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Polyvinyl Alcohol-*co*-Styrene Sulfonate/$FeCl_2$ Composite as Humidity Sensing Material

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Polyvinyl alcohol shows a significant impedance response with changing relative humidity (RH) only above 60% RH. Simply fabricated polyvinyl alcohol film as a humidity sensor lacks durability and also shows high impedance. To overcome this problem, polyvinyl alcohol was crosslinked with 4-styrene sulfonate (sodium salt) in the presence of ferrous ions. The best results with the material as a humidity sensor were obtained when polyvinyl alcohol was crosslinked with 4-styrene sulfonate in the presence of ferrous ions at a temperature of 140°C for about 1 h and when polyvinyl alcohol, 4-styrene sulfonate (sodium salt hydrate) and $FeCl_2 \cdot 4H_2O$ were used in a weight ratio of 10:2:3, respectively. The polymeric mixture of the three materials in water was cast on an alumina substrate (7.5 mm × 7.2 mm × 0.38 mm in size) prefabricated with interdigitized gold electrodes and was cured at a temperature of 140°C for 1 h. The results demonstrate that the logarithm of the impedance decreased linearly with increasing %RH in the range from 30 to 92% RH. Other factors, such as stability, sensitivity and response time for the fabricated sensor, were also determined.

1. Introduction

Organic polymers are potential materials for humidity sensors because of their low cost and easy fabrication as sensing materials in the form of thin films.[1–5] Another advantage of these materials with respect to inorganic sensing materials is that their properties can be

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tuned by adjusting chemical groups such as carboxylates, sulfonates and protonated amines associated with the polymeric molecules to yield better sensitivity and linearity on the part of the sensors.[1–3] Several organic polyelectrolytes have been suggested as humidity sensors, but these are usually water soluble and thus lack durability against moisture. Sakai *et. al*.[4] proposed grafting hydrophilic polymers that upon copolymerization with other molecules become water-insoluble but retain their moisture sensing capabilities.

Polyvinyl alcohol (PVA) is a common hydrophilic polymer having an -OH group on alternate carbon atoms in its backbone.[6,7] Due to its high affinity for water, PVA absorbs and desorbs moisture from the environment, thereby changing the water content in a fabricated polymeric film.[8,9] However, such films lack durability and also show high impedance.[8] To solve these problems, crosslinking PVA with other organic electrolytes has been proposed,[5] but the methods are long and tedious. In the last few years, organic polymer/inorganic composite materials have attracted attention for many electronic and optical applications, and it has been observed that composite materials have improved properties over organic polymers.[10–12] Only a few reports have been published on application of organic/inorganic composites as humidity or gas sensors.[13,14] As an example, recently Li et al.[13] used polystyrenesulfonate mixed with ZnO as a composite material in a humidity sensor. Suri et al.[14] reported humidity and gas sensors based on $FeCl_3$-polypyrrole nanocomposites. In this communication, we propose a very simple process for PVA-based polymeric film, namely crosslinking PVA with 4-styrenesulfonate (sodium salt) in the presence of ferrous ions on an alumina substrate and curing at a temperature of 140°C. The sensor thus fabricated had a good durability and showed linearity for the logarithm of impedance at relative humidities from 30 to 92% RH.

2. Materials and Methods

2.1 *Preparation of polymeric composite solutions*

Polyvinyl alcohol (PVA) [Mol.wt 500, purchased from Junsei Chem. Co.] was dissolved in doubly distilled water in a 1:10 ratio (W/V) and was allowed to swell for 24 h at room temperature. Varying amounts of 4-styrene sulfonate sodium salt (SS) [purchased from Aldrich Chem. Co.] dissolved in water were added to a known volume of PVA solution, mixed thoroughly, and were allowed to stand for 30 min. A 1 mM solution of $FeCl_2 \cdot 4H_2O$ was made by dissolving the calculated amount in a minimum amount of hydrochloric acid, evaporating it almost to dryness (repeated twice), and then finally diluting it to a known volume. Varying amounts of ferrous ion solution were added to a mixture of PVA-SS solution and mixed thoroughly.

2.2 *Sensor fabrication*

The polymeric mixtures were fabricated on alumina substrates (7.5 mm×7.2 mm×0.381 mm in size, printed with gold electrodes by screen printing and having a ten-toothed comb structure) by a process of either dip-coating or casting, as shown in the shaded portion in Fig. 1, and then curing at different temperatures between 80 and 160°C for different time intervals. Light brown colored films were obtained on the alumina substrate when cured

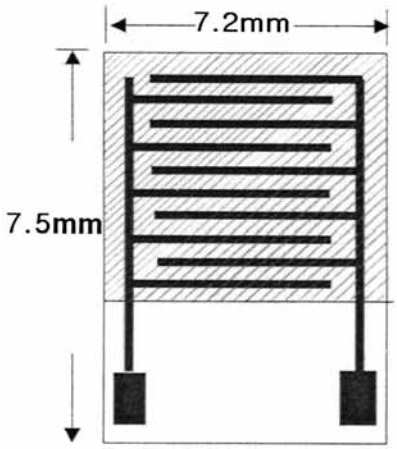

Fig. 1. Schematic view of the fabricated film on an alumina chip printed with gold electrodes.

below 120°C. Dark brown films were obtained if cured above 140°C. The films thus obtained were washed thoroughly with water. The structure of the polymeric material was established by spectroscopic methods to be a copolymeric material. The polymeric films were characterized by SEM, which showed a homogeneous distribution of ferrous ions in the mixture. EDAX data showed complete removal of sodium ions, while ferrous ions remained in the film.

2.3 *Measurement of impedance versus humidity*

Impedance of the films versus relative humidity was measured in a humidity chamber (30 cm × 30 cm × 45 cm in size) at 1 V, 1 kHz and at 22, 27, 35 and 40°C using impedance/gain-phase analyzer model HP 4194A. The fabricated sensor was mounted on an electronic circuit especially designed for determining the impedance/resistance of the sensors. The humidity chamber was flushed thoroughly with dry air until a constant impedance was recorded. Regulated humid air produced by an automatic electric humidifier was then introduced until it gave a constant humidity (%RH). These RH levels were independently monitored using a standard hygrometer. The measurement of the humidity detection output is done after 10 min have passed with the humidifier and temperature controller after the temperature and humidity setting. Impedance versus relative humidity in the range of 30 to 95% RH was plotted for absorption processes, and between 95 and 30% RH for desorption processes. Response time for the film upon an abrupt change in humidity was determined in the range of 30 to 80% RH for absorption as well as desorption.

3. Results and Discussion

The polymeric mixtures containing PVA and SS, when cast on alumina as given in the recommended procedure, were found to be able to bear very high impedance and showed very little response to humidity. However, it was observed that the addition of metal ions

such as alkali metal ions or transition metal ions to this polymeric mixture drastically changed the impedance when the film was exposed to moisture. Hence the polymeric mixtures were cured in the presence of inorganic cations. Better sensitivity was recorded against moisture when transition metal ions were added; this is shown in Fig. 2. Among the cations, cobalt(II), copper(II), iron(II) and iron(III) ions showed a good response for changes in impedance with moisture; however, the highest sensitivity was with ferrous ions. Hence, in further studies ferrous ions were selected to be added to polymeric mixtures to make an organic/inorganic composite as a humidity sensor material.

The polymeric mixtures were made in different proportions containing PVA, SS and $FeCl_2$ solutions and cast on alumina substrates. The films were cured at temperatures between 80° and 160°C for different time intervals. The films cured below 120°C were light brown and showed partial water solubility when dipped in water, while the films cured between 140° and 160°C for more than 30 min became dark brown and showed complete water insolubility. Charring started when the mixture was cured above 170°C. Similarly, it was observed that the films fabricated with a higher concentration of ferrous chloride in a ratio by weight with PVA above 9:25 were of course more sensitive to changes in impedance versus humidity but were attacked by the moisture, which damaged the surface of the film. These films also showed partial water solubility, which was

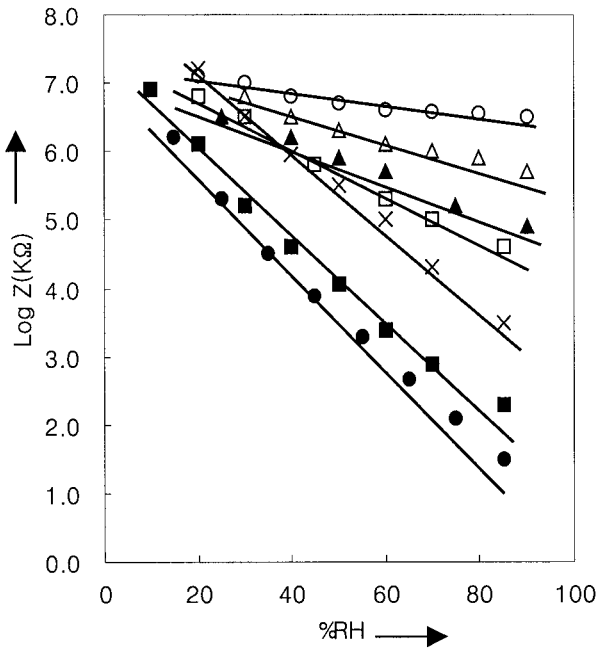

Fig. 2. Response of impedance vs %RH for the films fabricated with PVA/SS/Metal chloride in a weight ratio of 10:2:3 measured at 22°C, 1 V and 1 kHz: ○ no metal, △ Na^{I}, ▲ Ni^{II}, □ Cu^{II}, × Co^{II}, ■ Fe^{III}, ● Fe^{II}.

determined by analysis of the weight. Higher concentrations of SS in a ratio with PVA above 1:5 in the films were, however, completely insoluble in water but showed a smaller sensitivity to humidity. Figure 3 shows the dependence of impedance recorded *vs* relative humidity at 27°C and at 1 V and 1 kHz for polymeric films of PVA-SS-$FeCl_2$ constituted in varying proportions. Taking sensitivity and stability both into consideration, the best compromise was obtained for the film having PVA:SS:$FeCl_2 \cdot 4H_2O$ in a ratio by weight of 10:2:3. Figure 4 shows the dependence of impedance versus %RH recorded at different temperatures for this film. This ratio was chosen in the subsequent studies. However, it was concluded from this figure that the composite in this ratio is sensitive to increasing temperatures, presenting a variation of almost 1.4% RH/°C, and the highest sensitivity was therefore obtained at 40°C.

The response time shown by the films fabricated at a ratio by weight of 10:2:3 against absorption or desorption of moisture was plotted against time, as the sensor was changed from 30% RH maintained in one compartment to 80% RH maintained in another compartment. As shown in Fig. 5, 45 s was required by the films to respond to RH increasing abruptly from 30 to 80% RH (~1% change in RH/s). Similarly 60 s was required by the film to desorb moisture as RH decreased from 80 to 30% in a desorption process (~0.8% change in RH/s). The results obtained for the response time shown by the films for

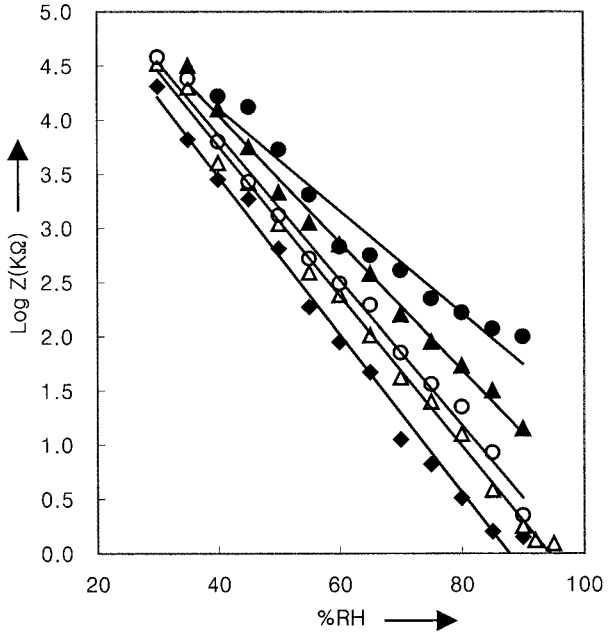

Fig. 3. Response of impedance vs %RH for the fabricated films with PVA/SS/$FeCl_2.4H_2O$ in different weight ratios (◆ 10:2:4, △ 10:2:3, ○ 10:2:2, ▲ 10:3:3, ● 10:4:3) measured at 27°, 1 V and 1 kHz.

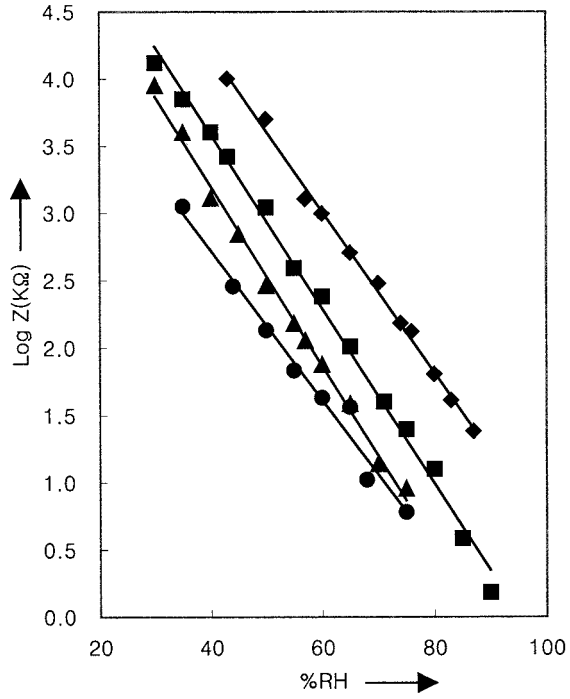

Fig. 4. Response of impedance vs %RH for the films with PVA/SS/$FeCl_2$.$4H_2O$ (10:2:3) measured at ◆ 22°, ■ 27°, ▲ 35° and ● 40° and at 1 V and 1 kHz.

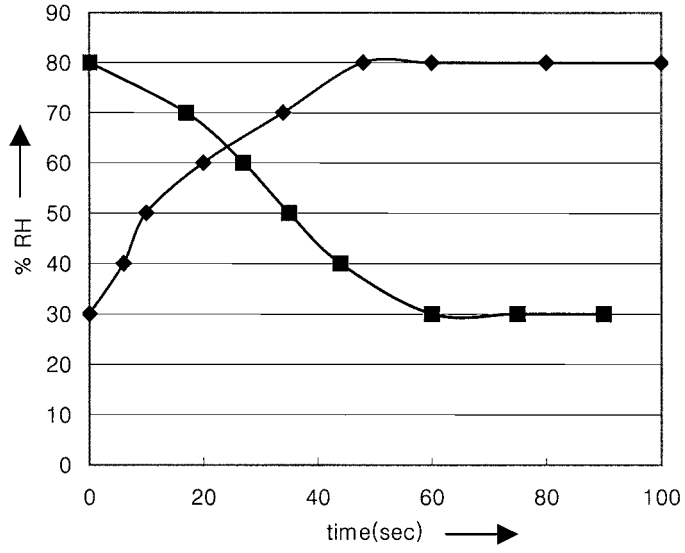

Fig. 5. Response time shown by the films containing PVA/SS/$FeCl_2$.$4H_2O$ in a 10:2:3 ratio against changing humidity: (◆) absorption (■) desorption.

absorption and desorption at different %RH are shown in Fig. 5.

The durability of the sensors, fabricated at the most preferred ratio, was tested by soaking them in water for different time intervals and then drying them in air. The impedance shown by the sensors was recorded at 40, 60 and 80% RH. These values were compared with those of a freshly prepared sensor which was washed with water to remove sodium ions and dried in air. The change in impedance was within 2% even after the sensors were soaked in water for 4 h and then dried. These results showed that the co-polymer formed was completely insoluble in water and was stable against an attack of moisture.

4. Conclusion

Sensors made by cross-linking PVA and SS in the presence of ferrous chloride and then curing the films cast on alumina substrates showed a good response against moisture. Increasing concentrations of ferrous ions increased the sensitivity, but the films were also sensitive to attack by moisture. Increasing the concentration of SS gave better durability but showed less sensitivity. The best results were obtained when the PVA-SS-$FeCl_2 \cdot 4H_2O$ weight ratio was 10:2:3 and when the films were cured at 140°C for 1 h. This composite showed a good linearity for the logarithm of impedance at relative humidities from 30 to 92% RH, and 45 s was required by the films to respond to RH increasing abruptly from 30 to 80% RH. The fabrication of the sensors is very simple and cheap as far as cost factors are concerned.

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