods for a hydrogen gas sensor were inspected for application methods in diffusion-type hydrogen sensors. As important elements of the standard test, the internal volume of a test chamber, conditions of a circulation fan, the location of the sensor in the chamber and the method of humidity control were examined from the viewpoints of the operability and precision of obtained sensing properties. We suggest a basic test method for the response of a hydrogen gas sensor and a precise test method for the response time.

Key Words : Hydrogen Gas Sensor, Response Test Method, Diffusion Chamber, Response Time

1 Introduction

Hydrogen is considered one of the most important energy sources in the future, because its combustion does not produce any hazardous chemicals. Currently, various facilities for hydrogen gas including a hydrogen refueling station are being developed and investigated. Hydrogen is also known to exhibit special properties; that is, it is lightweight and odorless and diffuses rapidly. Therefore, the treatment of hydrogen is not always the same as that of other flammable gases. A diffusion-type hydrogen sensor is an important component used in hydrogen facilities to maintain safety by monitoring and alarming hydrogen leakage or starting some safety control programs. However, there is no international or local standard that regulates specifically the requirements for a hydrogen detector or sensor. 1 Nowadays, the regularization of hydrogen leak detectors is being actively carried out by some government agencies or related organizations.

Generally, standards that regulate performance requirements and test methods are necessary for evaluating gas sensors. In this work, methods of testing the response of a diffusion-type hydrogen gas sensor using a diffusion chamber were carefully inspected, and some important parts and procedures were investigated from the viewpoints of the operability and precision of the obtained sensing properties. For the regulation of the hydrogen gas sensor, many tests should be conducted to check its properties, for example, sensitivity, hydrogen selectivity for other gases or poisoning tests. These properties should be assessed by comparing of the test results obtained under special conditions and under standard conditions. Here, the standard conditions are determined not only by the temperature, humidity and pressure of ambient air and the test gas, but also by the apparatus conditions such as the circulation of the atmosphere in a diffusion chamber.

In this work, the standard conditions for testing hydrogen sensor properties were investigated, and an appropriate internal volume of the test chamber, a method of realizing constant humidity, and an appropriate method of circulating the test gas in a diffusion chamber were discussed. Measuring sensor response properties are possible to be influenced by its location in the test chamber because the homogenization of hydrogen concentration in the chamber needs a little time. 2 Therefore, the effect of sensor locations in the diffusion chamber for the test result was also investigated. The response time is one of the most important properties for gas sensors, especially for hydrogen sensors, because the fast detection of hydrogen leakage is required in the safety control programs used in hydrogen facilities. We suggest an improved method of obtaining the response time, which is more precise and useful than a conventional method.

2 Experimental

2.1 Hydrogen gas sensors

Two different types of hydrogen gas sensors, namely, the micro-thermoelectric hydrogen sensor (THS) fabricated by our research group 3–7 and a commercial catalytic combustion-type hydrogen gas sensor (CHS) were used as sample devices. The THS used in this work was of the micro-THS type, 3 and the operating temperature was 100°C. It should be noted that, in principle, the THS and CHS consume hydrogen in oxidation, while another type of sensor, which is a semiconductor-type hydrogen gas sensor not considered in this work, does not consume hydrogen.

2.2 Type of test chambers

A flow chamber or a diffusion chamber is commonly used for gas sensor response tests as a container. In this work, a flow chamber and diffusion chambers were applied to the response tests and the operability and precision of the test results were compared.
The measurement system\textsuperscript{5, 6} with the flow chamber consisted of a reserve chamber of a test gas, \emph{i.e.}, hydrogen with a known concentration in air, and gas lines and mass flow controllers for clean air and the test gas. A sample sensor was set in the flow chamber, and the flow-controlled clean air and the test gas were allowed to flow in the flow chamber alternately. To test the sensor in humid conditions, the hydrations of clean air and the test gas were carried out by bubbling the gases through the temperature-controlled water in a gas-washing bottle. However, this method required the correct control of the temperatures of the water in the gas-washing bottle, of the gas line and of the atmosphere in the flow chamber for maintaining the target humidity;\textsuperscript{7, 8} and this was practically difficult.

The diffusion chambers of different internal volumes of 5.4 and 30 L have been tested for the gas sensor response tests. The small 5.4 L chamber is commercially available gas sensor test applications. The 30 L box is chosen because of its proper size on the table top, and also it is very close volume to that recommended in the UL standard for testing flammable gas detectors, 283 L.\textsuperscript{6} We have also carried out the test with a diffusion chamber of 100 L volume, but it was not practical. For instance, a large volume of hydrogen gas, 1 L for 1\% concentration, should be injected at high speed, and a long stabilization time for the humidity, over half a day, is necessary.

The schematic diagrams of the diffusion chamber of 30 L volume are shown in Figs. 1 (a) and (b). The chamber was made of polycarbonate, was cubic, and was equipped with a front door and an inlet near the center of the side wall that was needed to inject pure hydrogen gas with a syringe. A circulation fan (SANYO DENKI, 109-210) was set in front of the inlet facing outside. A temperature and humidity sensor (SENSIRION, SHT75) was set near the top side in the diffusion chamber, and data from this sensor were recorded. The wires as power supply lines and sensor signal lines passed from inside to outside through wire ports, and the ports were sealed.

The humidity in the diffusion chamber was controlled by the saturated salt solution method\textsuperscript{9, 10} or by silica gel. The saturated solution of NaBr or KCl was prepared using deionized water in a petri dish (diameter: 70 mm) for humid conditions, or silica gel was used alternatively for dry conditions. The atmospheric temperature in the diffusion chamber was confirmed to be maintained constant at 27°C in the range of ± 1.5°C during the sensor response tests with an air conditioner in the room. The humidities in the diffusion chamber controlled by NaBr and KCl saturated solution were measured as 62\% rh

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Schematic diagrams of the diffusion chamber of 30 L: the front view (a), the top view (b), layout of the sensor locations (c), and device holder used in the diffuse-burst method for response time measurement (d).}
\end{figure}
and 78% rh at 27°C, respectively, which were different from the specific humidities of 57% rh and 84% rh at 27°C for NaBr and KCl saturated solution. The uncertainty of the humidity in the diffusion chamber was about ±1% rh. In current standards for flammable gas detectors, the humidity for performance tests is regulated to be 65% rh ± 10% rh, 50% rh ± 20% rh, or within ±10% rh over the range of 30% rh to 70% rh. Therefore, the saturated salt solution method is considered appropriate for the standard test of a hydrogen sensor. The humidity in the diffusion chamber dehumidified by the silica gel is stable at around 30% rh. In principle, there is no specific humidity for the silica gel; however, the monitored humidity in the diffusion chamber showed a sufficient constant value, which indicated the silica gel is applicable for obtaining stable lower-humidity conditions.

To prepare a specific gas concentration in the diffusion chamber, a specific volume of pure hydrogen gas was injected into the diffusion chamber. The target hydrogen concentration can be easily calculated from the injected hydrogen gas volume and the internal volume of the diffusion chamber, 30 L. The error of the internal volume of the diffusion chamber was confirmed as not more than 0.3 L. Therefore, the error of hydrogen concentration comes from the internal volume error was estimated lower than 1% of each target concentration. The hydrogen concentrations of 0.1, 0.2, 0.5, 1 and 3% (v/v) in air were selected for the sensor response tests.

2.3 Procedure of sensor response test using diffusion chamber

The saturated salt solution or silica gel in the petri dish was placed in the diffusion chamber. The sensor was set at an adequate location and wired, and the front door was closed to maintain the atmosphere in the diffusion chamber. The internal atmosphere was circulated by a fan with a constant wind speed and the sensor was activated. The test was started after the temperature and humidity in the diffusion chamber and the sensor stabilized.

At the start of the test, the device signal was recorded for 60 s as the offset value. At the elapsed time of 60 s, the pure hydrogen gas was injected as quickly as possible through the inlet using a syringe, and the device signal was recorded for 240 s at intervals of 1 s.

2.4 Sensor location in diffusion chamber and wind speed of circulation fan

The effects of the sensor location and the wind speed of the circulation fan on the performances of the sensor were investigated. The tests were performed with different locations of the sensor: top (center of the chamber ceiling), A; bottom (center of the chamber floor), B; and two sides (center of the chamber side walls), C and D, as shown in Fig. 1 (c).

The relationship between the electrical power for the fan and its wind speed was determined beforehand by a wind speed meter. The wind speed was set to be 0, 1, 1.5 and 3 m s⁻¹ by controlling the power supply. The volume flow rates corresponding to these wind speeds were calculated using the performance data provided from the vendor as 0.16, 0.24 and 0.48 m³ s⁻¹ for 1, 1.5 and 3 m s⁻¹, respectively.

2.5 Response time

The response time, tᵣ, is defined as the “time interval between the time when an instantaneous variation in volume ratio is produced at the sensor inlet and the time when the response reaches the stated percentage, i, of the final indication”. Here, the final indication is defined as the “indication given by the sensor after stabilization”. Two methods of measuring response time were investigated using the diffusion chamber of 30 L to make sure the methods are appropriate for the hydrogen sensors. The first method, referred to as the “inject-diffuse” method, was similar to that indicated in 2.3. The second method, referred to as the “diffuse-burst” method, was devised as follows. The sensor was set in a small device holder (see Fig. 1 (d)), which was an open acrylic plastic box (70 mm × 70 mm × 50 mm), and the holder was sealed by a rubber film then placed in a diffusion chamber. After the warm-up of the sensor and stabilization of the conditions similar to those of the inject-diffuse method, the calculated volume of pure hydrogen gas was injected through the inlet. After waiting for 30 s, while the hydrogen concentration in the diffusion chamber was circulated by the fan with a volume flow rate of 0.48 m³ s⁻¹ to homogenize it; during this period the rubber film prevented the intrusion of the test gas into the device holder. The appropriate waiting time was determined beforehand by finding the elapsed time until the hydrogen concentration stabilized using the THS itself. After the appropriate waiting period, the measurement was started in the same manner as in the inject-diffuse method. After 60 s, the rubber film that sealed the device holder was cut by the remote manipulation of a cutter with a long stick, and then the sensor was exposed to the test gas. Other procedures of the test were the same as in the inject-diffuse method.

3 Results and Discussion

3.1 Response signal obtained using flow chamber

The increment of the voltage signal, ΔVₛ, was obtained by subtracting the offset value from the voltage signal, Vₛ, that was measured as the response signal of the THS. The results of ΔVₛ for dry 1% (v/v) hydrogen in air measured using the flow chamber system are shown in Fig. 2(a). The volume flow rate was controlled to be 100, 200, 300 and 400 ccm. The final indications were obtained clearly; however, the final indication values and the responsivity depend on the volume flow rate.

3.2 Tests with different diffusion chambers of 5.4 and 30 L

The ΔVₛ values of the THS for the hydrogen test gas of 0.5% (v/v) measured using the diffusion chambers are shown in Fig. 2 (b). The solid line indicates the result of the THS placed at E indicated in Fig. 1 (c) in the diffusion chamber of 30 L with a humidity of 60% rh controlled by the saturated salt solution method. For comparison, the diffusion chamber of 5.4 L was prepared, the THS was placed at the upper side of the chamber, and humidity was controlled to be 55% rh by the saturated
salt solution method. The result is shown as the dotted line in Fig. 2 (b). The solid line increased immediately after the hydrogen injection, and reached the final indication clearly, while the dashed line showed a spike immediately after the hydrogen injection, then decreased slowly and monotonically. The decrease in $\Delta V_s$ was attributed to the consumption of hydrogen by the THS itself. The hydrogen consumption rate, $R_c$, is defined as the ratio of the consumed hydrogen volume to the initially injected hydrogen volume per second ($% \ s^{-1}$). The $R_c$ values of THS and CHS for the initial hydrogen concentration of 0.5% (v/v) and 1% (v/v) in air are listed in Table 1. The $R_c$ values of the THS and CHS obtained from the chamber of 5.4 L were higher than those obtained from the chamber of 30 L.

From this result, we could suggest that the 30 L box is a better than the 5.4 L one for testing hydrogen sensors, as it reduces the possible errors such as the change in the hydrogen concentration during the test.

### 3.3 Effects of sensor location and fan setup

The increments of the current signal, $\Delta I$, of the CHS at several locations in the diffusion chamber of 30 L with several volume flow rates of the circulation fan are shown in Fig. 3. The test gas was 1% (v/v) hydrogen in air at room temperature and at a humidity of 55%rh for all measurements.

When the volume flow rate was 0.48 m$^3$ s$^{-1}$, the features of $\Delta I$ curves were not related to the sensor locations (Fig. 3 (a)). When the volume flow rate was 0.24 m$^3$ s$^{-1}$, a spike appeared in the curve when the device was placed at A, and the responsibility of $\Delta I$ became different for each location (Fig. 3 (b)). In the case of a volume flow rate of 0.16 m$^3$ s$^{-1}$, the difference between the responsibilities of $\Delta I$ increased (Fig. 3 (c)). When the volume flow rate was zero, the feature of $\Delta I$ was clearly related to the sensor location (Fig. 3 (d)).

In comparison with other locations, $\Delta I$ for A showed the fastest responsibility when the volume flow rate was not greater than 0.24 m$^3$ s$^{-1}$ and the change in responsibility was not so large. In contrast, the responsibility of $\Delta I$ for B markedly decreased with the volume flow rate. The responsibilities of $\Delta I$ for C and D showed that their variations depend on the volume flow rate, and their tendency was intermediate of those for A and B. The difference in $\Delta I$ features between the sensor locations was similarly observed in the additional experiments for the hydrogen concentrations of 0.5% and 3%.

The results in the case when the volume flow rate was zero were considered to reflect the behavior of the injected test gas: immediately after the injection, the injected hydrogen gas was considered to be a flux, and the flux flowed immediately to the upper side of the diffusion chamber with hydrogen dispersing, then it diffused down to the lower side of the chamber along the chamber side wall. This behavior of the hydrogen gas attributable to the light weight of hydrogen and it is unfavorable for the test method of the sensor. However, this problem was reduced by the circulation of the atmosphere in the chamber by the fan, and the volume flow rates of 0.48 m$^3$ s$^{-1}$ or higher were considered to be sufficient to obtain a sensor signal that was independent of the sensor location and hydrogen concentration. To eliminate any suspicious effect of the fast hydrogen flux along the chamber ceiling, in this work, the location E (see Fig. 1 (e)) was selected as an appropriate location of the sensor for the response test.
Fig. 3 Increment of the current signal, $\Delta I$, of the CHS for 1 % (v/v) hydrogen in air at room temperature and a humidity of 55 %rh measured using the diffusion chamber of 30 L. The volume flow rates of the circulation fan were 0.48, 0.24, 0.16 and zero m$^3$ s$^{-1}$ for (a), (b), (c) and (d), respectively. The sensor locations in the diffusion chamber, A, B, C and D, are indicated in Fig. 1 (c).

3.4 Test method for response time
To obtain the intrinsic response time of the hydrogen sensors, the sensor must ideally be exposed directly to the specified concentration gas. However, in the case of the measurement method using the flow chamber, it is impossible to instantly exchange the atmosphere in the chamber from the clean air to the test gas, and there is a gradual change in the hydrogen concentration at the first step of the measurement. The result shown in Fig. 2(a) indicates this delay can be eliminated to some extent by increasing the frequency of the fan; however, it is not the ultimate solution. In addition, the test condition with the high volume flow rate is considered to be far from the practical condition, especially for the diffusion-type sensors. Therefore, the flow chamber is not recommended for the response test of hydrogen sensors.

In the case of using the diffusion chamber without the device holder, i.e., the inject-diffuse method, a similar problem existed. The hydrogen concentration in the chamber was inhomogeneous immediately after the injection, and it took some time until the hydrogen concentration in the chamber became homogeneous as observed in Fig. 3.

In contrast, the diffuse-burst method is considered more appropriate for evaluating the response time of hydrogen sensors, because in this method, the sensor was directly exposed to the specified test gas without the delay of gas diffusion in the large box. The volume of the device holder, $2.45 \times 10^{-2}$ L, was 0.82% of the volume of the diffusion chamber; this is then sufficiently small to neglect its effect on the hydrogen concentration.

The final indications obtained by the inject-diffuse and diffuse-burst methods for the same THS were compared, and the values were confirmed to be the same. The response times, $t_{50}$ and $t_{90}$, of the THS devices measured by these methods are listed in Table 2. The response times, $t_{50}$ and $t_{90}$, obtained by the two methods are different; the values measured by the inject-diffuse method increase with the hydrogen concentration; in contrast, the values measured by the diffuse-burst method show the opposite results. The response times, $t_{50}$ and $t_{90}$, of the THS for low hydrogen concentration obtained by the diffuse-burst method were longer than those obtained by the inject-diffuse method. However, for percent hydrogen concentration, the diffuse-burst method showed fast response. The origin of the slow response of the inject-
Table 2  Response times, $t_{63}$ and $t_{90}$ of the THS measured by the inject-diffuse and diffuse-burst methods. The humidity and temperature were controlled to be 60~67 %rh and room temperature, respectively. The volume flow rate of the circulation fan was 0.48 m$^3$ s$^{-1}$, and the sensor location was E indicated in Fig. 1 (c).

<table>
<thead>
<tr>
<th>Hydrogen concentration in air (v/v) (%)</th>
<th>$t_{63}$/s</th>
<th>$t_{90}$/s</th>
<th>$t_{63}$/s</th>
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<tr>
<td>0.1</td>
<td>3</td>
<td>3</td>
<td>5</td>
<td>8</td>
</tr>
<tr>
<td>0.2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>6</td>
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<tr>
<td>0.5</td>
<td>4</td>
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<td>1</td>
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<tr>
<td>3</td>
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<td>10</td>
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diffuse method could be the delay time to diffuse out high gas concentration. As for the inversion for low gas concentration, we could not explain the slow response of the THS in the diffuse-burst method, and more details are currently under investigation.

For practical use, the response time for 1% (v/v) hydrogen in air is the most important. A quarter of the lower explosive limit (LEL) of hydrogen, 4% (v/v), is 1%, which is the alarm level of flammable gas leak detectors$^{11}$ required by the regulation on fire protection. The response times, $t_{63}$ and $t_{90}$ of the THS for 1% (v/v) obtained by the diffuse-burst method, 2 and 3 s, were smaller than those obtained by the inject-diffuse method, 3 and 4 s, respectively. From this result and the result in 3.3, the response time obtained by the diffuse-burst method is considered to be appropriate for evaluating the response speed of the hydrogen sensor, for practical applications.

4 Conclusions

An adequate method for the standard response test of diffusion-type hydrogen gas sensors using a diffusion chamber is proposed as follows:

1) The internal volume of the diffusion chamber should not be very small so as not to decrease the hydrogen concentration of the test gas in operation, particularly in testing the hydrogen-consuming-type sensor. The internal volume of around 30 L is considered to be appropriate.

2) A circulation fan is necessary and the recommended volume flow rate is not lower than 0.48 m$^3$ s$^{-1}$.

3) The sensor location in the diffusion chamber is optional when the circulation fan is running with the recommended volume flow rate.

4) The saturated salt solution method is feasible in controlling the humidity of the atmosphere and the test gas in the diffusion chamber. For example, the saturated NaBr solution is recommended for the response test with a humidity of about 60%rh.

5) Monitoring or recording of the temperature and humidity in the diffusion chamber is required. The standard response test cannot be applied to the response time test without being modified, and the following method is recommended for use in obtaining precise values.

6) The response time test should be performed to expose the sensor directly to the homogenized test gas of the specified hydrogen concentration. Two different methods, the diffuse-burst method and inject-diffuse method, are bench-marked and the former is considered to be appropriate for evaluating the response speed of the hydrogen sensor, for a 1% hydrogen concentration (1/4 of LEL).

References

1) IEC 61779, JIS M 7626, JIS M 7653, CSA 222 No. 152-M1984 and UL 2075 are examples of the standards for a flammable gas leak detector, and hydrogen is included as one of the target gases.


9) OIML R 121, The scale of relative humidity of air certified against saturated salt solutions (1996).

