Paper

A Temperature-compensated Sensor System for Ozone Detection

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A new type of a temperature-compensated sensor system, which detects dissociation heat caused by ozone decomposition, is suggested. The detection principle is almost identical to that of a catalytic combustion (pellister-type) sensor except that the suggested sensor does not utilize catalytic materials. A sensing device with catalyst and a compensating device without catalyst have been utilized at the same operating temperature in a conventional catalytic combustion sensor to form a bridge configuration. In the proposed sensor system, sensing devices of identical characteristics without any catalysts are adapted for both sensing and compensating devices. However the operating temperatures of the two devices are different. The sensing device is operated well above the decomposition temperature of ozone, whereas the operating temperature of the compensating device is below the decomposition temperature. Signals of the two devices are amplified with the corresponding gains to cancel the temperature dependences of the two devices, when ozone is not present. Ozone decomposes by itself upon contact with the sensing device owing to thermal decomposition and generates the heat. The thermal decomposition does not take place at the compensating device.

Keywords: ozone, gas sensor, temperature compensation, dissociation heat

1. INTRODUCTION

Ozone has been widely used as disinfectant for a filtration plant, in Europe and USA. Ozone has also favorable characteristics for sterilization of drinking water, because it deodorizes water simultaneously. In Japan, the usage of ozone for the filtration plant has been limited because of cost and public regulations. The quality guideline for drinking water of Japan recommends the residual chlorine of 1 ppm for sanitary reason. Chlorine sterilization may create some organochloro-compounds, which may be strongly carcinogenic and odor-generating.

Ozone is self-dissociating and oxidative substance. It can sterilize or deodorize various substances without any long-term residual effects to the environment. Usage of ozone to drinking water as sterilizer should be contrasted with usage of chlorine; ozone reduces water odor whereas chlorine would add extra odor and may create carcinogenic substances.

Recently much attention has been paid to utilization of ozone because of its superior chemical and environmental characteristics. Hospitals and other indoor public spaces were sterilized by formaldehyde until recently, but health hazard by residual formaldehyde stimulated the introduction of ozone sterilization. Ozone also becomes popular in food industry. It is used for the food sterilization as well as for the deodorization of its sewage plant. Deodorization at small sewage plants at stockyards or fish plants is another industrial area where effective use of ozone is expected.

Ozone is usually generated at the usage site by electric discharge. Since the generation cost of ozone is rather high and the residual ozone after usage has to be decomposed before release to the environment, it is desirable to keep the ozone level just above the minimum required level. Usually an ozone monitor is used to control the level. Among the several types of existing ozone monitors, Ultra-Violet (UV) ozone monitors are widely used because of better stability and easy maintenance. A UV ozone level meter(1) measures strong UV absorption (Hartley band) around 255 nm accurately and reliably with the adaptation of double beam configuration. But the cost of the measuring system is high and a drastic cost reduction in the measuring system has been desired especially for the small system. Possible cost reduction with the existing UV ozone monitor is limited. So we have developed the detecting system based on different mechanisms.

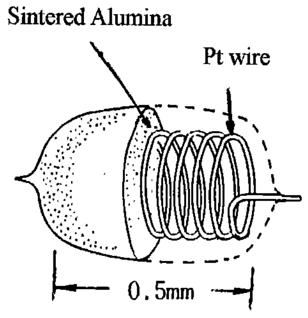

Fig. 1 Structure of the sensor (reference) device

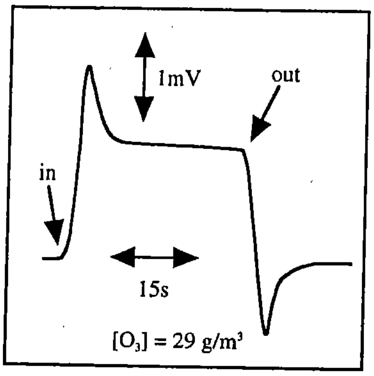

Fig. 2 Ozone signal from the bridge circuit of the catalytic combustion sensor

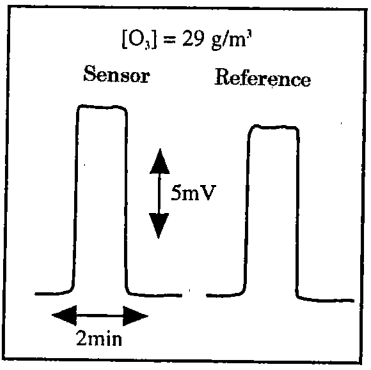

Fig. 3 Response signals of the sensor and the reference

2. SENSOR SYSTEM

2.1 Principle

In addition to the UV method$^{(1)}$, oxide-semiconductor$^{(2,3)}$ and amperometric$^{(4)}$ sensors have been suggested. In the present investigation, the possibility of a new ozone sensor based on completely different principle that had not been utilized in the existing sensors was explored. Ozone generates considerable amount of heat (142.7 kJmol^{-1}) upon decomposition. A catalytic combustion gas sensor detects flammable gas by measuring the heat generated by catalytic combustion. The fact persuaded us to apply a catalytic combustion sensor for ozone. As a preliminary trial, we measured ozone with a catalytic combustion sensor. The catalytic combustion sensor consists of 2 devices, the sensor device and the reference device. The two devices were connected to form two arms of the bridge and operated at the same temperature. The physical structure of the sensing device was shown in Fig. 1$^{(5)}$. Alumina powder with appropriate catalyst were sintered on Pt coil as an elongated sphere. The reference device has the same structure without any catalyst.

Figure 2 shows an output signal response of the bridge circuit with a catalytic combustion sensor (CS-type, New Cosmos Co. Ltd.). It could be seen that the sensor showed relatively small response during the steady state period, but showed strong response at the transient period. Since two devices were heated up to several hundred ℃, it was likely that ozone decomposed at the surfaces of the sensing and reference devices. This was confirmed by the signals of the sensor and reference devices upon ozone exposure in Fig. 3. The small ozone response during the steady state period might be caused by the cancellation of temperature rises of the two devices. The large transient response could be attributed to the difference of the transient characteristics and of the geological locations for the two devices. To explore the sensing characteristics in detail, the steady state sensor responses of the two devices were plotted as a function of temperature in Fig. 4. Sensitivity was expressed as relative resistance change normalized by unit ozone concentration, i.e., the ordinate value indicates the relative resistance change caused by 1 g/m^3 ozone change. Although signal from the reference device was smaller, both the sensing and reference devices responded to ozone, suggesting thermal decomposition. The thermal decomposition rate increased as the device temperature increased. The signal of the sensing

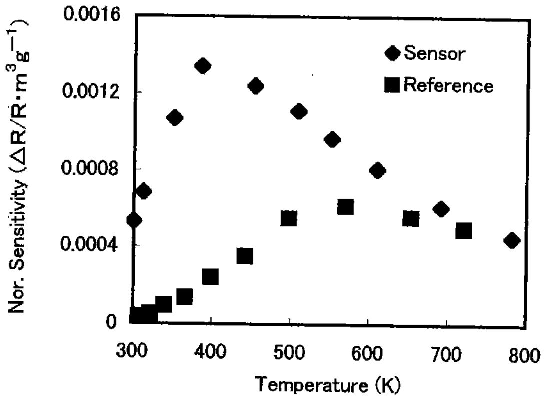

Fig. 4 Sensitivities of the sensor and the reference

device showed a large peak at about 400 K. Around the peak, ozone was decomposed mainly by catalysts upon contact with the device surface, heating up the sensing device efficiently. As the temperature increased, more ozone thermally decomposed before ozone molecules reached the device surface, which resulted in the reduction of signal. The reference device also responded to ozone because of the thermal decomposition. As a nature of thermal decomposition, the signal was small at low temperature, but became large as the temperature increased. The signal of the reference device also exhibited a peak because ozone started to decompose before it reached the device surface above the peak temperature. But the peak was broad and located at higher temperature in comparison to that of the sensor device. It may be crudely said that the difference of the two response curves was attributable to the catalytic decomposition promoted by the catalytic additives.

2.2 Catalyst Poisoning

The catalyst combustion sensor worked stably when the source gas was pure oxygen, but it exhibited distinguishable sensitivity degradation when the source gas contained N_2. Figure 5 shows the temporal response of the sensing device operating at 392 K under exposure to ozone at a concentration of 22 gm^{-3} with O_2 and air source gas. The sensor response stayed at a constant level when the source was pure oxygen, but the response decreased within a few minutes when source gas contained nitrogen. This degradation may be attributed to a catalyst poisoning. NO_x would be generated upon discharge when source gas contains N_2, and NO_x might cause catalyst poisoning. Small amount of N_2, however, is often included in the source gas to increase ozone generation efficiency. Catalyst poisoning or sensitivity degradation should be avoided for practical applications. The initial difference of the response to the two gases was caused partly by the difference in thermal conductivity of air and oxygen and partly by the catalyst poisoning. Although the data was not shown, the response of the reference device also showed distinguishable degradation in time when the source gas was air. The phenomenon suggested that alumina powder might work as catalyst for ozone decomposition.

2.3 Platinum Coil Resister

Since both the sensing device and the reference device of the catalytic combustion sensor were affected by NO_x, we have investigated the detection characteristics of the bare coil without any catalyst or metal oxide powder (Fig. 6). Even with Pt coil alone, response degradation was observed when the operating temperature was low and source gas contained N_2. The degradation was not observed when the device was operated at high temperature as is evidenced by the plots at 925 K. And the response degradation generated at the low temperature operation could be remedied when the device was heated to more than 900 K for a while. The degradation might be resulted by the deposition of some NO_x compounds.

2.4 Temperature Compensation

Since the sensor of this type measures temperature to detect ozone, the temperature variation in the gas under measurement directly affects the data. In a catalytic combustion sensor, this variation was cancelled by the bridge configuration of a sensing and a reference device. This method, however, could not be applied for ozone detection, because thermal decomposition would equally take place at the reference device. Operation temperature of the reference device should be below the thermal decomposition

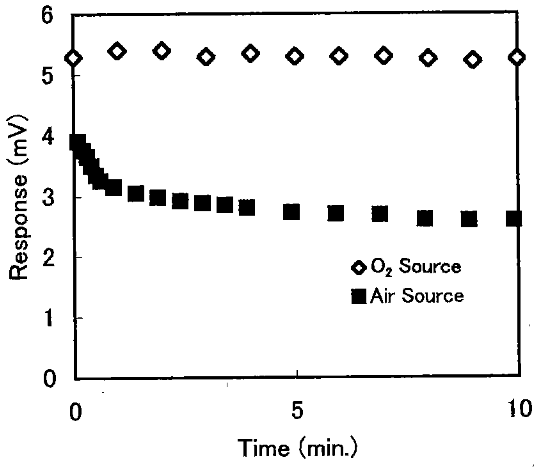

Fig. 5 Source gas dependence of the response

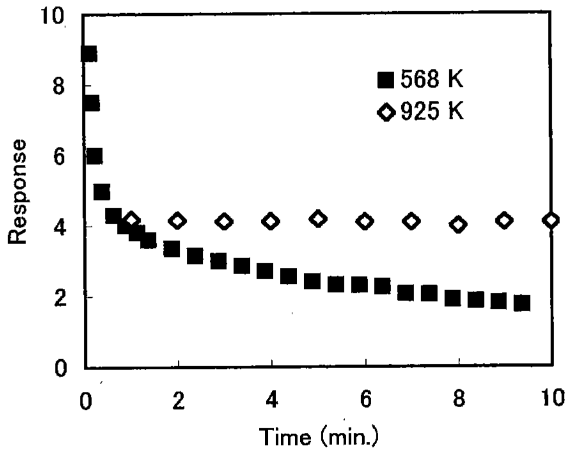

Fig. 6 Response change for Pt coil with air source gas

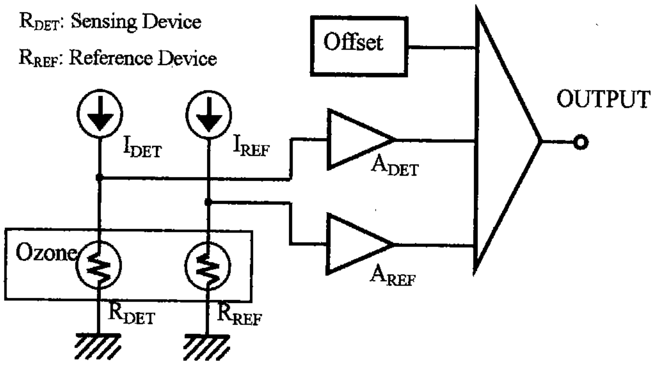

Fig. 7 Temperature compensation scheme for the thermal decomposition sensor

temperature and the cancellation of the temperature dependence by simple bridge configuration was not feasible. It may be possible to operate the reference device below the thermal decomposition temperature by feeding small driving current. The signal from the reference device is also small, but an operational amplifier may easily amplify the signal to the same magnitude of that of the sensing device. The method was schematically presented in Fig. 7. In the measurement a current of 100 mA was flown to the sensor device to heat it up to 925 K whereas 10 mA was flown to the reference device. Gain of A_{REF} was set to about 7 times larger than that of A_{DET} to adjust the difference in current and temperature coefficient of Pt coil at the operating temperatures. Calibrations curves for 95% O_2 and 5% N_2 source gas and for pure O_2 source gas, are presented in Fig. 8. It could be seen that two calibration curves were almost linear up to 80 $g\cdot m^{-3}$ and coincided with each other within the experimental error. In principle, two calibration curves may not coincide since gas composition was different, but the small difference in the composition might not have affected the calibration curve. It should be noted that the sensor was tested continuously for 30 days at an ozone concentration of 80 $g\cdot m^{-3}$ for 95% O_2 and 5% N_2 source gas without noticeable sensitivity change.

3. CONCLUSION

A new ozone sensor for high ozone concentration range with low cost and easy maintenance was reported. The sensor detected the dissociation heat caused by the thermal decomposition. It has been shown that catalyst poisoning by the interfering gas (NO_x) may be eliminated by high temperature operation. A new scheme to compensate the sensor signal with gas temperature variation was suggested.

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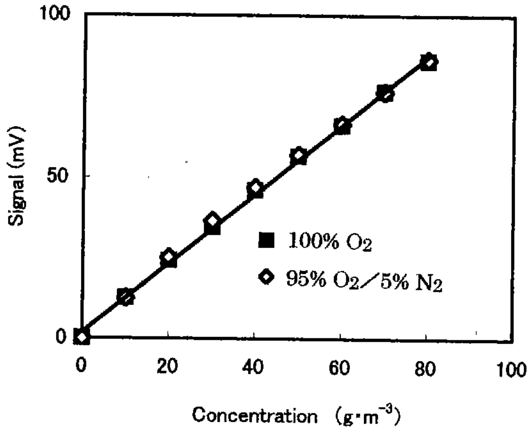
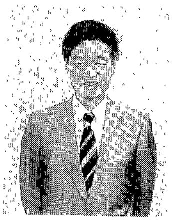


Fig. 8 Calibration curve of Pt Coil

Hidemoto Nakagawa (Member) obtained his M.Appl.Sci. and Ph.D. degrees from University of Toronto in 1974 and 1978 respectively. His research centers on various sensors and their applications since he joined Yokohama National University in 1993. He is also interested in electrochemistry and micromachining.



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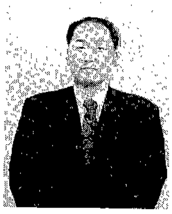

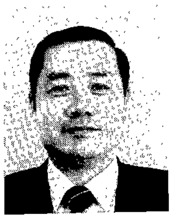

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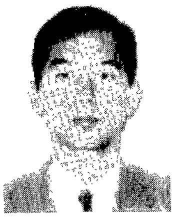

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