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A resistive-type humidity sensor using composite films prepared from poly(2-acrylamido-2-methylpropane sulfonate) and dispersed organic silicon sol

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Abstract

A composite material of dispersed organic silicon sol and poly(2-acrylamido-2-methylpropane sulfonate) (poly-AMPS) was used to make humidity sensor without protective film or complicated chemical procedures. The organic silicon sol was dispersed well in the poly-AMPS without using dispersion agent. Parameters that may affect the water-resistive but humidity-sensitive characteristic of composite material, the adding amount of organic silicon sol solution and the film of thermal treatment time, were investigated. The microstructure of the material was analyzed, and the humidity sensing and electrical properties of the sensor were measured. The sensor well responded to humidity with a relatively good linearity, though it depended on the applied frequency. The temperature influence between 15 and 35 °C was within −0.17 % relative humidity (RH)/°C in the range of 30–90% RH. The activation energy was maximum around 40% RH. The sensor showed the hysteresis within 5.9%, fast response time, long-term stability (75 days at least) and satisfactory resistance to high humidity atmosphere (97% RH) and chemical environment (20% C_2H_5OH vapor). Analyzing the structure and complex impedance plots of organic silicon sol/poly-AMPS was used to explain improvement in humidity sensing properties in comparison with nano-sized SiO_2 powder/poly-AMPS films.

Keywords: Humidity sensor; Composite material; Dispersion; Organic silicon sol; Poly-AMPS; Impedance spectra

1. Introduction

There are many kinds of ceramics and organic polymers have been studied for the development of humidity sensors for measurement and control of humidity in human comfort and a myriad of industrial processes. The polymer electrolytes are one of interesting materials because they have a better humidity-sensitive characteristic, such as long-term stability, reliability, ease of processing and the low fabrication cost, than the ceramic materials or hygroscopic resin containing an electroconductive powder distributed therein. The resistive-type humidity sensors are fabricated with polymer electrolytes. The conductivity of polymer electrolyte usually increase with humidity due to that the polymer electrolyte ionizes and produces conductive ions migration inside the material [1]. For example, poly(2-acrylamido-2-methylpropane sulfonate) (poly-AMPS) polymer electrolyte with acidic groups or their salts, such as $–SO_3^-H^+$ or $–SO_3^-M^+$, where M is an alkali metal has been used for humidity sensors material [2–6]. However one of serious shortcomings of the hydrophilic electrolytic-type polymer is that when exposed to a highly humid atmosphere for a long time, then the humidity sensing layer is liable to swell, shrink or peel off from the substrate [7,8].

Many kinds of methods have been studied to solve the problem of resistant to high humidity atmosphere using polymer electrolyte as sensing material. Sakai et al. [3,9] used the graft polymerization method to prepare the polymer electrolyte on the surface of the pores of porous polyethylene

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films. Many papers reported that using the cross-linking method of copolymer of hydrophilic and hydrophobic monomers as the humidity-sensitive materials [10,11]. Sakai et al. [12] applied the interpenetrating polymer net-work (IPN) technique, the cross-linked hydrophilic polymer chains and the cross-linked hydrophobic chains interpenetrated each other, to prepare a sufficiently resistive materials to water. Kinjo et al. [7] proposed that coating a protective organosilane film on the surface of hydrophilic polymer. Some composite materials of inorganic/polymer have been reported, such as SiO_2/Nafion [13], TEOS/poly-AMPS [6], $BaTiO_3$/RMX [14,15] and $BaTiO_3$/polystrene sulfonic sodium [16]. There are some disadvantages of these methods, such as the rather complicated chemical procedures and the bad degree of dispersion of reinforcement in polymer for preparing the water-resistive humidity sensing material using polymer electrolyte. In our previous study [17], poly-AMPS was mixed with nano-sized SiO_2 powders to form organic/inorganic composites. However, the mixture was not very stable and nano-sized SiO_2 particles tend to coagulate or precipitate from solution, which makes it difficult to prepare thin film humidity sensors by dip coating. In order to solve the problem, the directly addition of dispersed organic silicon sol solution into polymer was used to form a water-resistive but humidity-sensitive characteristic of composite material by simple blending fabrication in this study. The humidity sensing and electrical properties of the organic silicon sol/poly-AMPS composite films and compared with nano-sized SiO_2 powder/poly-AMPS composite films were investigated.

2. Experimental

2.1. Sample preparation

Organic silicon sol solution (serial number STK-300) used in this work was kindly supplied from Yamaichi Kagaku Corp. (Japan). The precursor solution for the poly-AMPS were prepared by adding AMPS (4 g, Merck), triethylamine (TEA) (0.4 ml, 99.9%), sodium persulfate (0.8 ml, Merck), H_2O (10 ml) into a reflux system in all at 100 °C (1 h) with high speed stirring (850–900 rpm). The precursor solution for the poly-AMPS and organic silicon sol composite films was prepared by blending of poly-AMPS and organic silicon sol solution (1:2, w/w). With the precursor solution, films composed of poly-AMPS and organic silicon sol were coated on the alumina substrate with a pair of comb-like electrodes by dip-coating and then thermal treatment at 90 °C for 0.5 h and then 180 °C for 5 min in air, whereby the humidity sensor of resistive-type was obtained.

2.2. Instruments and analysis

A field emission scanning electron microscopy (FE-SEM; LEO 1530; Oberkochen, Germany) was used to investigate the surface morphology. The complex impedance of the sensor as a function of the relative humidity was measured with an LCZ meter (Philips PM6304) in a cell in which the humidity was controlled by mixing the dry and wet air using mass flow controllers (Hastings) as described elsewhere [6]. The frequency ranged from 1 to 100 kHz and relative humidity (RH) varied from 30 to 90% RH under the temperature of 15, 25, and 35 °C. The highest humidity atmosphere (97% RH) for stability test was controlled by using a saturated K_2SO_4 solution.

3. Results and discussion

3.1. The morphology and optimal fabrication of composite films

From the results of scanning electron microscopy analysis, Fig. 1a shows that the organic silicon sol was ball-type structure, particle size was about 300 nm in diameter, and had good degree of dispersion in liquid. When the dispersed organic silicon sol was added into poly-AMPS, compared to the pure poly-AMPS film (Fig. 1b), the composite film's (Fig. 1c) sturdiness increased was observed so that it had less porosity in comparison with pure poly-AMPS film. The powder can be stably dispersed in the solution because of the effect of electrostatic and steric stabilization [18,19]. It is mainly due to the organic silicon sol is charged during the preparation to increase the interface interaction with poly-AMPS so that it could be easily and homogeneously dispersed in an electrolyte polymer solution. The schematic model representation of organic silicon sol in the poly-AMPS is shown as Fig. 2.

The measurement was made at 25 °C and an ac voltage of 1 V, 1 kHz. The effect of adding amount of organic silicon sol into the poly-AMPS to form composite material is shown as Fig. 3. The humidity sensing range (30–90% RH) of composite material decreased with increasing the adding amount of organic silicon sol. It is thought to be due to that the organic silicon sol (STK-300) had water-resistive character [20] so that the hydrophilic of poly-AMPS was restrained. The segmental motion space of polymer chain was occupied by the adding organic silicon sol so that the impedance of composite material was increased with increasing the adding organic silicon sol. Therefore, for a further study, the ratio of STK 300 to poly-AMPS as 2:1 (w/w) was used.

The effect of thermal treatment time on the film is shown as Fig. 4. It was observed that when the thermal treatment time was 5 min the sensor had the longer humidity working range (30–90% RH). It is mainly due to that the tightness of film increased with increasing the thermal treatment time so that the water permeation of film surface decreased.

The composite film showed excellent stability after the sensor was placed in the high RH (97% RH) and in the chemical environment containing 20% C_2H_5OH vapor for 7 days as shown as Fig. 5.

3.2. Humidity sensing properties

The impedance of the organic silicon sol/poly-AMPS humidity sensor is shown as function of relative humidity in Fig. 6. The sensor was measured at 25 °C and an ac voltage of 1 V, 1 kHz. It is seen that the impedance changes from 10^2 to 10^6 Ω and the curves show acceptable linearity ($Y = -0.0653X + 7.77$; $R^2 = 0.9491$, where Y is log-impedance; X the RH; R^2 is the correlation coefficient) between log-impedance and RH at the range of 30–90% RH. The differences between humidification and desiccation process in the range of 30–90% RH were within 5.9%.

The impedance of the sensor was dependent on the ambient temperature as shown in Fig. 7. When the temperature increased, the RH characteristic shifted to the lower impedance. The temperature coefficient between 15 and 35 °C was −0.005, −0.17 and −0.024% RH/°C at 30, 60, and 90% RH, respectively. When the data were plotted as the measured resistance versus $1/T$ at 30, 60, and 90% RH, the activation energy of sensor was obtained from the Arrehenius plot of resistance. The obtained activation energy was plotted against the relative humidity in Fig. 8. There was a maximun around 40% RH. According to Sakai et al. [5] the sorbed water molecules act as a plastisizer, which induces the increase in the mobility of cation. At lower RH (<40% RH), this may be the cause of the carrier ion Na^+ obtained more hydrating water molecules as the humidity increased, so that the mobility decreased with increasing in humidity. Above 40% RH, the amount of sorbed water is sufficient to promote the transfer of hydrated Na^+ ion. In addition the protons from

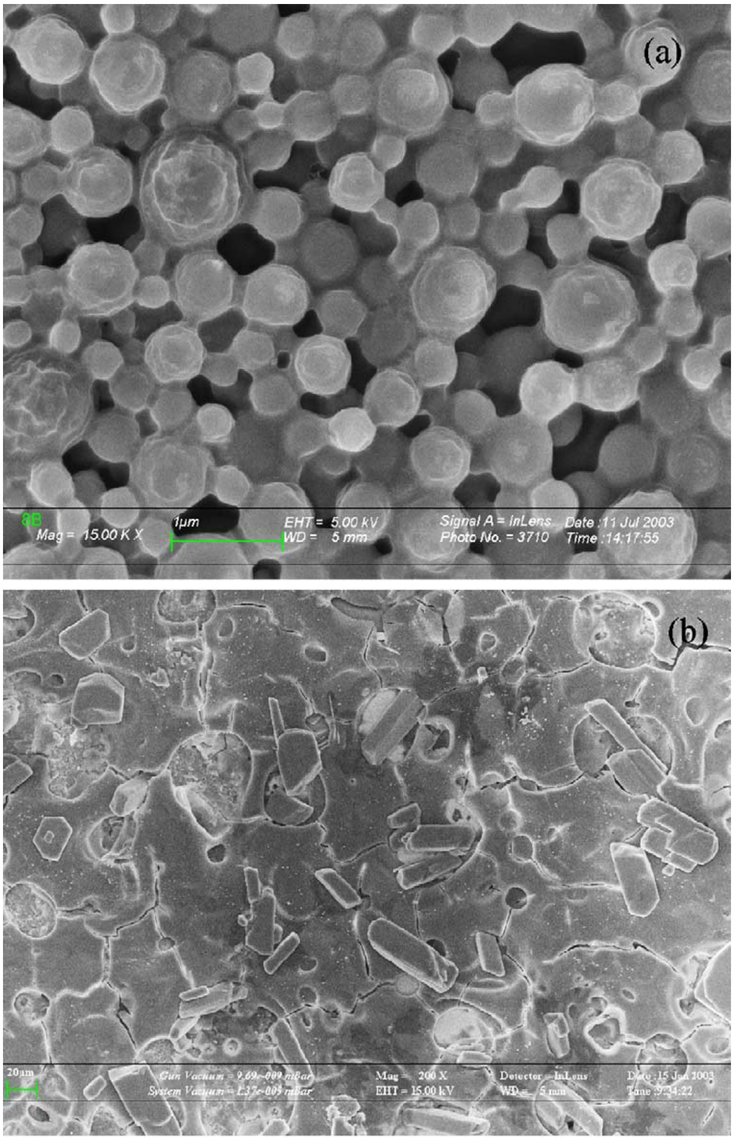

Fig. 1. FE-SEM images of: (a) organic silicon sol (STK 300); (b) poly-AMPS; (c) composite of organic silicon sol/poly-AMPS.

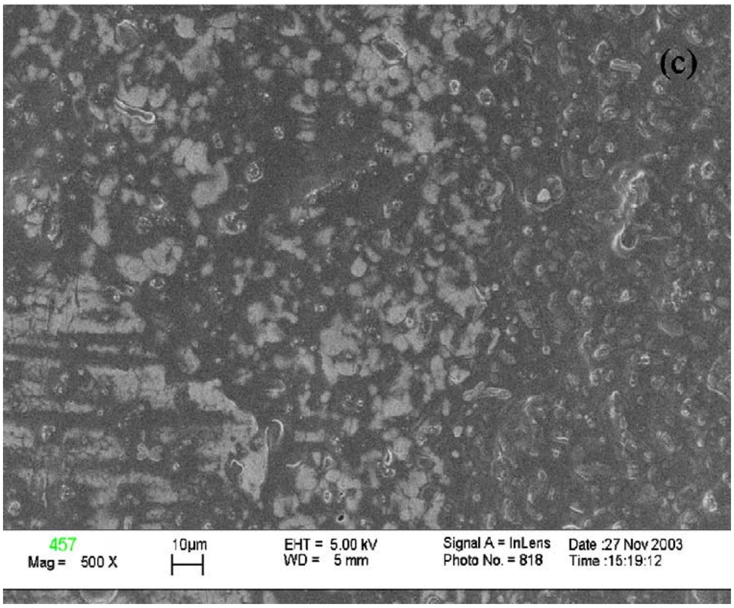

Fig. 1. (*Continued* .)

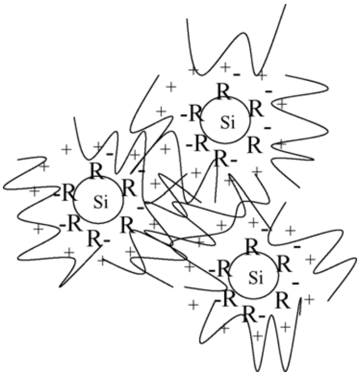

Fig. 2. Schematic representation of organic silicon sol dispersing in the poly-AMPS.

the water also could become the carrier at high humidity [21].

Dependences of sensor impedance on applied frequency were measured at frequencies of 1, 11, and 100 kHz as shown in Fig. 9. At low RH, the frequency influence on the impedance was bigger than the one at high RH. Because at a very high frequency the adsorbed water can not be polarized (at RH < 50%), the dielectric phenomena does not appear, and the impedance is determined by the geometric of the sample [22].

The response–recovery property of the sensor, measured at 25 °C and 1 kHz, are shown as Fig. 10. The response time (humidification, as humidity changed from 30 to 90% RH) was about 60 s, and the recovery time (desiccation, as humidity changed from 90 to 30% RH) was about 180 s.

The effect of long-term stability is shown in Fig. 11. The sensor impedance had no obvious deviation at three testing point 30, 60, and 90% RH for 75 days at least.

The comparison of humidity sensing characteristics between organic silicon sol/poly-AMPS composite films and nano-sized SiO_2 powder/poly-AMPS composite films is shown in Table 1. The organic silicon sol/poly-AMPS composite films had better linearity ($R^2 = 0.9491$) and less temperature dependence due to the dispersed organic silicon sol

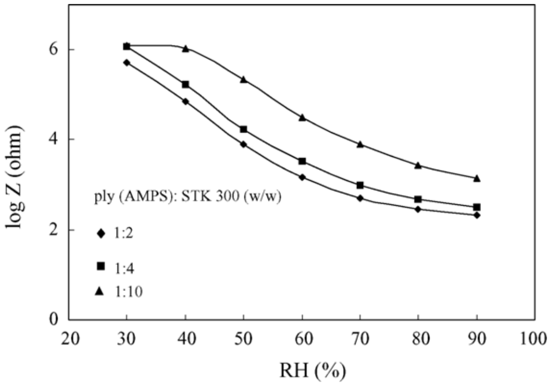

Fig. 3. Effect of adding amount of organic silicon sol into the poly-AMPS measured at 1 V, 1 kHz.

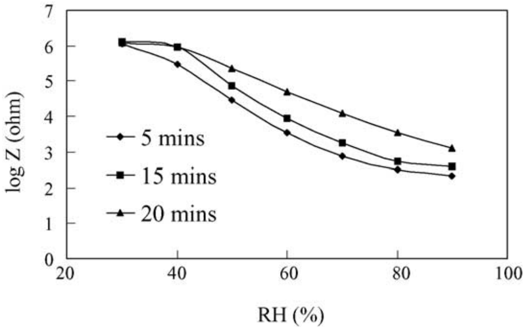

Fig. 4. Effect of thermal treatment time on composite film measured at 1 V, 1 kHz.

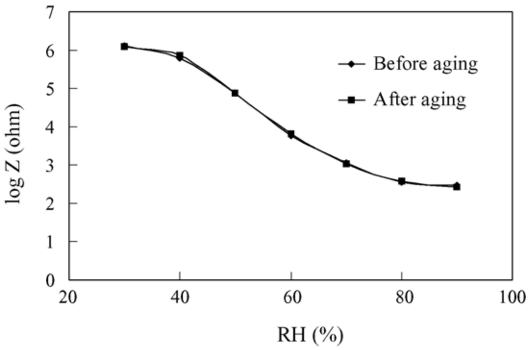

Fig. 5. Impedance vs. relative humidity an organic silicon sol/poly-AMPS sensor before and after aging under a highly humid (97% RH) and alcoholic (20% CH_3CH_2OH) environment.

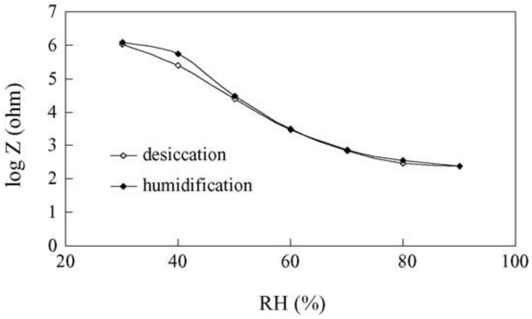

Fig. 6. Impedance vs. relative humidity between humidification and desiccation process for an organic silicon sol/poly-AMPS (1:2, w/w) sensor measured at 1 V, 1 kHz.

increasing the interface interaction with poly-AMPS and then increased the composite film's sturdiness. However, the hysteresis (at low RH) and the recovery time of the organic silicon sol/poly-AMPS composite films were slightly bad. It could be due to the porosity of organic silicon sol/poly-AMPS composite film decreased with increasing in composite film's sturdiness. Therefore, after the adsorbing water at high RH for organic silicon sol/poly-AMPS the composite films, the moisture inside of composite film was removed slowly at low RH.

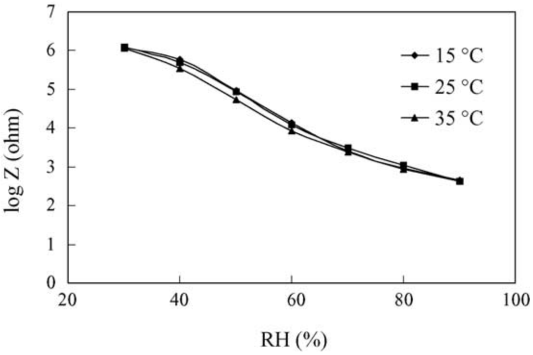

Fig. 7. Impedance vs. relative humidity for an organic silicon sol/poly-AMPS (1:2, w/w) sensor at various temperatures measured at 1 V, 1 kHz.

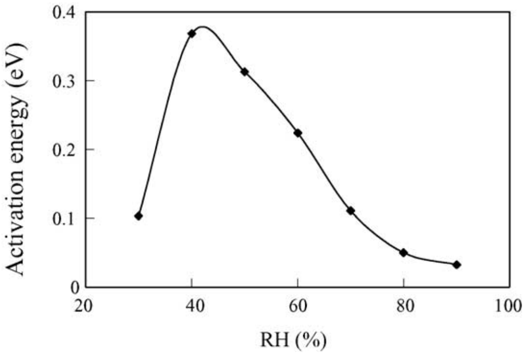

Fig. 8. Activation energy vs. relative humidity for an organic silicon sol/poly-AMPS (1:2, w/w) sensor.

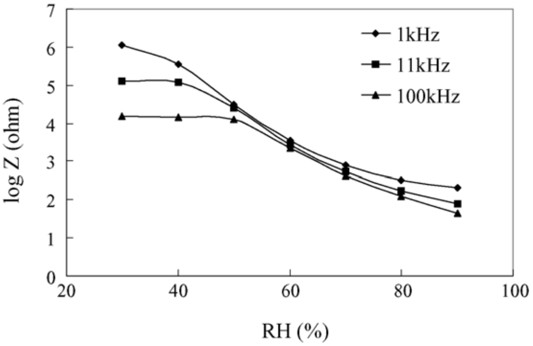

Fig. 9. Impedance vs. relative humidity for an organic silicon sol/poly-AMPS (1:2, w/w) sensor at various frequencies.

3.3. Complex impedance

The LCR meter cannot give real (Zr) and imaginary (Zi) impedance at low applied frequency and low RH. Therefore, the frequency range from 1 to 100 kHz and the RH range from 20 to 90% at 25 °C were chosen for the complex impedance analysis. The typical complex impedance spectra of the organic silicon sol/poly-AMPS composite film at different humidities are shown in Fig. 12. At low humidity, a semicircle

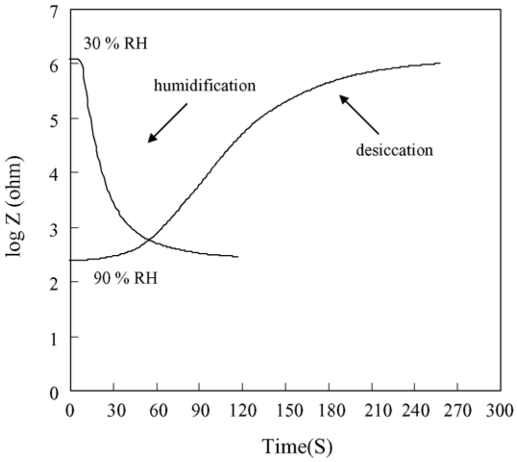

Fig. 10. Response–recovery property of an organic silicon sol/poly-AMPS (1:2, w/w) sensor measured at 1 V, 1 kHz.

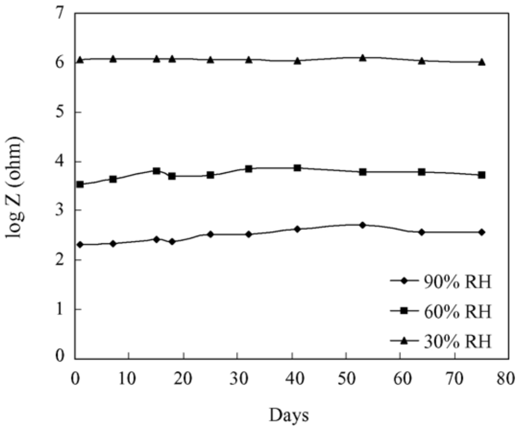

Fig. 11. The long-term stability of an organic silicon sol/poly-AMPS (1:2, w/w) sensor measured at 1 V, 1 kHz.

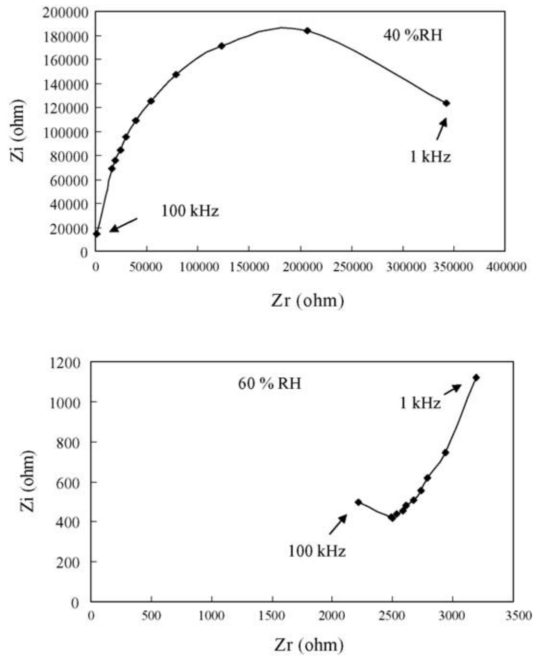

Fig. 12. The complex impedance plots of an organic silicon sol/poly-AMPS (1:2, w/w) sensor at different RH.

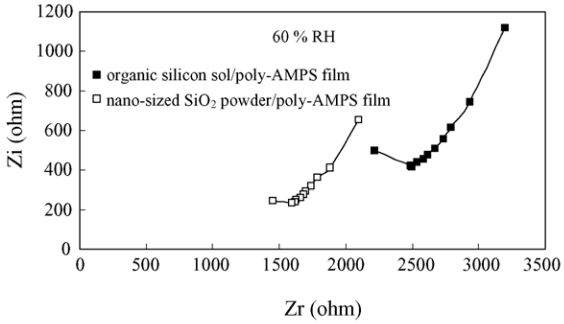

Fig. 13. The complex impedance plots of the organic silicon sol/poly-AMPS and nano-sized SiO_2 powder/poly-AMPS film at 60% RH.

due to film impedance was observed. As RH increased, a line appeared at the low frequency range, and the line became long when RH further increased. The semicircle plot of the impedance have been explained by many authors [13,15,16] that it is due to a kind of polarization and can be modeled by an equivalent circuit of parallel resistor and capacitor. The line at the low frequency range represented a Warburg impedance, which was caused by the diffusion process of redox ions at the interface of electrode and sensing film [23,24]. The existence of Warburg impedance always makes the impedance response deviate from the linear line. Therefore, the linearity of the response curve is closely related with the weight of the components in the composite impedance of sensors [13,25]. The complex impedance plots of organic silicon sol/poly-AMPS and nano-sized SiO_2 powder/poly-AMPS film are shown in Fig. 13. A semicircle with slightly larger diameter was observed in the plot of organic silicon sol/poly-AMPS film. This leads to the decrease in the weight of Warburg impedance in the composite impedance. Thus, the linearity of the response curve of organic silicon sol/poly-AMPS composite film was slightly improved reported in Table 1.

Table 1
The comparison of humidity sensing characteristics between organic silicon sol/poly-AMPS and nano-sized SiO_2 powder/poly-AMPS

Sensing characteristics	Organic silicon sol/poly-AMPS	Nano-sized SiO_2 powder/poly-AMPS [a]
Linearity[b]	$Y = -0.0653X + 7.77$; $R^2 = 0.9491$	$Y = -0.0627X + 7.383$; $R^2 = 0.9231$
Temperature coefficient[c] (% RH/°C)	−0.17	−0.71
Hysteresis[d] (%)	5.9	1.17
Response-recovery time[e]	60 s for response and 180 s for recovery	60 s for response and 120 s for recovery

[a] The data refers to reference [17].

[b] The humidity sensing range from 30 to 90% RH.

[c] The ambient temperature range from 15 to 35 °C.

[d] The deviation between humidification and desiccation process in the range of 30–90% RH.

[e] The response time as humidity changed from 30 to 90% RH; the recovery time as humidity changed from 90 to 30% RH.

4. Conclusion

The organic silicon sol could be dispersed well in poly-AMPS to form a humidity sensor that was sufficiently resistance to water and chemical environment. From the structure of composite and complex impedance plots analysis, the sensor based on organic silicon sol/poly-AMPS composite film showed better linearity over humidity range (30–90% RH), lower temperature dependence and excellent stability in a high RH atmosphere and even in an alcoholic environment than nano-sized SiO_2 powder/poly-AMPS film. The response and recovery time of the sensor were 60 and 180 s, respectively. There was a maximum activation energy around 40% RH. The complex impedance plots in different RH showed that the shapes of the curves changed from a semicircle to a line with increasing RH, indicating different sensing mechanisms at low and high RH.

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