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Application of Woodceramics for Ammonia Sensor

Kazuhiko Kakishita and Toshikazu Suda
Polytechnic University, 4-1-1 Hashimotodai, Sagamihara, Kanagawa, 229-1196, Japan
Fax +81-427-63-9168 E-mail: kakisita@uitec.ac.jp

Response of electrical resistance to ammonia gas and temperature dependence of sensitivity to ammonia in woodceramics have been measured aiming at the application of woodceramics as ammonia sensor. The resistance of woodceramics increases and then saturates when exposed to ammonia gas at extremely low working temperature of 40°C. Saturated value of resistance increases as ammonia gas concentration increases. Temperature dependence of ammonia sensitivity indicates minimum at about 50°C. The amount of ammonia gas adsorption decreases as working temperature increases. Assuming the reaction such as thermal catalysis enhances as working temperature increases, temperature dependence of the ammonia sensitivity has been explained. Consequently, it seems that woodceramic is suitable for ammonia sensor which can be used at extremely low temperature. Mechanism of resistance change due to ammonia gas has also been discussed.

Key words: woodceramics, ammonia sensor, porous carbon, electrical properties

1. INTRODUCTION

Woodceramics (WCMs hereafter) are the new functional carbon materials and have recently shown a strong promise of constituting the next generation of industrial materials [1-9]. WCMs are fabricated by sintering woody materials impregnated with phenolic resin to form glassy carbon which reinforces the fibrous structure of wood. It is known that WCMs can be fabricated from waste wood, waste paper, saw dust and so on; thereby WCMs are environment conscious materials (ecomaterials) designed for minimizing the environmental impacts. The WCMs have the prominent characteristics of lightweight, hardness, corrosion resistance and heat resistance.

WCMs particularly have the porous structure caused by woody fiber, so that WCMs has been developed as a humidity sensor [3-9]. The electrical resistance of WCMs decreases with humidity resulting from the supply of electrons and/or ions with adsorption of water molecules on WCMs porous surface. Similar to water molecules, if resistance change occurs by adsorbing some gases to the WCMs surface, WCMs can be used as a gas sensor. In this work, ammonia was used as target gas. Detection of the ammonia gas is important in many technological fields such as clinical diagnosis, industrial processes and environmental monitoring. Recently, ammonia is increasingly used as coolant of refrigerator and heat pumps in place of Freon gas which has permeated the atmosphere and begun to destroy the ozone layer. Although semiconductor oxide is widely used as gas sensor, high temperatures are necessary for the operation and, in general, this type of sensor has critical limitations in gas selectivity. Thus, a low cost and easy-to-use ammonia sensor is strongly required.

In this report, aiming at the use of WCMs as ammonia sensor, the response of electrical resistance to ammonia gas and the temperature dependence of the ammonia sensitivity in WCMs have been measured and the mechanism of resistance change due to ammonia gas has also been discussed.

2. EXPERIMENTAL

Fabrication process of WCMs is as follows: medium density fiber boards were impregnated with phenolic resin using an ultrasonic impregnation system. The impregnated fiber boards were dried at 130°C and then they were sintered at 600°C in a vacuum furnace to form WCMs. Aluminum was evaporated as electrodes onto the WCMs to make ohmic contacts for measuring electrical resistance. In order to remove physical strain of the

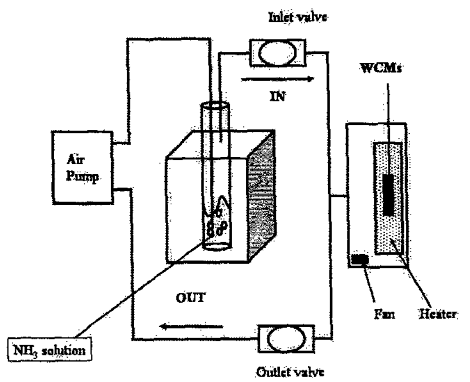

Fig.1 Experimental setup to measure the response of electrical resistance to ammonia gas

samples, the samples were annealed at 600°C in vacuum for 10 min.

Figure 1 shows the experimental setup to measure the response of electrical resistance to ammonia gas. Ammonia gas concentration was controlled by changing the ammonia solution concentration through which air was supplied. Ammonia solution was diluted with distilled water for various concentrations. Ammonia gas concentration was measured by ammonia gas detector tube at 130 seconds after the inlet of ammonia gas. In this experiment, initial gas concentration was varied from 230ppm to 3600ppm. The working temperature of the sensor was varied from 30°C to 70°C using heater.

3. RESULTS AND DISCUSSION

The resistance response to ammonia gas at working temperature of 40°C is shown in Fig.2. Ammonia gas concentration was 2000ppm. When ammonia gas is put into the box, the resistance increases and then saturates after 100 min from the inlet of ammonia gas. When opening the box so as to remove the ammonia gas from the box, resistance decreases. However, after 200 min from removing the ammonia gas, the resistance value was 10% larger than the initial value because ammonia is still adsorbed on WCMs surface. Therefore, degassing process is needed for continuous use of WCMs as ammonia sensor. In this work, the pretreatment, which is the annealing at 75°C for 30 min in air, was carried out before each experiment. After this treatment, the resistance returns to the initial value.

It is assumed that resistance response to ammonia gas is expressed by exponential form,

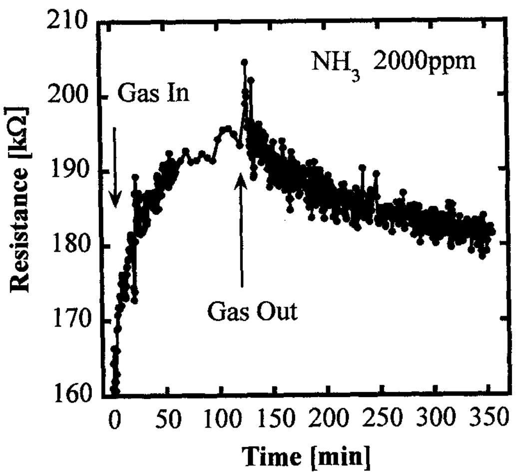

Fig.2 The resistance response to ammonia gas at working temperature of 40°C

$$R(\infty) - R(t) = A\exp\left(-\frac{t}{\tau}\right) \quad (1),$$

where R(t) is resistance at time (t) after the inlet of ammonia gas, A is constant, and τ is response time. The response time τ was determined from fig.2 by eq.1 as about 40 min. This value is too large to use WCMs as sensor, so the improvement such as mixture of metal oxide in WCMs is needed for practical use.

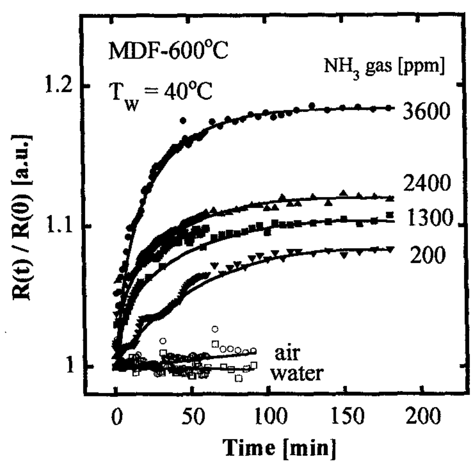

Fig.3 Resistance response to ammonia gas for various gas concentrations at working temperature of 40°C

Figure 3 shows resistance response to ammonia gas for various gas concentrations at working temperature of 40°C. Saturated value of resistance increases as the ammonia gas concentration increases. When air or moisture is put into the box taking over the ammonia gas,

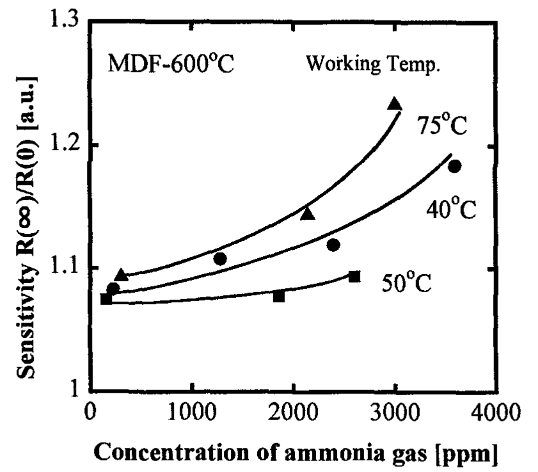

Fig.4 Sensitivity of WCMs to ammonia gas for various working temperature

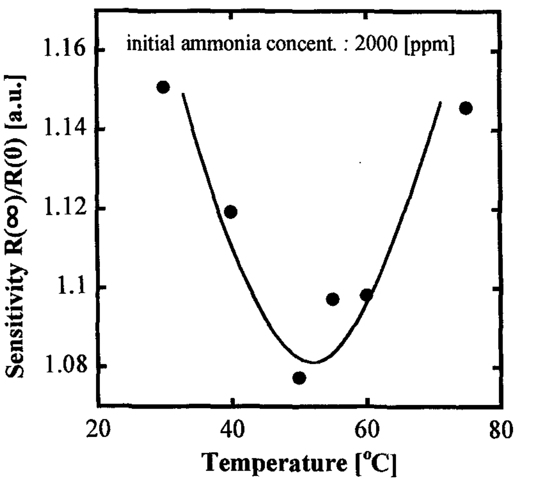

Fig.5 Temperature dependence of the sensitivity for the ammonia gas with concentration of 2000ppm

resistance does not change.

It is reported that phenolic resin pyrolytically decomposes at 300 – 700°C and carboxylic group was formed significantly. Honma reported that noticeable amount of carboxylic and lacton groups were formed in charcoal obtained by carbonization in air [10]. Since WCMs was manufactured by sintering at 600°C in vacuum furnace with phenolic resin which contains oxygen, it seems reasonable to suppose that WCMs have noticeable amount of carboxylic and lacton groups. Acid functional group such as carboxylic and lacton groups acts as adsorbent for basic material such as ammonia. Therefore, the resistance changes by adsorbing ammonia molecules on WCMs surface.

Figure 4 shows sensitivity of WCMs to ammonia gas for various working temperature. Sensitivity is defined as resistance ratio of the saturated value to the initial value. Sensitivity increases as ammonia gas concentration increases irrespective of working temperature. However, the slope of sensitivity depends on working temperature. Temperature dependence of the sensitivity for the ammonia gas with the concentration of about 2000ppm is shown in Fig. 5. The sensitivity indicates minimum at about 50°C. This result suggests that two or more processes are involved in the mechanism of resistance change.

Ammonia gas was put into box and was adsorbed on WCMs surface, so that the ammonia concentration in the box decreased during the measurement. The magnitude of concentration reduction was measured after 3 hours from the inlet of gas. For the initial ammonia concentration of about 3000ppm, the magnitude of concentration reduction was about 2000ppm at working temperature of 40°C, while that was about 1000ppm at 80°C. Irrespective of initial gas concentration, the magnitude decreases as the working temperature increases. It suggests that the amount of ammonia adsorption decreases as working temperature increases. On the other hand, the reaction such as thermal catalysyis enhances as working temperature increases. In fact, most of gas sensors made by semiconductor oxide are operated at the working temperature above 200°C and the sensitivity of these sensors is low at low temperature.

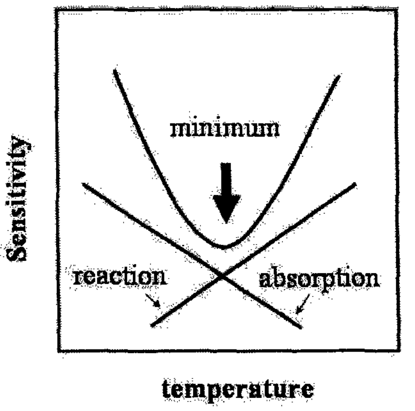

Fig.6 Schematic diagram of the temperature dependence of sensitivity

When these results are taking into consideration, the temperature dependence of sensitivity is explained as in Fig.6. The amount of ammonia adsorption decreases and the reaction such as thermal catalysis enhances as working temperature increases, so that the sensitivity shows the minimum.

4. CONCLUSION

Aiming at the usage of WCMs as ammonia sensor, the response of electrical resistance for WCMs to ammonia gas and the temperature dependence of ammonia sensitivity have been measured and the mechanism of resistance change has been discussed. The resistance of WCMs increases and then saturates with ammonia gas exposure even at extremely low working temperature of 40°C. Saturated value of resistance increases as ammonia gas concentration increases. These results suggest that the resistance changes due to the adsorbing ammonia molecules on WCMs. Temperature dependence of ammonia sensitivity indicates minimum at about 50°C because the amount of ammonia adsorption decreases and the reaction such as thermal catalysis enhances as working temperature increases. Consequently, it seems that WCM is suitable for ammonia sensor which can be used at extremely low temperature.

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