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Preparation of New Polyelectrolyte/ Silver Nanocomposites and Their Humidity-Sensitive Properties

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Abstract: A simple strategy was developed based on polyelectrolyte/silver nanocomposite to obtain humidity-sensitive membranes. The major component of a humid membrane is the polyTEAMPS/silver nanocomposite obtained by thermal heating the mixture of a polyelectrolyte and silver isopropylcarbamate complex. Humidity sensors prepared from polyTEAMPS/silver (w/w=100/0 and 100/6) nanocomposites had an average impedance of 292, 8.83 and 0.86 kΩ, and 5,327, 140 and 0.93 kΩ at 30, 60 and 95% relative humidity (RH), respectively. Hysteresis, temperature dependence and response time were also measured. Activation energies and complex impedance spectroscopy of the various components of the polyelectrolyte/silver nanocomposite films were examined for the humidity-sensing membrane.

Keywords: silver nanoparticles, humidity sensor, polyelectrolyte/Ag nanocomposite, silver alkylcarbamate complex.

Introduction

Various types of humidity-sensitive polymers have been used as humidity sensing material.[1-11] Chemical structure of the base polymer determines the sensitivity, stability, reliability, and electrical characteristics of the sensor. Incorporating nanoparticles into polymeric matrices is proven to be an effective method to enhance the function of polymeric materials.[12] Metal nanoparticle/polymer nanocomposite materials exhibit novel combinations of the metal nanoparticles and polymers properties that are attractive for their potential applications in catalysis, optics, electronics, sensor and biomedicine.[13] Silver is an important commercially available metal and its nanoparticles are superior to other nanosized metal particles for their excellent electrical conductivity,[14] antimicrobial effects[15] and optical properties.[16] Therefore, the combination of silver nanoparticles and polyelectrolyte is expected to create a new functional nanocomposite with properties of both polyelectrolyte and silver nanoparticles, such as humidity sensitive and electrical properties. Some inorganic/polymer composite materials have been tested as humidity sensors, such as SiO_2,[17,18] $BaTiO_3$,[19,20] $BaTiO_3$[21], and ZnO.[22]

Silver organic salts was reported as a new method to obtain silver nanoparticles and conductive silver tracks, where the silver alkylcarbamate complex[23-25] and silver carboxylate[26] were reduced to silver metal by thermal heating at 130-250 °C.

In this work, the polyelectrolyte containing quaternary ammonium salt and amide groups were used directly as the anchoring reagents for the silver nanoparticles. Novel humidity-sensitive polyelectrolyte/silver nanocomposites were successfully prepared by *in situ* thermal heating the polyTEAMPS and silver isopropylcabamate complex solution and their humidity sensitive characteristics were investigated.

Experimental

Chemicals and Instrument. Tetraethylammonium 2-acrylamido-2-methyl-1-propanesulfonate (TEAMPS) was prepared by reacting 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS) with tetraethylammonium hydroxide. Silver isopropylcarbamate complex, $i\mathrm{PrNHCOO_2Ag_2{\cdot}2}i\mathrm{PrNH_2}$ solution was supplied by Inktec Co. Ltd (silver content, 20%). 2-Methoxyethanol was dried over calcium hydride and purified by distillation.

The humidity and temperature controller (Jeio Tech Korea, Model: TM-NFM-L; 20%-95%RH) was used at a constant temperature for the measurement of relative humidity. Tooth-comb gold electrode (width: 0.15 mm; thickness of

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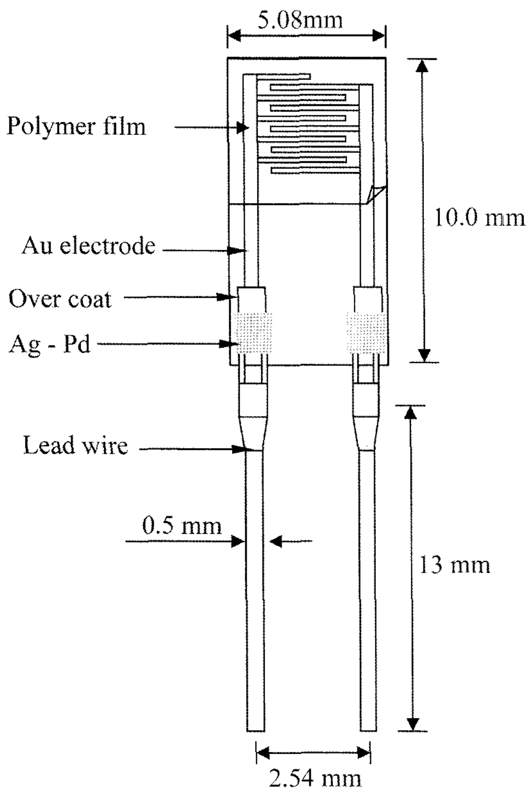


Figure 1. Schematic view of the gold electrode on the alumina substrate.

electrode: 8-10 μm) was silkscreen-printed on the alumina substrate (10 mm × 5.08 mm × 0.635 mm) using a 280-mesh sieve. A soldering pad and over-coat was formed using silver-palladium alloy and glass paste, respectively, as shown in Figure 1. The surface impedance of the gold electrode was found to be less than 0.04 Ω. The impedance was measured with an Impedance Analyzer (HP 4192).

Polymerization of Tetraethylammonium 2-Acrylamido-2-Methyl-1-Propanesulfonate (TEAMPS). Radical initiator 4,4′-azobis(4-cyanovaleric acid) (1 mole% of monomer) and ammonium hydroxide (0.5 g) dissolved in water (5 mL) were poured into a solution of AMPS (6.21 g, 30 mmol) and tetraethylammonium hydroxide (30% solution, 17.18 g, 35 mmol) dissolved in distilled water (35 mL), with vigorous stirring. The reaction mixture was heated and maintained at 65 °C for 24 h. After polymerization was completed, the reaction mixture was precipitated in acetone and the resulting powdery product was filtered. The final product was dried at 60 °C under vacuum to produce a hygroscopic white powder with an 84% yield.

Fabrication of Humid Membrane. A solution of silver carbamate complex solution (3.0 g) was added to a solution of polyTEAMPS (9.4 g) dissolved in anhydrous 2-methoxyethanol (30 g). The mixture was put onto the gold/alumina electrode by dip-coating method. The sensor chips were heated at 130 °C for 30 min to induce the decomposition reaction of silver isobutylcarbamate. Other humidity sensors obtained from nanocomposites with polyTEAMPS/Ag=100/4, 100/2, and 100/0 were prepared by similar procedures.

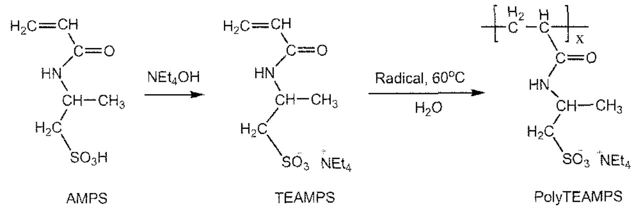
Measurement of Impedance Characteristics. The hysteresis characteristics was measured by first humidification process using fresh samples from 30 to 95%RH and directly return to the desiccation process from 95 to 30%RH at 1 V, 1 kHz and 25 °C at equilibrium state. The temperature dependence was measured at temperatures between 15 and 35 °C at 1 V and 1 kHz. Response and recovery time was determined using the saturated salt solution of KNO_3 for 94%RH and $MgCl_2 \cdot 6H_2O$ for 33%RH. The response time from 33 to 94%RH was measured by transferring the humidity sensor from the chamber in equilibrium at 33%RH to the chamber in equilibrium at 94%RH. Complex impedance measurements were carried out over a frequency range of 100 Hz to 1 MHz at 1 V and 25 °C at various relative humidity levels. The resistance (R_p) was estimated by extrapolating the semicircle or the pile to the real axis based on the assumptions of an equivalent circuit of parallel combination of the resistance R_p and the capacitance C_p.

Results and Discussion

Monomer Synthesis and Polymerization. Monomer, tetraethylammonium 2-acrylamido-2-methyl-1-propanesulfonate (TEAMPS) was prepared by the neutralization reaction of 2-acrylamido-2-methyl-1-propanesulfonic acid with tetraethylammonium hydroxide. PolyTEAMPS was prepared by the radical polymerization of an aqueous TEAMPS solution as shown in Scheme I.

The polymer was hygroscopic and soluble in polar aprotic or protic solvents such as ethanol, 2-methoxyethanol, 2-ethoxyethanol, dimethylsulfoxide and *N,N*-dimethylformamide. PolyTEAMPS had an inherent viscosity of 1.22 dL/g in 2-methoxyethanol and average molecular weights of 64,520, and polydispersity of 2.23. The radical polymerization produced polymer with somewhat moderate molecular weight judging from the data of viscosity and GPC.

Preparation of PolyTEAMPS/Silver Nanocomposites. *In situ* preparation of a humidity sensor using polyelectrolyte/silver nanocomposite was performed after the gold electrode/alumina fabricated with a solution of polyTEAMPS and silver isopropylcarbamate complex was heated to 130 °C.



Scheme I

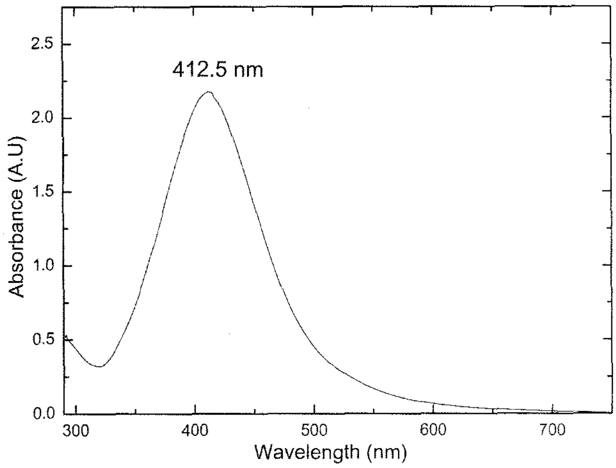


Figure 2. UV-vis absorption spectrum of ethanol solution of polyTEAMPS/Ag (w/w=100/6) nanocomposite.

PolyTEAMPS molecules absorb on the surface of the silver nanoparticles through the formation of a coordination bond between silver and oxygen atoms of the amide carbonyl group, C=O. The polyelectrolyte/silver nanocomposite was stable enough to use as a humidity-sensitive membrane. No cracks developed in the film since the humid membrane adheres tightly to the electrode and alumina substrate. As the amount of silver carbamate solution was increased, the content of silver nanoparticles in the nanocomposites was also increased.

There is a lot of evidence that shows the prepared materials are polyTEAMPS/silver nanocomposite. The UV-vis spectrum for the sample solution heated to 130 °C shows only one absorption peak at around 412 nm corresponding to a peculiar characteristic of the silver surface plasmon, as shown in Figure 2. Transmission electron microscopy (TEM) image shows that the silver nanoparticles have a spear-like structure with a diameter of about 5-20 nm, and are well dispersed in the solid polyelectrolyte, as shown in Figure 3. The XRD pattern shows three peaks positioned at 2θ equal to 38.00, 44.38, 64.54, 77.54 and 81.56°, as shown in Figure 4. They are indexed to the {111}, {200}, {220}, {311} and {222}. The XRD pattern matched with the literature reported values of pure silver.[27,28] Electron dispersive X-ray (EDX) analysis of individual particles was carried out to determine the composition of the particles, by focusing the electron beam on the particles. EDX analysis showed the atomic percentage of silver equivalent to 99.1%.

Humidity-Sensing Properties. Complex impedance measurements were carried out in the frequency range from 100 Hz to 100 MHz. Assuming an equivalent circuit of a parallel combination of resistance and capacitance, we determined R_p values from the intercept of the real axis in a Cole-Cole plot for devices at various measurement system (from 30 to 95%RH at 25 °C). The dependence of impedance on relative humidity is shown in Figure 5. The average

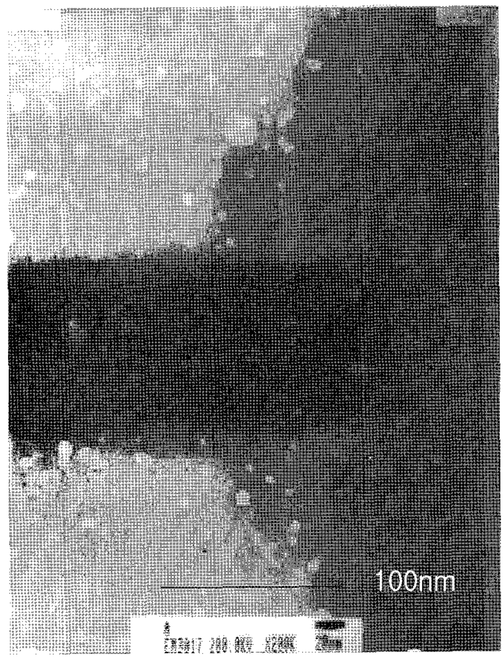


Figure 3. TEM micrograph of the humidity-sensitive membrane obtained from polyTEAMPS/Ag nanocomposite (w/w=100/4).

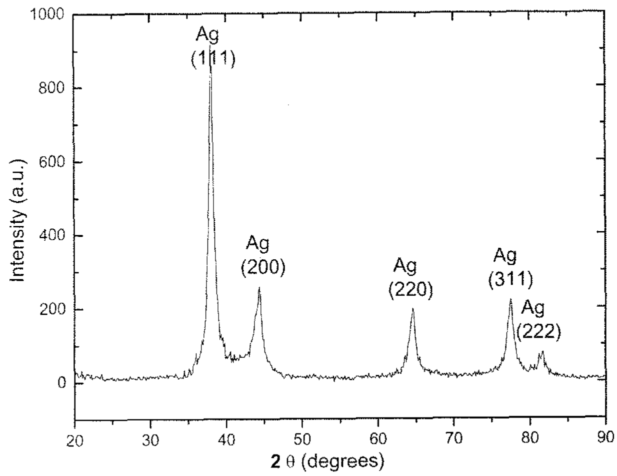


Figure 4. X-ray powder diffraction pattern of silver nanoparticles dispersed in polyTEAMPS.

impedances at 30, 60 and 95%RH were 292, 8.83 and 0.86 $k\Omega$ polyTEAMPS/Ag (w/w=100/0), while the corresponding values for the polyTEAMPS/Ag (w/w=100/6) system were 5,327, 140 and 0.93 $k\Omega$, respectively. The absorption of water vapor resulted in the swelling of the film and mobility of the ammonium ions, causing the impedance to decrease with increasing relative humidity.

It is observed that impedance of the nanocomposite film greatly increased in the lower relative humidity range and the linearity of the response curve improved. The increase in sensitivity, as seen in Figure 5, is probably due to the fact that silver nanoparticles lead to acting as islands interfering

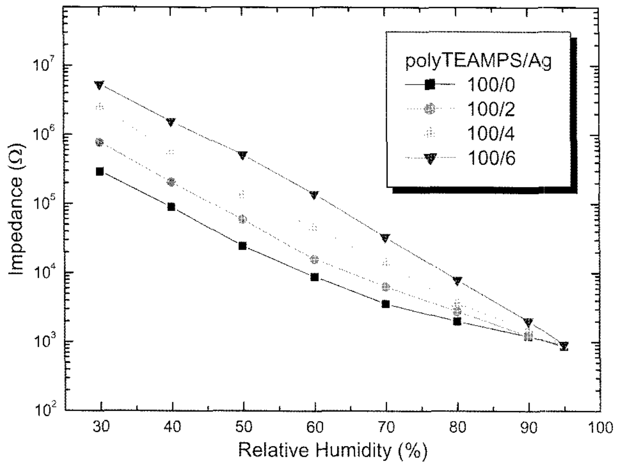


Figure 5. Dependence of impedance on the relative humidity of the humidity sensor obtained from the polyTEAMPS/Ag=(■) 100/0, (●) 100/2, (▲) 100/4 and (▼) 100/6 at 25 °C, 1 kHz and 1 V.

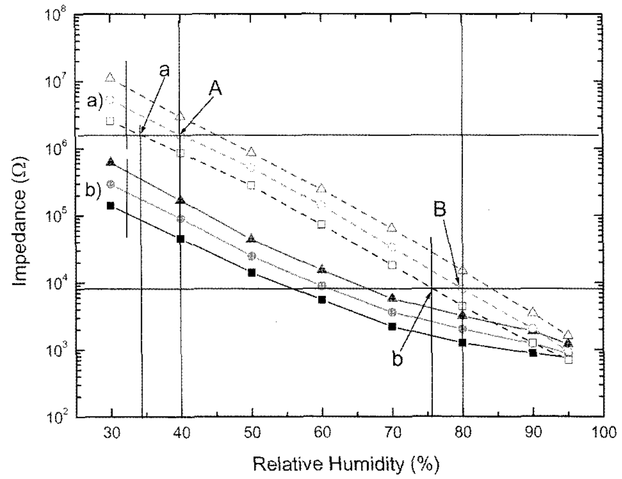


Figure 7. The impedance dependence on relative humidity of the humidity sensor obtained from polyTEAMPS/Ag (w/w=a) 100/6 and b) 100/0) at 15, 25 and 35 °C at 1 kHz and 1 V.

ion mobility in the lower humidity range. Another important point to be noted is that impedance for a film with nanoparticles is found to be convergent at around 95 %RH. Such behavior suggests that activation energy is low enough for the ion mobility to improve in the higher humidity range.

Hysteresis. Little hysteresis (-1.46%RH) was observed for the polyTEAMPS/Ag nanocomposite films, which is comparable to that of polyTEAMPS film (-3.95%RH), as illustrated in Figure 6. Desiccation process appeared at the bottom of the loop. The adsorbed water molecules had a stronger interaction with the -SO_3NEt_4 group than that of surface of silver nanoparticles. Therefore, the moisture was removed more easily from the nanocomposite film, which shortened the desiccation process and resulted in little hysteresis.

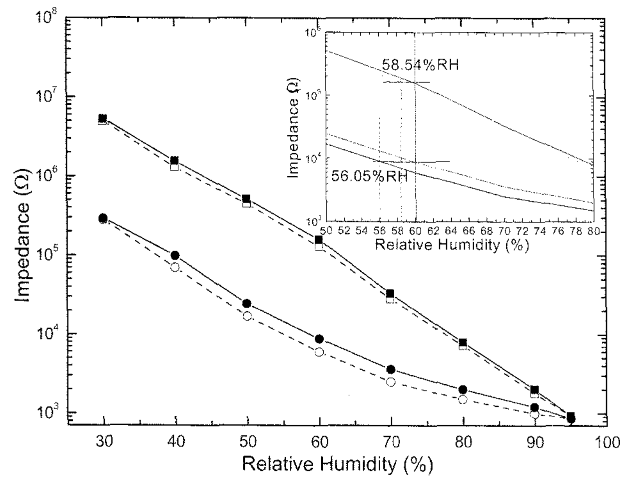


Figure 6. Hysteresis characteristics of the humidity sensor obtained from polyTEAMPS/Ag (w/w=(●) 100/0 and (■) 100/6) at 25 °C, 1 kHz and 1 V; (●, ■) humidification and (○, □) desiccation process.

Temperature Dependence. Ion transport in the polyelectrolyte strongly depended on the operating temperature. The impedance was decreased at higher temperatures, due to improvement in the mobility of the ammonium ions. Impedance of the sensor fabricated with polyelectrolyte/silver nanocomposite was also dependent on ambient temperature, with a negative coefficient, as shown in Figure 7. The temperature-dependent coefficient between 15 and 35 °C was about -0.54~-0.46%RH/°C, therefore, compensation of temperature is considered to be necessary for the application as a humidity sensor. The dependence of the humidity change upon temperature can be calculated from the following equation in the humidity range of 30-95%RH.

$$\%RH/^{\circ}C = [\%RH(a) - \%RH(A)]/10^{\circ}C \text{ or } [\%RH(b) - \%RH(B)]/10^{\circ}C$$

Activation Energy. Activation energy was determined in order to understand the role of adsorbed water in the transport of charges between pure polyelectrolyte and nanocomposite films. The impedance of the sensor followed the Arrhenius equation, with straight line plots for the semi-log of impedance against $1/T$. It was observed that the slopes of these straight lines increased as the relative humidity decreased. From the slopes of the Arrhenius plot of the impedance, the activation energy, E_a, was calculated according to the formula $R_p=R_o\mathrm{Exp}(E_a/kT)$ in the range of 30-95%RH. In the case of the sensor obtained from polyTEAMPS, the activation energy decreases monotonously from 0.52 to 0.19 eV. The relationship between the activation energy and the amount of silver particles is shown in Figure 8. It was known that ion conductivity is affected by the content of dispersed nanoparticles. At 30%RH, appreciable differences in activation energy were observed between the polyTEAMPS and the polyTEAMPS/Ag nano-

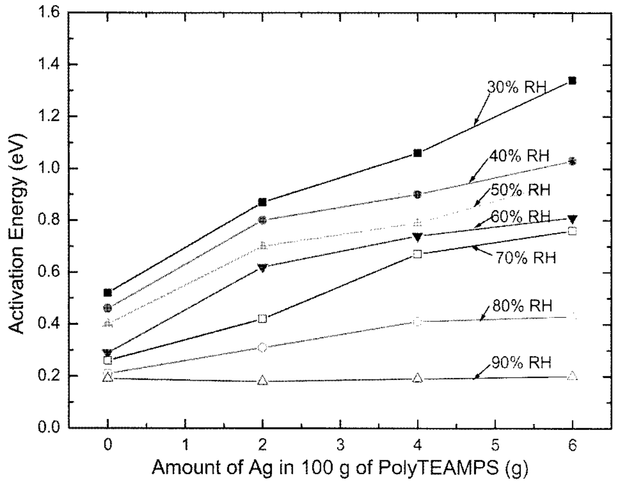


Figure 8. Activation energy change of the humidity sensors obtained from various polyelectrolyte/silver composites.

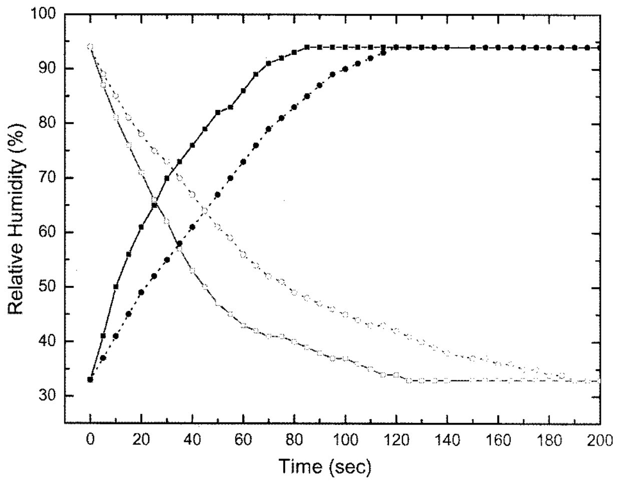


Figure 9. Response time of the humidity sensor obtained from (■, □) polyTEAMPS/Ag (w/w=50/3) and (●, ○) 50/0) polyTEAMPS between humidification and desiccation process at 25 °C.

composites films.The differences in activation energy the conductivity reflect that conduction mechanisms in the polyTEAMPS/Ag and polyTEAMPS films can be distinguished.

Response and Recovery Time. Figure 9 shows the response and recovery time of the humidity sensor, in which the relative humidity is plotted against time in seconds. For the polyelectrolyte film only, most of the trapped water was released or absorbed on the ammonium salt of polyelectrolyte and hence the absorbed water strongly reacted with ionic salts, resulting in a long response time. The response time (humidification process) of the devices obtained with silver composite films is less than 85 s in the case of an abrupt change of humidity from 33 to 94%RH, whereas the recovery time is 125 s, which is slower by 40 s than that of response time.

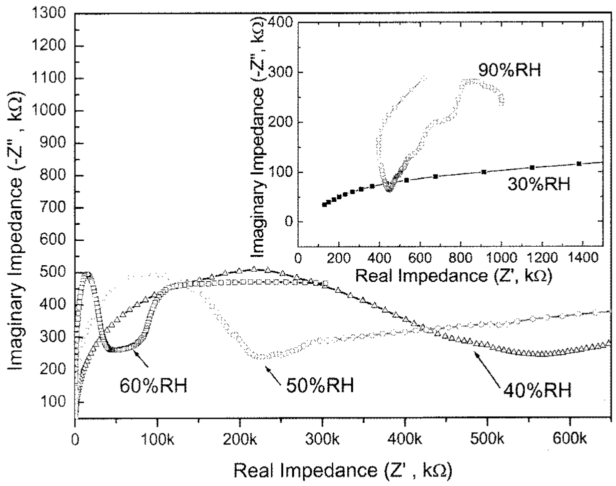


Figure 10. The complex impedance spectra of polyTEAMPS/Ag (w/w=50/3) at various humidity at 25 °C.

Complex Impedance. The typical complex impedance spectra of the composite film at different humidities are shown in Figure 10. At low humidity (30-70%RH), semicircle due to film impedance was observed. The larger radius of the semicircle at lower humidity was observed. With increase of humidity (80-95%RH), the polyTEAMPS/Ag composite film absorbed more water molecule so that small resistance was observed and the semicircle was invisible. These results suggested that the electrical conduction occurs essentially by the different mechanism for the polyTEAMPS/Ag composite between low and high humidity; that is, the transport process of counter ion plays a predominant role for the electrical conduction at high humidity.

Conclusions

New polyelectrolyte/silver nanocomposites were prepared *in situ* through heat treatment of a silver isopropylcarbamate complex in the presence of polyTEAMPS and adopted for use in the humidity-sensitive membrane. The humidity sensor obtained from polyTEAMPS/silver (w/w=100/6) nanocomposite film had an impedance varying from 5327 to 0.93 kΩ in the humidity range of 30-95%RH. Nano silver dispersion techniques are very efficient in improving humidity-sensitive characteristics and this type of humidity sensor is very sensitive and considered to be applicable as a common humidity sensor.

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