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Gas Sensor for Volatile Organochlorine Compounds Using Percolation Conduction of Organic Montmorillonite-Carbon Composites

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Gas sensor material, which shows a resistivity change in response to change in concentration of volatile organochlorine compounds, is first developed based on a percolation principle. A composite of organic montmorillonite and carbon shows a reversible resistivity change in response to the concentration change of chloroform, dichloromethane, trichloroethylene, tetrachloroethylene, and tetrachloromethane, because the resistivity of the composite is closely dependent on the volume fraction of the insulating phase and the volume of the insulating phase is increased by incorporation of the organochlorine molecules. The response time is substantially improved by fabricating thick-film composites using classified organic montmorillonite.

Introduction

Volatile organochlorine compounds such as dichloromethane, chloroform, trichloroethylene, and tetrachloroethylene are hazardous substances having central nervous system toxicity and carcinogenic risk, although widely used for solvents and detergents in var-

ious industrial processes. Their allowable concentrations in working environment are regulated by the laws of most countries to prevent health hazards. The gas concentrations of volatile organochlorine compounds are usually determined by gas chromatography (GC) equipped with an electron capture detector or a flame ionization detector, or a gas chromatography–mass spectrometer (GC-MS).^{1–3} Such analyses are not performed *in situ* because of the need for sample pretreatment and the unportability of the equipment. Gas

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sensors for organochlorine compounds have not been developed so far, whereas the concentrations of flammable gases such as hydrogen, methane, propane, and ethanol are easily monitored by resistivity measurements of semiconductor gas sensor materials.⁴ This is because the flammability affects the amount of oxygen adsorbed on the semiconductor surface, whereas the organochlorine compounds are inflammable and generally unreactive. Simple detection methods of volatile organochlorine compounds are highly desirable to monitor the working environment.

We have been investigating the percolation behavior of electrical conductivity and its application to sensors.^{5–9} The electrical resistivity of a composite prepared by mixing conducting and insulating particles is closely dependent on the volume fraction of each phase, and thus an extremely small volume change of the phase due to an extrinsic perturbation brings about the resistivity change of the composite. Pressure can be electrically detected by monitoring the resistivity of the composite because the volume fraction of each phase changes with pressure. Carbon-dispersed rubber has been put to practical use as pressure sensors, because the stress to the rubber brings about the decrease in the volume fraction of the rubber matrix, and consequently, the decrease in the resistivity. Our idea is that an objective substance can also be electrically detected on the condition that the volume of one phase increases by incorporation of the objective substance. Carbon-loaded polymers have been found to show resistivity increase when exposed to solvents and hydrocarbons due to the volume change of the polymer matrix.^{10–13} One of the authors has first observed an anomalous resistivity increase of hexagonal tungsten bronzes in a humid atmosphere at room temperature.^{7–9} The resistivity was increased because the conduction path along the *c*-axis was separated by water incorporation into oxygen vacancies existing every six layers perpendicular to the *c*-axis. In our previous paper, we have prepared a humidity sensor consisting of the mixture of montmorillonite and carbon and have demonstrated the operating principle based on percolation conduction.⁵ The resistivity was increased in the humid atmosphere because the volume of the insulating montmorillonite was increased by water incorporation.

In the present study, we used organic montmorillonite for an insulating phase and first developed a sensor material whose resistivity changes with the gas-phase concentration of the volatile organochlorine compounds.

Material and Methods

Organic montmorillonite (average particle size: 40 μm , Esben NX80, Hojun, Gumma, Japan) containing 49.9 wt% of dimethyl dioctadecyl ammonium ion (DMDO) in the interlayer was used to prepare pellets and thick films.^{14–21} The chemical composition of the host montmorillonite is $\text{Na}_{2/3}\text{Si}_8(\text{Al}_{10/3}\text{Mg}_{2/3})\text{O}_{20}(\text{OH})_4$, and all of the Na^+ ion in the host interlayer are exchanged with the DMDO ion in the organic montmorillonite. The organic montmorillonite and carbon powders (average particle size: 5 μm , Kojundo Chemical Laboratory, Saitama, Japan) were mixed in the weight ratio of 90:10 in an agate mortar, and molded into pellets of 0.116 g, 13 mm diameter and 0.63 mm thickness with relative density 76% by monoaxial pressing at 450 MPa. The pellets were dried in an oven at 115°C for 24 h after gold electrodes were coated on both sides of the pellets using gold paste (No. 8563, Tokuriki Chemical Research, Tokyo, Japan). As for the thick-film samples, the organic montmorillonite powder was suspended in acetone and the turbid supernatant was gathered by decantation in order to classify the powder by particle size and to fabricate smooth thick films. The average particle size in the supernatant was estimated at 26 μm by the laser scattering method, and coarse particles above around 90 μm were completely removed by the classification. The carbon powder was mixed with the supernatant. A viscous suspension was obtained by evaporating most of acetone at room temperature, and the thick films of carbon-organic montmorillonite composites were prepared by applying the suspension to a slide glass without adhesives and drying it at room temperature. The two gold electrodes were coated at a distance of 10 mm on the same surface, and the thickness of the thick film was 0.03 mm. The content of the carbon in the thick films was 17.0 wt% (18.5 vol%).

The resistivity was measured by the dc two-probe method using a digital multimeter (34401A, Agilent Technologies, Palo Alto, CA) after drying at 115°C for 24 h and subsequently cooling down to room temperature in dry air. The resistivity changes were investigated in response to stepwise changes of the gas concentration of volatile organochlorine compounds such as chloroform (trichloromethane), dichloromethane (methylene dichloride), trichloroethylene, tetrachloroethylene (perchloroethylene), and tetrachloromethane (carbon tetrachloride). Flammable gases such as acetone, ethanol, and

2-propanol were also used for comparison. The gas concentrations over 4 vol% were controlled by passing dry air through a gas bubbler filled with a liquid of the compound and mixing the gas with the other dry air using mass flow controllers. The gas concentrations as low as 6200 ppm or below were controlled by injecting the liquid compound into a sample chamber using a microsyringe. The morphology of the sample composites was observed using an SEM (S-3000N, Hitachi, Tokyo, Japan) after carbon coating. The structure change of the organic montmorillonite by incorporation of the chloroform was also investigated by powder X-ray diffraction (Miniflex, Rigaku, Tokyo, Japan).

Results and Discussion

The resistivity of the carbon–organic montmorillonite composite pellets is shown in Fig. 1 as a function of the volume fraction of the organic montmorillonite. Similar to the case with the inorganic montmorillonite,⁵ the resistivity began to increase above around 80 vol% and showed a steep jump by four orders of magnitude at 93–94 vol%. The critical threshold of percolation (p_c), the volume fraction of the conducting phase, is estimated as 7 vol%, and thus the composites containing 7 vol% or a little more of carbon is expected to show a sensitive resistivity increase by the volume increase of the insulating phase. The earlier studies theoretically predicted that the p_c is 7.6 vol% when the particle size ratio of insulating to conducting particles is 8 to 1.²² This theoretical prediction is coincident with the present result.

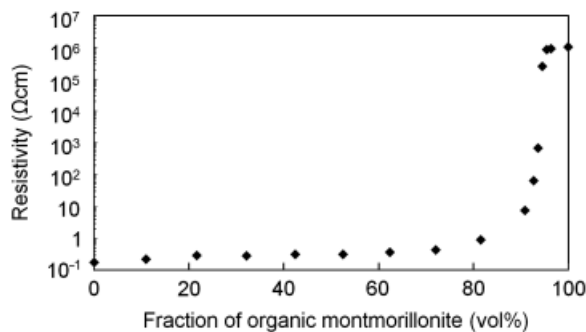


Fig. 1. Resistivity of an organic montmorillonite–carbon composite as a function of the volume fraction of the organic montmorillonite.

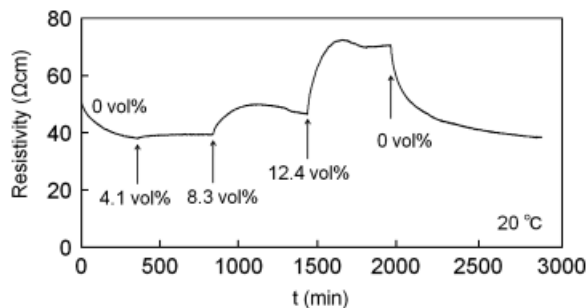


Fig. 2. Resistivity change of a composite pellet containing 10.0 wt% of carbon when the air containing chloroform was introduced and its concentration was changed stepwise at 20°C.

As shown in Fig. 2, the resistivity of the composite pellet containing 10.0 wt% (10.9 vol%) of carbon showed a stepwise increase when the gas concentration of chloroform was increased stepwise, and it returned to its initial level when chloroform-free air was introduced. It is well known that organic montmorillonite incorporates organic compounds in the interlayer.^{14–16,18,20,21} The volume of the organic montmorillonite phase is considered to be increased due to the extension of the interlayer spacing. The 90% response time was in the range of 180–230 min and not fast enough for practical use. Figure 3 shows the result for the thick-film sample containing 17.0 wt% (18.5 vol%) of carbon in response to the change of dichloromethane concentration. The 90% response time was drastically improved to 2–5 min by fabricating thick films using the collected finer particles. We can say that the response time reached the level of practical use. The contact area with the gas was substantially increased compared with the pellet sample,

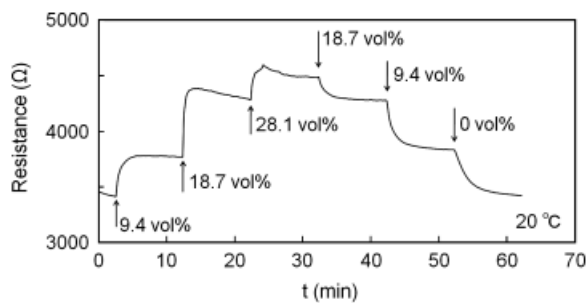


Fig. 3. Resistivity change of a composite thick film containing 17.0 wt% of carbon when the air containing dichloromethane was introduced and its concentration was changed stepwise at 20°C.

and this accelerated the diffusions into both the composite and the interlayer. From our adsorption rate study using pellets, thick films, and powders, we found the form of the thick films contributes greater to the improvement of the response time than using smaller particles. We must mention that the resistance values were slightly different at the same dichloromethane concentration in increasing and decreasing processes. We consider this is because smaller particles that surround larger particles in the thick film are difficult to return to their original position after expansion and contraction. This can be solved by using homogeneous nanoparticles. Figure 4 shows the resistance change in response to increase of trichloroethylene in low concentration range 476–6188 ppm. The resistance reached equilibrium values in 10 min after going through sharp maximum values. Such overshooting behaviors are considered to become obvious in the low concentration range due to competitive adsorption by the composite and the chamber walls. The detection limit for trichloroethylene was estimated at 116 ppm from the S/N ratio of the resistance change.

The resistance changes similar to Fig. 3 were also observed for chloroform, trichloroethylene, tetrachloroethylene, tetrachloromethane, acetone, ethanol, and 2-propanol so far. The composites of organic montmorillonite and carbon detect the flammable volatile organic compounds as well as the inflammable volatile organochlorine compounds, because the organic molecules are incorporated due to the organic affinity of the interlayer compound (DMDO) in organic montmorillonite. The inflammable organochlorine compounds can be distinguished from the flammable organic com-

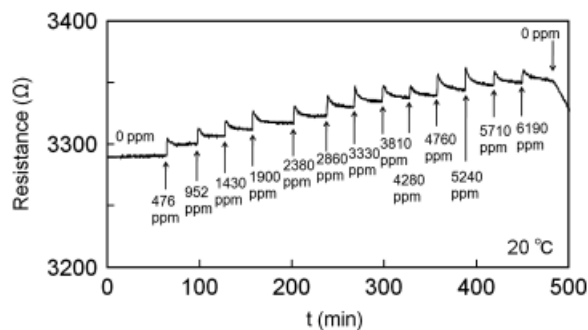


Fig. 4. Resistivity change of a composite thick film containing 17.0 wt% of carbon when the concentration of trichloroethylene was increased stepwise from 476 to 6190 ppm at 20 °C.

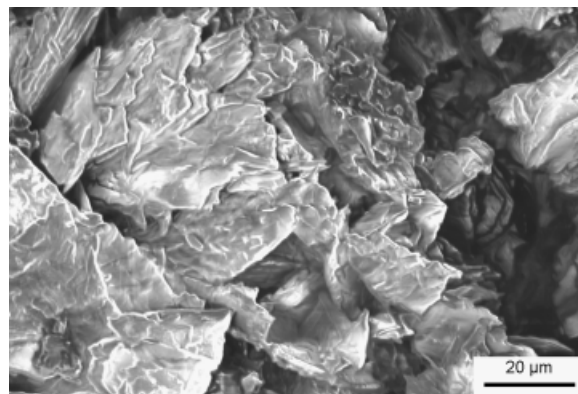


Fig. 5. SEM image of the composite thick film. The flake-like organic montmorillonite particles are observed in the left two-thirds. The conduction path is provided by the carbon powders segregated and aggregated in the grain boundaries between the montmorillonite particles as observed in the crack in the right one-third.

pounds by using concurrently with the flammable gas sensor. Our future challenge is to give the composites the selectivity among the organochlorine compounds.

Figure 5 shows the SEM image of the thick-film surface. The flake-like organic montmorillonite particles are accumulated and oriented along the [001] plane in the left two-thirds of the image. The carbon powders are segregated and aggregated providing a conduction path in the grain boundaries between the montmorillonite particles, which is observed in the crack in the right one-third of the image. Figure 6 shows powder XRD patterns of the organic montmorillonite powders before and after exposition to chloroform-saturated atmosphere for 24 h. In general, powder XRD patterns of two dimensional crystals show asymmetric ($hk0$) reflections tailing to higher angles, ($00l$) reflections like those of the three-dimensional crystals, and no (hkl) reflections ($h, k, l \neq 0$).^{23,24} The organic montmorillonite showed the XRD pattern characteristic of the two dimensional crystals. The d value 3.633 nm for (001) is three times larger than that of ordinary inorganic montmorillonite 1.241 nm, and this corresponds with the fact that the organic montmorillonite contains 49.9% of DMDO in the interlayer and the density is about two-thirds of the ordinary one. The d values of (001), (002), and (003) calculated from peak positions after Lorentz-polarization correction were increased by 6.9–7.8% from 3.344, 1.847, and 1.230 to 3.603, 1.975, and 1.322 nm, respectively, by the incorporation of

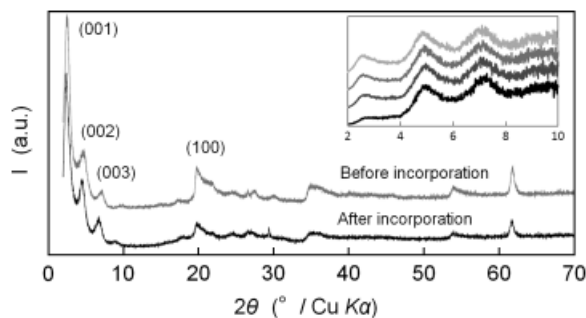


Fig. 6. Powder XRD patterns of the organic montmorillonite before and after chloroform incorporation. The organic montmorillonite powder was left in a chloroform-saturated atmosphere at 20°C for 24 h. Inset shows the XRD pattern change in the desorption process of the organic montmorillonite having adsorbed chloroform (the bottom black line, the sample having adsorbed 127 wt% of chloroform; the second line from the bottom, the sample left for 8 min in air; the third line, the sample left for 16 min in air; the top gray line, the sample left for 24 min in air). The patterns in the inset are deviated for clarity after Lorentz-polarization correction.

chloroform, whereas the d value of (100) remained the same at 0.4485 nm. This indicates that the interlayer spacing was increased by the incorporation of the organic compounds due to the organic affinity of the interlayer DMDO and supports the sensing mechanism that the volume increase of the insulating phase brings about the resistivity increase. A little discrepancy in lattice parameters c calculated from each (00 l) ($l = 1-3$) reflection is due to profile broadening derived from both size and distortion of interferential coherence domain, and such discrepancy has been also reported for ordinary hydrated montmorillonite.²⁵ It is interesting to note that the intensity of (001) was remarkably decreased by the incorporation and increased by the desorption whereas the intensities of (002) and (003) showed little changes. This suggests that the incorporation of chloroform brought about the distortion of the domain rather than the change in the size, because the size effect on the profile is independent of the orders (00 l) and the distortion effect is dependent on the orders.²⁴ Additionally, the XRD pattern of the sample pellet showed higher relative intensities of (00 l) than those of the powder sample, indicating the orientation along [001] plane in the pellet.

In our present and previous papers,⁵ the new chemical sensing principle based on the percolation was formulated using the composite of clay and carbon. So far,

we demonstrated the detection of volatile organochlorine compounds and flammable organic compounds using organic montmorillonite as well as water vapor using ordinary montmorillonite. The sensing principle is inherently advantageous in sensitivity as well as cost reduction, and thus there are various potential applications such as gas alarms in working environment, disposable test strips, water quality monitor, odor sensors, and taste sensors. Selectivity in detection can be achieved by combining the present principle with antigen-antibody reactions, for example, by modifying the interlayer with antibody, which specifically reacts with the objective substance. It is our future challenge to apply specific immune reactions to the present gas sensors and to establish a new category of biosensors. Furthermore, immunoassay tests using the absorptimetry have been used for semiquantitative analysis of environmental pollutants such as pentachlorophenol, polychlorinated biphenyl, *p,p'*-dichlorodiphenyltrichloroethane, and these test methods were approved by the U.S. EPA.²⁶ Electrical detection in immunoassay tests will be possible by using antibody-modified clay composites instead of test tubes or microtiter plates, and this technique will be useful in detection on a microchip.

Conclusions

We demonstrated that volatile organochlorine compounds such as chloroform, dichloromethane, trichloroethylene, tetrachloroethylene, and tetrachloromethane can be detected by a gas sensor consisting of the composite of organic montmorillonite and carbon. The resistivity of the composite was increased in response to the concentration increase of the volatile organochlorine compounds, because the volume of the insulating phase in the composite was increased by incorporation of the organochlorine molecules. The response time was greatly improved from 180–230 to 2–5 min by changing the sample form from the pellet composite to the thick film composite, because the diffusions into both the composite and the interlayer is accelerated due to the increase of the contact area with the gas. The XRD patterns indicated that the lattice parameters c was increased by incorporation of the organochlorine compounds, and this supports the mechanism that the volume increase of the insulating phase brings about the resistivity increase. The detection limit for trichloroethylene was estimated at 116 ppm. The

resistivity change was also observed for flammable gases such as acetone, ethanol, 2-propanol, and water vapor. More sensitive and more selective detection will be possible by modifying the interlayer with peptide or antibody, which specifically reacts with the objective substance.

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