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Optical Humidity Sensor Using Nafion-Dye Composite Thin Films

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By using Nafion[R] film with crystal violet or pink FGH[R], the optical humidity sensor has been fabricated. In the reflection mode, the optical intensity of the peak at 630 nm for crystal violet and at 540 nm for pink FGH decreases with relative humidity. The raising and recovery times are less than 1 min.

The development of optical fibres has given to new technology. A great number of optical fibre sensors have been devised for the measurement of physical parameters like temperature and position. Recently, optical fibre system is currently of interest technique to detect gas species in atmosphere.[1-5] In this paper, we propose a new type humidity sensor composed of immobilized dye with Nafion film.

Crystal violet(C.I.Basic Violet 3,42555) and Aizen cathilon pink FGH[R] (C.I.Basic Red 13,5-1950) were used as dyes. For thin film preparation, Nafion[R] powder dispersed in water-alcohol solution with the prescribed ratio of dye was used. The films were prepared on alumina substrate and quartz oscillator with gold electrodes by using spinner. The humidity of the atmosphere to be measured was controlled by mixing humid air prepared by bubbling and synthesized air. The setted humidity was achieved within 20 s in the humidification and dessication processes by using the special chamber to measure the optical response. The Y-type quartz fibre was fixed just front of the sensor. Light from D_2/I_2 lamp was launched into the fibre and directed to the sensor; the reflected and modulated light was collected by the same optical fibre. The collected light was analyzed by using a spectro multi channel photo detector in the region 400 nm to 800 nm. By using the film prepared on quartz oscillator, the changes of the oscillating frequency were measured as a function of the relative humidity. All of the measurements were executed at 30 °C.

It is well known that crystal violet and pink FGH take solvato-chromism in which the color is very sensitive to the activity of acidic protons. Nafion is well known as a strong polyelectrolyte acid. For the composite film of Nafion and dye, the dye can be entrapped as a result of the formation of a new ionic salt and the solubility of dye in water is greatly depressed. Crystal violet and pink FGH are intensely colored to violet and pink, respectively, and the entrapped dyes on Nafion, crystal violet and pink FGH are slightly yellowllish in dry air. It is expected that the acid strength of solid acid is weakend by the sorption of a water molecule. This change induces the color change of dyes caused by the change of the molecular structure. The spectra in reflection mode of the composites were examined as a function of the relative humidity. The reflection peak was observed at 630 nm for crystal violet and 540 nm for pink FGH,respectively. For crystal violet entrapped on Nafion, the color was changed by the sorption of a water molecule to blue with an increase in the sorbed water and the good reversibility for the changes of the humidity was confirmed. The results are shown in Fig.1-a. The signals were measured as the ratio of the reflected intensity to that in the dry air. The reflectance at 630 nm decreases with an increase in the relative humidity and the reverse tendency is confirmed at 470 nm. For the composite film with pink FGH,the reflectance at 540 nm decreases with an increase in the humidity as shown in Fig.1-b. In the humidification process, the steady state values are achieved within 30 s, furthermore, the recovery times are 1 min or less. The heat pretreatments induced the deteriorations of humidity sensitivity while the response time was hardly influenced.

Nafion is a hydrophilic polymer and can sorb a considerable amount of

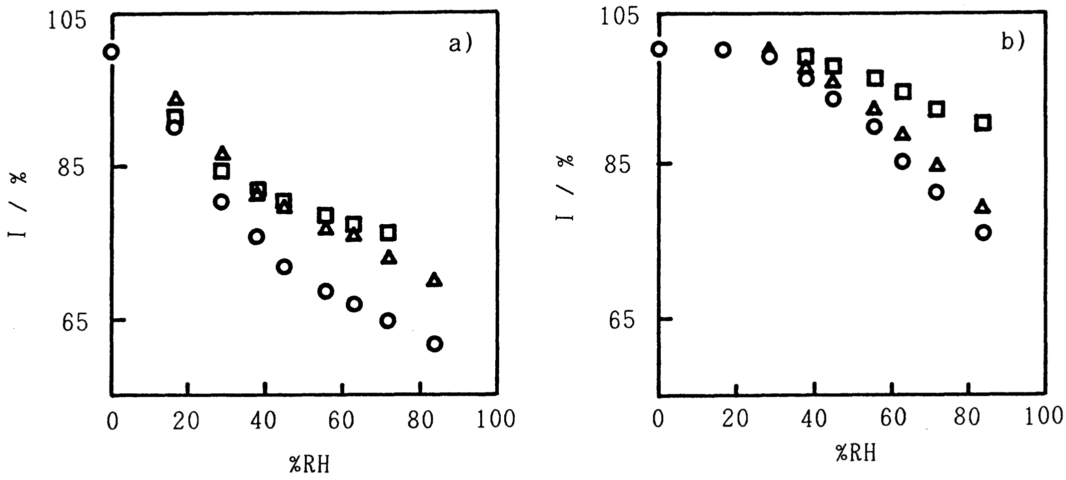

Fig. 1. Humidity dependence of intensity at 630 nm for crystal violet(a) and at 540 nm for pink FGH(b) composite. Annealing temp ; O)60 °C, Δ)120 °C, □)150 °C.

water. The water sorption ability was decreased by the heat pretreatments, for example, the water content of 6 water molecule per ionic group was decreased to 2 at 80% relative humidity by the annealing at 120 °C. For the composite films, similar annealing effects on water sorption ability were confirmed. The correlations between water

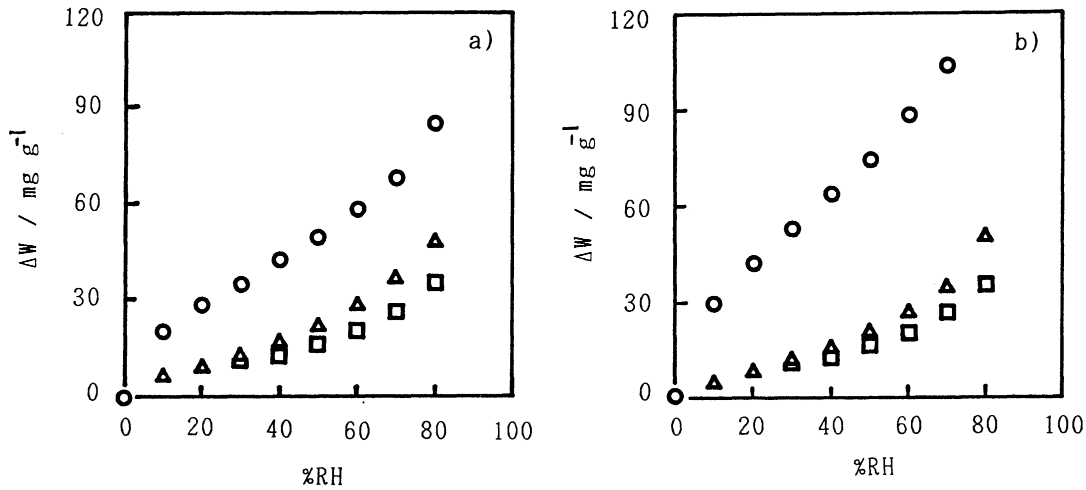

Fig. 2. Water sorption isotherms of composite films with crystal violet(a) and with pink FGH(b) at 30 °C. Annealing temp ; O)60 °C, Δ)120 °C, □)150 °C.

content (ΔW) and relative humidity for crystal violet and pink FGH composites are shown in Fig.2-a and b, respectively. For the composite film annealed at 60 °C, the water sorption ability was less than Nafion singly and grealty decreased by the annealing at 120 °C or more. It will be quated from the reliable datum by W.G.Grot of Du Pont [6] that we believe that the liquid obtained is not a true solution. If the solvent is evaporated at room temperature,the morphology of the discontinuous fluorocarbon phase is largely preserved. Such a film is weak and will readily re-dissolve in alcohol. If, however, the solvent is evaporated hot or if the cast film is heated to 100 to 120 °C, the dispersed fluorocarbon phase will some extent fuse together and the film will become insoluble. Furthermore, it is believed that the heating at 120 °C induce the formation of micelles surrounded by the hydrophobic phase. The proposed model convinced us the heat pretreatment effects on the water sorption characteristics. The deterioration of the humidity sensitivity and the decrements of water sorption ability by the heat pretreatments are qualitatively interpretable in terms of the phase inversion of the micelles surrounded by ionic groups to that surrounded by fluorocarbon chain.

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