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Percolation-Type Chemical Sensor: Electrical- and Humidity-Sensing Properties of Carbon–Montmorillonite Composites

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A chemical sensor based on the percolation principle is newly developed by fabricating a composite comprising of a conducting phase and an insulating phase whose volume increases by the incorporation of a desired substance. We find a composite of montmorillonite with carbon shows a remarkable resistivity increase in a humid atmosphere, because the volume of the montmorillonite phase increases by the incorporation of water. The resistivity increases in response to stepwise water vapor increases like a humidity sensor. The response time is substantially improved by fabricating a composite thick film using classified fine montmorillonite particles.

Introduction

The electrical resistivity of a composite prepared by randomly mixing conducting and insulating particles is closely dependent on the volume fraction of the conducting phase. When the volume fraction of the conducting phase is relatively small, the resistivity of the composite shows a gradual decrease with the increasing fraction. However, the resistivity decreases drastically by

several orders of magnitude around a certain volume fraction of the conducting phase. This drastic resistivity decline is due to the percolation of the conducting phase, that is, the formation of the conducting paths. This volume fraction is termed a critical threshold (p_c) and experimentally estimated from the inflection point of the volume fraction dependence of the resistivity. The percolation properties of composite materials have been investigated extensively by many researchers from both theoretical and practical aspects.^{1–6}

The volume fraction dependence of the resistivity of cermets has been quantitatively analyzed using a

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general effective media equation, which combines percolation and effective medium theories.⁷ Influence of particle size ratio on the electrical resistivity of the compacted mixtures has been investigated, and it has been theoretically and experimentally confirmed that p_c is reduced when the particle size of the conducting phase is much smaller than that of the insulating phase.^{8–10} Composite conducting polymers have been developed by loading an insulating polymer matrix with a conductive filler based on the percolation principle.¹¹ Such composite materials have potential applications to sensors or transducers, because an extrinsic change that affects the volume fraction of the conducting phase gives rise to the resistivity change of the composite. 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.^{12–15} 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 due to the percolation. Furthermore, one of the authors has first observed an anomalous resistivity increase of hexagonal tungsten bronzes in a humid atmosphere at room temperature.^{16–18} The resistivity increase was percolation-like behavior, 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.

Chemical sensor materials have been widely investigated and a number of operating principles have been proposed. With regard to the humidity sensor, many researchers focused on the resistivity decrease of materials including clay minerals due to water adsorption or hydration.^{19–21} The principle of the resistivity decrease due to the dissociation of H_2O molecule into H^+ and OH^- at the interfaces between electron donor and acceptor in composite materials was also proposed.²² The composite of TiO_2 and $MgCr_2O_4$ has been put to practical use in the humidity sensor of microwave ovens.²³ The permittivity change of polymers due to water adsorption has also been applied to electric hygrometers.²⁴ Although the conventional humidity sensors are widely used to measure relative humidity (RH), they cannot detect a slight amount of humidity in a dry atmosphere and are not sensitive to humidity change. This is because the conductivity or permittivity of the conventional sensor materials changes linearly in response to the adsorbed amount of water molecules.

The conductivity increases due to an increase of ionic conduction derived from water molecules, and the permittivity increases due to an increase of orientation polarization of water molecules. Enhancement mechanism of slight change is not incorporated in the conventional humidity sensor materials. It is essential to detect and control the slight amount of humidity in materials processing plants such as battery factories, semiconductor plants, and thus the inexpensive humidity sensors sensitive to the slight amount of humidity and to the small change of RH are highly desirable. We considered the percolation-type chemical sensor to be appropriate for this purpose.

In this paper, we design and present a percolation-type chemical sensor. A desired substance can be detected by monitoring the resistivity of a composite comprising of a conducting phase and an insulating phase whose volume increases by the incorporation of the substance, according to the percolation principle. In order to verify the applicability of this principle, we fabricate a composite using a montmorillonite as an insulating phase and carbon as a conducting phase. Here, we exploit the well-known property of montmorillonite that it swells by water incorporation. Contrary to the conventional humidity sensors, the resistivity of the composite increases in a humid atmosphere, because the volume of the insulating phase increases by water incorporation.

Experimental Procedure

The sample composites were prepared by mixing montmorillonite particles [particle size: 5–120 μm , average: 40 μm , typical chemical formula: $Na_{2/3}Si_8(Al_{10/3}Mg_{2/3})O_{20}(OH)_4$, Kunipia-F, Kunimine Industries, Tokyo, Japan] and carbon powders [average particle size: 5 μm , Kojundo Chemical Laboratory, Saitama, Japan] in an agate mortar. The mixtures were molded into pellets by monoaxial pressing at 450 MPa. The pellet was 13 mm in diameter and 0.40–0.68 mm in thickness. After gold electrodes were coated on both sides of the pellets using gold paste [No. 8563, Tokuriki Chemical Research, Tokyo, Japan], the pellets were dried in an oven at 115°C for 24 h. The density of the pellet was 2.0 g/cm^3 (relative density 82%).

Moreover, the montmorillonite powder was classified by particle size in order to improve the response time. The powder was suspended in water and centri-

fused at 1000 rpm for 10 min. The turbid supernatant was separated by decantation and carbon powder was mixed with the suspension. Thick films of carbon–montmorillonite composites were prepared by coating and drying this suspension on a slide glass.

The resistivity was measured by the dc two-probe method using a digital multimeter (34401A, Agilent Technologies, Palo Alto, CA). Resistivity measurements of the pellet as a function of the volume fraction of the montmorillonite were carried out after drying at 115°C for 24 h and subsequently cooling down to room temperature in a dry atmosphere. The time course of the resistivity at RH 60% and 20°C was also monitored after the drying process, and thus this measurement started from the water-free state. The resistivity change in response to the stepwise increase of RH was monitored after leaving the pellet at RH 60% and 20°C for several days and subsequently at RH 0% and 20°C for 24 h. At the starting point of this measurement, the pellet already incorporated water to some extent, because some incorporated water does not desorb reversibly at room temperature. Water incorporation into the sample was monitored by gravimetry. The desired water vapor pressure ($P_{\text{H}_2\text{O}}$) was prepared by mixing a dry gas with a wet one using mass flow meters. The morphology of the sample composites was observed using a SEM (S-3000N, Hitachi, Tokyo, Japan) after carbon coating and an optical microscope (VHX-900, Keyence, Osaka, Japan). The structure change of montmorillonite by water incorporation was also investigated by powder X-ray diffraction (XRD) (Ultima IV, Rigaku, Tokyo, Japan) using monochromatized $\text{CuK}\alpha$ radiation, and the water content was determined by DTA/TG measurement (DTG-50, Shimadzu, Tokyo, Japan) at a heating rate 20°C/min.

Results and Discussion

The resistivity of the carbon–montmorillonite composites is shown in Fig. 1 as a function of the volume fraction of the montmorillonite. The resistivity was increased gradually with the increasing volume fraction when the fraction was below about 80%. Above about 90%, however, the resistivity was drastically increased by eight orders of magnitude from 5.55 Ωcm to 273 $\text{M}\Omega\text{cm}$, and became almost steady in the vicinity of 100%. The percolation critical threshold (p_c), the volume fraction of the conducting phase, is estimated as

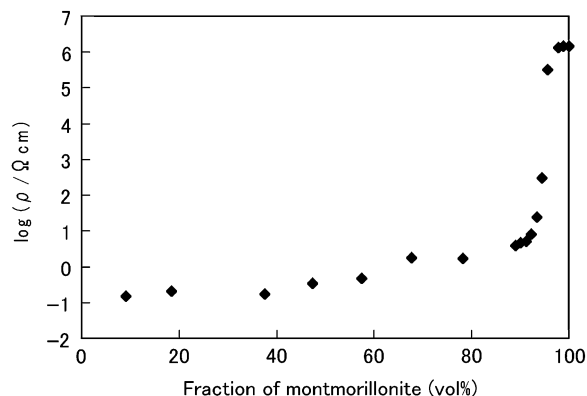


Fig. 1. Resistivity of a montmorillonite–carbon composite as a function of the volume fraction of the montmorillonite.

7 vol% (6 wt%) from an inflection point of the curve. This is much lower than the reported experimental values of p_c such as 47% for $\text{W}-\text{Al}_2\text{O}_3$ films, 35% for Bakelite–silver mixtures.^{9,25} The low p_c is due to the segregation of carbon powders around the montmorillonite particles,¹⁰ because the carbon powder is much smaller than the montmorillonite. Figures 2 and 3 show the surface morphology of the pellet. In Fig. 2, the carbon phase was not randomly distributed in the pellet, but it was segregated and partly continuous between the montmorillonite phase. In Fig. 3, the flake-like montmorillonite particles were oriented perpendicular

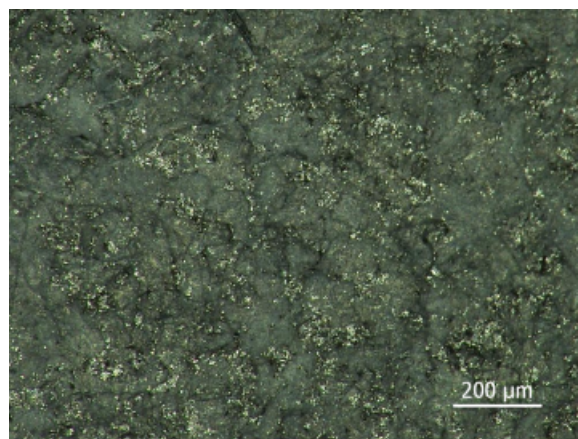


Fig. 2. Optical microscope image of the surface of the composite pellet. The white points are the carbon powders naked on the surface, and the black nets are the segregated continuous carbon phases buried shallowly in the pellet.

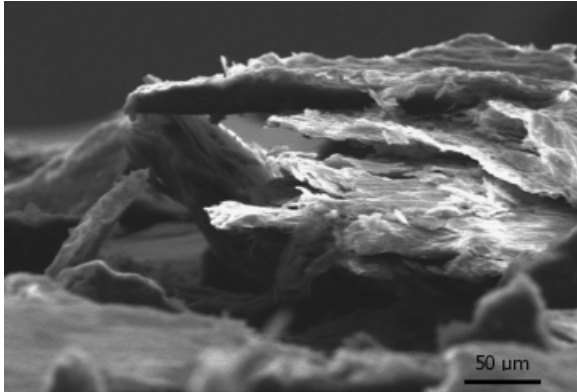


Fig. 3. Scanning electron microscopic image of the composite pellet. The flake-like particles of the montmorillonite were oriented and agglomerated. The carbon powder was not observed in the agglomerate.

to the c -axis, and the carbon powder was not distributed inside the agglomerates of the montmorillonite powder. The p_c is theoretically predicted as 7.6% for the present particle size ratio ($R_M/R_C = 8$) according to the segregation model.^{9,10} This is in good agreement with our present experimental value. It is appropriate to fabricate the composites containing around 7 vol% of carbon to obtain a sensitive resistivity change by water incorporation.

As shown in Fig. 4, the composite containing 7.7 vol% of carbon showed a remarkable resistivity increase from 6 to 1200 Ω cm at 60% RH at 20°C. This unusual resistivity increase is due to the separation of the conducting paths based on the percolation principle,

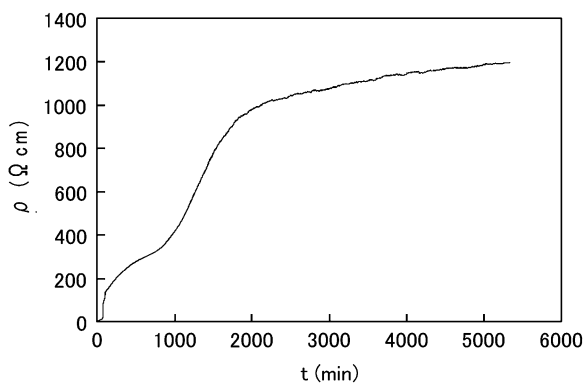


Fig. 4. Resistivity change of a composite pellet containing 7.7 vol% of carbon at RH 60% and 20°C after drying at 115°C for 24 h.

whereas almost all of inorganic materials including the montmorillonite show resistivity decrease by water incorporation. Interestingly, the time evolution of the resistivity showed two inflection points, although resistivity as a function of the volume fraction showed only one inflection point in Fig. 1. This is probably because the curve reflects two factors: the rate change of water incorporation and the volume fraction dependence of the resistivity. The two inflection points are explained by the faster water incorporation rate at the initial stage and the greater volume fraction dependence at the middle stage.

The composites with the mixing ratios far from the value of p_c showed a relatively small resistivity change in a humid atmosphere (RH 85%, 20°C), for example, the composite with carbon 22 vol% changed from 10 to 15 Ω cm. In addition, the composites with carbon 2 vol% or below showed resistivity decrease in humid atmosphere due to the proton conductivity of montmorillonite similar to a pure montmorillonite pellet, whereas those with carbon 3 vol% or above showed resistivity increase due to the percolation effect. The decrease of electrical conductivity due to the separation of the conducting path was balanced with the increase of the proton conductivity through the montmorillonite phase, when the carbon phase was 2–3 vol%.

After the resistivity almost reached a saturated value at room temperature, a dry gas was introduced to the pellet and an equilibrium was established between the pellet and the dry gas at room temperature. The resistivity at this point was greater than that immediately after drying at 115°C, and we investigated a humidity sensor property from this point to reduce the response time. As shown in Fig. 5, the resistivity of the composite (6.6 vol% carbon) was increased and reached an equilibrium in response to stepwise water vapor increases (RH 20%, 40%, and 60%). The resistivity was decreased again by the introduction of a dry gas. The 90% response time was estimated to be 540, 512, and 476 min for RH 20%, 40%, and 60%, respectively. The mass change of the montmorillonite powder in response to the stepwise water vapor increases showed almost the same tendency as the resistivity change (Fig. 6). The 90% response time was estimated to be 1010, 434, and 400 min for RH 20%, 40%, and 60%, respectively. The equilibrium values of water content for P_{H_2O} 0.467, 0.935, and 1.40 kPa were 1.06, 1.99, and 2.79 wt%, respectively. This relationship followed the Langmuir isotherm written as

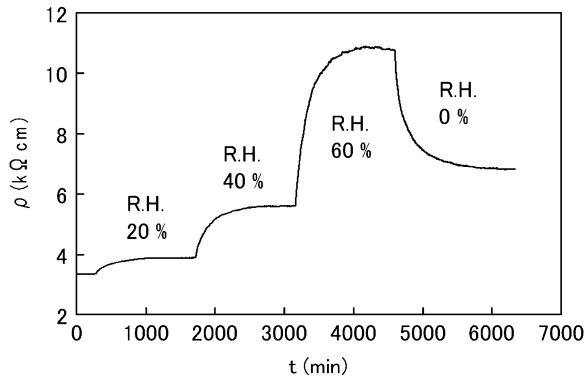


Fig. 5. Resistivity change of a composite pellet containing 6.6 vol% of carbon in response to stepwise relative humidity change (RH 0%, 20%, 40%, and 60%) at 20°C.

$$\frac{P_{\text{H}_2\text{O}}}{x} = \frac{P_{\text{H}_2\text{O}}}{x_\infty} + \frac{1}{Kx_\infty} \quad (1)$$

where x is the amount of adsorbed water molecules and x_∞ is the amount of all adsorption sites. The $\frac{P_{\text{H}_2\text{O}}}{x}$ vs ($P_{\text{H}_2\text{O}}$) plot indicated $x_\infty = 15.2 \text{ wt}\%$ and $K = 1.61 \times 10^{-4} \text{ Pa}^{-1}$. The relationship between the chemical potential of water molecules ($\mu_{\text{H}_2\text{O}}$) and the adsorption potential energy E is expressed by¹⁶

$$\begin{aligned} \mu_{\text{H}_2\text{O}} &= \mu_{\text{H}_2\text{O}}^\circ + kT \ln P_{\text{H}_2\text{O}} \\ &= E + kT \ln \frac{\theta}{1 - \theta} \end{aligned} \quad (2)$$

where $\mu_{\text{H}_2\text{O}}^\circ$ is the chemical potential of water molecules at 101.3 kPa and θ is the coverage of the adsorption site

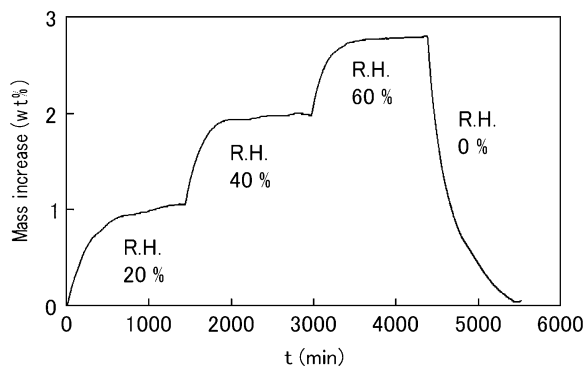


Fig. 6. Mass change of montmorillonite powder in response to stepwise relative humidity change (RH 0%, 20%, 40%, and 60%) at 20°C.

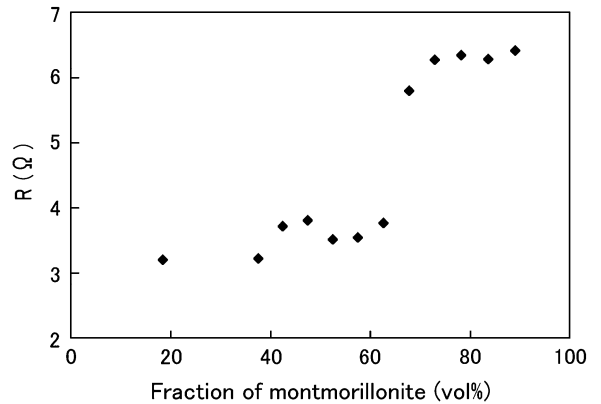


Fig. 7. Resistance of a montmorillonite-carbon composite thick film prepared from the classified fine montmorillonite particles as a function of the volume fraction.

($= x/x_\infty$). The adsorption energy of water molecules onto the montmorillonite was estimated at $E - \mu_{\text{H}_2\text{O}}^\circ = -6.74 \text{ kJ/mol}$. It is important to note that the response time of the powder was similar to that of the pellet. This indicates that the pellet density hardly affected the response time and that not the diffusion in the pellet but the diffusion in the particle is crucial to the sensor response time. We considered the response time would be diminished by the classification of the powder because it is dependent on the particle size.

Figure 7 shows the resistance of the carbon-montmorillonite thick films prepared from the fine montmorillonite particles as a function of the volume fraction. The thickness was in the range of 0.016–0.047 mm. The critical threshold (p_c) is estimated as 35 vol%, because the resistivity was abruptly increased in the range of 62.6–67.7 vol%. The increase of the critical threshold compared with the pellet reflects the reduction of the particle size of the insulating phase.^{9,10} The resistance change of the thick film containing 56 vol% of carbon in response to stepwise water vapor increases is shown in Fig. 8. The 90% response time was 24, 25, and 56 min for RH 20%, 40%, and 60%, respectively. The response time was substantially improved by fabricating a thinner sample comprised of smaller particles of the montmorillonite. The resistivity was rapidly increased when liquid water was dropped on the surface of the thick film, in contrast to the conventional films.

The DTA/TG measurement of the montmorillonite powder indicated that the water desorption proceeded in two stages. The interfacial water desorbed

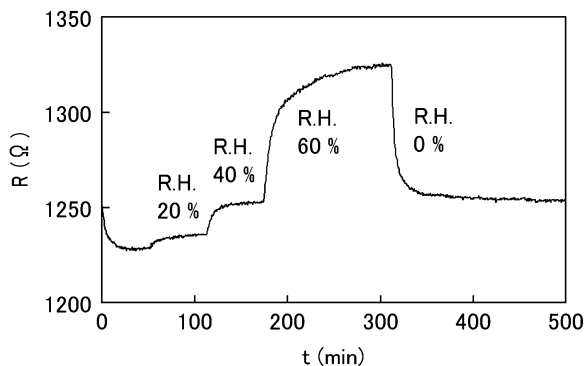


Fig. 8. Resistance change of a composite thick film containing 56 vol% of carbon in response to stepwise relative humidity change (RH 0%, 20%, 40%, and 60%) at 20°C.

from room temperature to 110°C, and the structural water desorbed at 600–700°C indicating the change from $\text{Na}_{2/3}\text{Si}_8(\text{Al}_{10/3}\text{Mg}_{2/3})\text{O}_{20}(\text{OH})_4$ to $\text{Na}_{2/3}\text{Si}_8(\text{Al}_{10/3}\text{Mg}_{2/3})\text{O}_{22}$. The content of the interfacial water was determined from the mass decrease below 110°C. Powder XRD patterns of the montmorillonite are shown in Fig. 9. The lattice parameters were $a = 4.471 \text{ \AA}$, $c = 12.48 \text{ \AA}$ when retained at RH 60% for more than a week, and they changed to $a = 4.503 \text{ \AA}$, $c = 12.10 \text{ \AA}$ by drying at 115°C for 24 h. The water content of the former sample was estimated at 14 wt% by the TG measurement. Because of the water incorporation, the lattice parameter c was increased by 3.14%, whereas the lattice parameter a was decreased by 0.71%. The total volume change of the unit cell corresponding to the water incorporation of 14 wt% was 1.68%. The volume change of the unit cell involved by the resistivity change in Fig. 5 is much lower

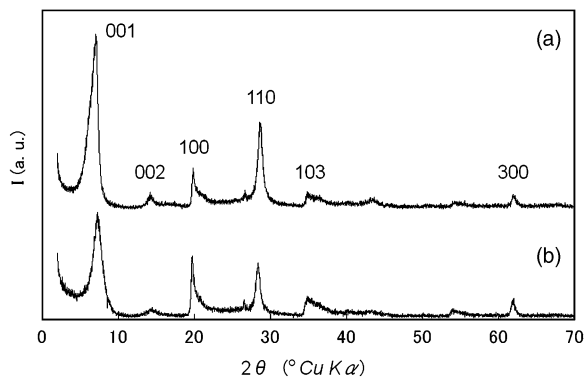


Fig. 9. Powder X-ray diffraction patterns of montmorillonite: (a) with interfacial water of 14 wt%, and (b) water free.

than this value, because the mass change of the sample in Fig. 6 was within 3 wt%. If we assume a linear relationship between the water content and the volume change of the montmorillonite, the resistivity change in Fig. 5 corresponds to the volume change within 0.34%. Our results demonstrate that the composite comprising of a conducting phase and an insulating phase is an effective tool for detecting not only the incorporation of substance but also a slight volume change.

The resistance did not return to the initial value at RH 0% when a dry gas was reintroduced in Figs. 5 and 8, in contrast to the fact that the mass change almost returned to the initial value in Fig. 6. This is probably due to the change of contact resistance between the electrode and the composite, and the change can be cancelled by the improvement of the attachment of the electrodes or the adoption of the dc four-probe method. The resistivity changes in Figs. 5 and 8 remained within one order of magnitude, whereas the resistivity in Fig. 4 increased three orders of magnitude. This is due to the difference in the initial conditions. The measurement in Fig. 4 started immediately after drying at 115°C, while those in Figs. 5 and 8 were carried out using the samples left in an ambient atmosphere for several days. It is appropriate to start immediately after drying at 115°C when we prioritize the sensitivity or the detection limit for a water vapor detector over the reversibility of the resistance. In this case, the detection limit is roughly estimated at 0.6 ppm from the S/N ratio in Fig. 4. In contrast, it is appropriate to use the composite almost saturated with water vapor in application to an RH sensor. Our results suggest that controlling the initial state is critical for the practical use of the percolation-type sensors.

Conclusions

We demonstrated that a percolation-type chemical sensor can be fabricated using a composite of a conducting phase and an insulating phase whose volume increases by the incorporation of a desired substance, because the resistivity of the composite increases abruptly with the increasing volume fraction of the insulating phase at a certain threshold of the volume fraction. Water vapor (4.6×10^2 – $1.4 \times 10^3 \text{ Pa}$, 20°C) was successfully detected by monitoring the resistivity of the composite comprising of montmorillonite and carbon. Contrary to the conventional humidity sensors, the re-

sistivity showed an increase by water incorporation. The response time was substantially improved from 400–1010 to 60–128 min by using a thick film prepared from classified finer montmorillonite particles. Simultaneously, the critical threshold (p_c) of the volume fraction of the conduction phase increased from 7 to 35 vol% by reducing the particle size. This was in agreement with the earlier reports on the influence of particle size ratios. This percolation-type humidity sensor has advantages in cost, sensitivity, and durability, and thus it will be a powerful tool to detect a water vapor at high temperature up to about 150°C in a corrosive atmosphere. Furthermore, this new working mechanism of chemical sensor can be easily applied to the other sensor systems. Selective and sensitive detection of a desired substance will be feasible by modifying the interlayer of the montmorillonite with functional groups. Biosensors will also be possible by fabricating a composite of a conductor and a receptor containing an enzyme or an ion channel whose volume or morphology change by the incorporation of a desired substance. We believe that the new working mechanism will occupy an important position in the principles of chemical sensors in the near future.

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