



Development of Highly-reliable Gas Sensor for Domestic Use Gas Alarm Working on Batteries

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1. Background

The number of accidents in Japanese city gas business is very close to zero. Nevertheless, CO poisoning accident happened fairly infrequently. Hence domestic gas alarm is needed to prevent an accident during gas consumption.

Domestic gas alarm which detects leaked methane and CO evolving by incomplete combustion has been contributing to decrease in the number of accidents during gas consumption along with efforts of improving safety of gas appliances. Nevertheless, the adoption rate of domestic gas alarm in Japan recently stays about 40 %. The reason is that domestic gas alarm requires AC power code which restricts its installation position and spoils the appearance of the kitchen. Therefore, new domestic gas alarm working on batteries for 5 years, called "codeless gas alarm", is required for domestic gas alarm to prevail.

2. Objective

CO sensor and methane sensor are key components in the gas alarm, therefore these reliability are required to be kept at a very high level. Domestic gas alarm is required to work reliably with maintenance-free for 5 years in Japan. Hence the target of gas sensor's power consumption must be less or equal than 0.1 mW for gas sensor to work on batteries. Recently new sensors whose power consumption is below 0.1 mW have been developed by using nanotechnology and MEMS (Micro Electro Mechanical Systems) technology. But new sensors' material and structure are different from conventional ones proven commercially as domestic gas alarms. For such new sensors, reliability under various installation environments has not been proven based on actual performance data. Therefore, we install new sensors in house kitchens to obtain sensors' characteristic change data at various installation environments and analyse factors causing those changes. We also try to establish a method of an accelerated laboratory test that simulates same characteristic changes as in kitchens as fast as possible, based on the mechanism of characteristic change, to evaluate a reliability of new sensor in minimum period.

We have carried out this development with sensor manufacturers since FY2008. In FY2008, we carried out it, commissioned by the New Energy and Industrial Technology Development Organisation (NEDO).



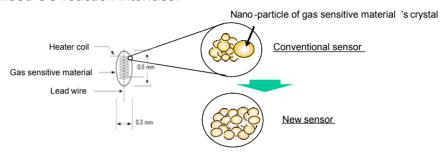


3. The new sensors under development

We selected semiconductor CO sensor, electrochemical CO sensor and micro methane sensor as a new low power consumption sensor.

1) Semiconductor CO sensor

The semiconductor CO sensor has been developed to reduce power consumption by improving conventional technology applied to an existing domestic gas alarm. The conventional one consumes much power by frequent heating to clean up impurities attached on the surface of the sensor. Therefore, it is tried to reduce the power consumption and the frequency of the heating for cleaning the sensor by inhibiting affects of impurities; water, CO₂, oil and so on. The way of the inhibition is enlarging the surface area of gas sensitive particles by miniaturization and homogenization of gas sensitive material's crystal with controlling a crystal growth. The concept of a new sensor is shown in Figure 3-1. The miniaturization and homogenization could become easy for CO to adsorb on a sensor surface and react because of expanded CO reaction interface.



The surface area of gas sensitive material's particle of the new sensor is larger than the conventional by leading edge nano technologies.

Figure 3-1 Schematic of sensitive material of semiconductor CO sensor

2) Electrochemical CO sensor

The electrochemical CO sensor is expected as a drastic low power sensor because it detects CO at ordinary temperature and doesn't need heating for cleaning surface. The schematic of a sensor is shown in Figure 3-2. It is used at an industrial plant where scheduled maintenance is done, but it cannot be used for a domestic gas alarm that is required maintenance-free for a long period. The reason is that a conventional sensor shows a trend of a reduction in sensitivity along with decreasing a reaction activity of electrodes over time. In the development of the electrochemical CO sensor, a technology that inhibits the reduction in the sensitivity, a fatal disadvantage for a domestic gas alarm, must be established in various installation environments.

CO CO₂ Catalytic electrode layer (sensing electrode) $CO+2 \underbrace{0 \ H^-}_{OH} \rightarrow CO_2 + H_2O + 2 \underbrace{e^-}_{H_2O+2 \ e^-}$ Electrolyte membrane $Hydroxide \ ion \ moves \ in \ hydrophilic \ porous membrane \ impregnated \ with electrolyte.$ Catalytic electrode layer (counter electrode) $1/20 \ _2 + H_2O + 2e^- = 20H -$

Mechanism of sensing

Total reaction $2CO + O_2 \rightarrow 2CO_2$

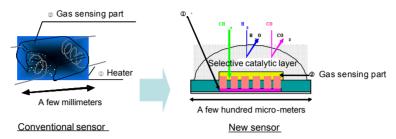
Figure 3-2 Sensing mechanism of electrochemical CO sensor





3) Micro methane sensor

A methane sensor has to be heated to 400°C in order to activate chemically stable methane to detect. A conventional methane sensor consumes much power to heat continuously to 400°C. It is effective to heat by short-pulse at intervals for saving power consumption. It has been achieved that the sensor can be heated to 400°C within a few dozen milliseconds by miniaturizing the gas detection part and the heater to hundreds of micrometers using MEMS technology. The concept of a new sensor is shown in Figure 3-3.



The new sensor makes power distribution time significantly short er owing to gas sensing part and micro heater that are made by MEMS technolo gies.

Figure 3-3 Schematic of micro methane sensors

4. Field test method

We made the sensor unit, whose size is 130 mm wide, 50 mm depth and 200 mm high, to mount sensors. We installed the sensor units that mount all of these new sensors provided by six sensor manufacturers in actual house kitchens to obtain data of sensors' output signals, temperature and humidity under various installation environments. We also collect sensor units once a half-year in order to calibrate sensor's CO, CH_4 and H_2 sensitivity at laboratory. We selected the installation environments, considering the combinations of four conditions, to obtain various data. The conditions are climate, architecture, date of build and family composition. The factors, related to each condition, which were presumed to affect sensor's variability characteristic are shown in Table 4-1.

Table 4-1 Factors being presumed affect to sensor's characteristic

Condition	Factor
Climate	Temperature
	Humidity
Architecture	Ventilation air volume
Date of built	Ventilation air volume
	Quantity of Volatile organic compounds (VOC)
Family composition	Time at home
	Frequency of cooking





In the climate, the sensor units have been installed at the houses in five regions of Japan. The regions are shown in Figure 4-1.

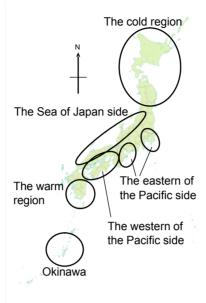


Figure 4-1 Regions in which the sensor unit installed

In the architecture, we considered the difference of a detached house made of wood and an apartment with reinforced concrete. In the date of build, we took regulation related to construction into account. In Japan, the rule for energy saving excessively accelerated draft-free houses to be built in 2000 to 2003. Additionally, revised Building Standards Act has promoted building houses which is less VOC and equipped an automatic ventilation system since 2003. In the family composition, we compared single to family.

We have installed sensor units in 660 houses widely spread in Japan with varieties and obtained data for two and a half year since 2008.

We also placed activated carbon on the sensor unit in the kitchens to identify suspicious impurities adsorbed on the activated carbon.

5. Result

We obtained variant data of temperature and humidity throughout a year by each factor such as in climate, in architecture (detached house or apartment), date of build (change in the regulation of ventilation) and family composition. These variant data showed to correlate with sensor's characteristic changes. We also found out substances to be possible to affect sensor's characteristic changes by impurities adsorbed on the activated carbon. These data are utilised for sensor manufacturers to improve developing sensors. We are going to carry on obtaining data to help for sensor manufacturers to establish a method of an accelerated test.

We obtained data showing correlation between sensor's characteristic changes and temperature and humidity by means of putting sensor units in 660 houses. The variant mean temperature and mean relative humidity at each region in December 2008 to May 2011 are shown in Figure 5-1 and 5-2. In winter, the mean temperature at the cold region was equal or high than the other regions, which are in southern of the cold region, except for Okinawa. It supposed that a heater made temperature higher at the cold region. In summer, it was lower





than the other. As a result, it changed less than the other in a year. Okinawa's temperature was higher than the other throughout the year. In addition, the fourth term's temperature was higher than another term at all regions except for Okinawa because of the extremely hot weather in 2010.

The mean relative humidity at the cold region was lower than the others in winter. It was the same as another in summer. As a result, it changed more than the other in a year. Okinawa's one changed at higher level throughout the year. Additionally, the mean relative humidity was higher at all regions and was little different among regions in summer. However, it was more different in winter.

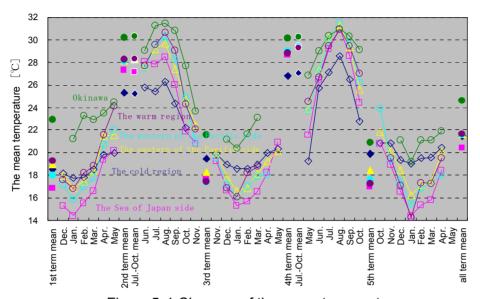


Figure 5-1 Changes of the mean temperature

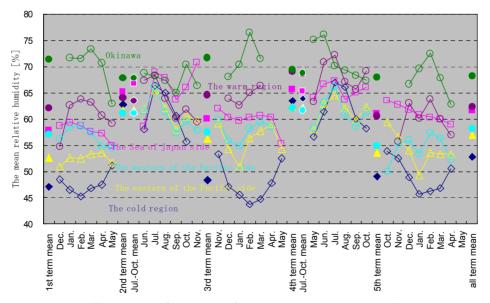


Figure 5-2 Changes of the mean relative humidity

We also found out substances to be possible to affect sensor's characteristic changes by identified substances adsorbed the activated carbon that was placed on the sensor unit. These data made it easy that we deduced causes of affecting sensor's characteristic changes. As a result, we acquired the method of evaluating a reliability of developing new





sensor in minimum period with our accelerated test. Furthermore, we found out some new sensors which could be commercialised in the near future.

6. Conclusion

We established the method to obtain data of sensor's variability characteristic material under various installation environments. In addition, we have obtained data for maximum three years. The data were utilised for sensor manufacturers to extract causes changing sensor's characteristic and to establish a method of an accelerated laboratory test. Furthermore, actual conditions related to temperature, humidity and existing substances under various environments were also clarified. Consequently, we found out some new sensors which could be commercialised in the near future.