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Humidity-sensitive properties of a cross-linked polyelectrolyte prepared from mutually reactive copolymers

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Two mutually reactive three component copolymers were synthesized to utilize as humidity-sensitive membranes. The major ingredient of a humid membrane is the cross-linked polyelectrolyte obtained from the copolymers 4-vinylpyridine (VP)–(methacryloxyethyl)trimethylammonium chloride (METAC)–*n*-butyl acrylate (BA) = 1 : 2 : 1, 2 : 2 : 1, 2 : 3 : 1 and 3 : 2 : 1, and 2-chloroethyl acrylate (CEA)–METAC–BA = 1 : 2 : 1, 2 : 2 : 1, 2 : 3 : 1 and 3 : 2 : 1. The humidity sensor prepared from the reaction of VP–METAC–BA = 3 : 2 : 1 with CEA–METAC–BA = 3 : 2 : 1 showed average impedance of 620, 41.9 and 3.38 kΩ at 30, 60 and 90% relative humidity humidity (RH), respectively. Temperature dependence, frequency dependence and response time were measured. The variation of humidity on temperature between 5 and 35 °C was −0.62 to −0.67% RH $^\circ C^{-1}$ and the hygrometric hysteresis between humidification and desiccation processes were less than ±2% RH. The humidity sensors using polyelectrolyte cross-linked were quite resistant to water.

Introduction

Several kinds of polymeric films with different chemical structures have been used as sensing materials for humidity sensors. The principal ingredient of the polymeric humidity-sensitive membrane is the polyelectrolyte.[1] The linear polyelectrolytes are soluble in water and homopolymers of polyelctrolyte show reliability and long-term stability because of the high solubility in water. In order to solve these problems, several methods have been proposed to modify the hydrophilic polymers.

The cross-linking,[2–5] copolymerization,[6–11] interpenetrating polymer network (IPN) system[12] and anchoring of humid membrane to electrode,[13] have been tried to modify these polyelectrolytes to be insoluble in water in order to construct a reliable humidity sensor. Recently, we have developed a new method to overcome this shortcoming using the cross-linking of epoxy function[14] or simultaneous cross-linking of reactive copolymer with dihalide cross-linker film.[15–16] Two mutually reactive copolymers were simultaneously cross-linked to form a cross-linked humidity-sensitive membrane.[17]

In this study, a new type of ammonium salt-containing cross-linked polyelectrolyte humidity-sensitive films derived from two mutually reactive copolymers were prepared as the humidity sensor, and coated onto the tooth-comb electrode. The impedance characteristics of the film were examined and evaluated as a function of the relative humidity.

Experimental

Chemicals and instrument

4-Vinylpyridine (VP), *n*-butyl acrylate and 2-chloroethyl acrylate (CEA) were purified by passing through an inhibitor removal column (Aldrich Chem. Co.). (Methacryloxyethyl)-trimethylammonium chloride (METAC) was purified after evaporation of water. 2-Methoxyethanol was dried over calcium hydride and purified by distillation. Dimethyl sulfoxide (DMSO) was purified by vacuum distillation after drying by azeotropic distillation with benzene using a Dean–Stark separator.

The humidity and temperature controller (Tabai Espec Model PL-2G, −40 – 150 °C, 20 – 95% RH) was used for the measurement of relative humidity at constant temperature. The impedance was measured with an LCR meter (Model EDC-1635) and an impedance analyzer (HP 4192A). Tooth-comb gold electrode (width: 0.15 mm; thickness of electrode: 8 – 10 μm) was silkscreen printed on the alumina substrate (10 mm × 5.08 mm × 0.635 mm). A soldering pad of lead wire and overcoat were formed using silver–palladium alloy and glass paste, respectively. The surface resistance of the gold electrode was found to be less than 0.04 Ω.

Preparation of copolymers of 4-vinylpyridine, (methacryloxyethyl)trimethylammonium chloride and *n*-butyl acrylate

Into a glass ampoule was added a mixture of VP (1.051 g, 50 mmol), METAC (2.081 g, 10 mmol), BA (0.642 g, 5 mmol) and AIBN (0.041 g, 0.25 mmol) dissolved in 2-methoxyethanol (20 ml). The solution was degassed by the freeze–thaw method. The glass ampoule was sealed, and maintained at 65 °C for 24 h. The polymerized mixture was precipitated into a large amount of diethyl ether. The white precipitate was filtered and redissolved in 2-methoxyethanol, and precipitated into *n*-hexane. The solid powdery product was dried at 50 °C for 12 h under vacuum. Copolymers with different content, VP–METAC–BA = 1 : 2 : 1, 2 : 3 : 1 and 3 : 2 : 1 were prepared by a similar method to that described above.

FT-IR (KBr) 3120 (aromatic C–H), 2920 (aliphatic C–H), 1720–1740 (C=O), 1610 (aromatic C=C), 1235–1100 (C–O and C–N) cm^{-1}. ^1H NMR ($CDCl_3$) δ 7.4–7.1 (m, -*Py*), 4.1–3.6 (m, -O-$\mathit{CH_2}CH_2CH_2CH_3$ and -O-$\mathit{CH_2}CH_2N^+(CH_3)_3$), 3.2 (br, -O-$CH_2\mathit{CH_2}N^+(\mathit{CH_3})_3$), 2.6–2.3 (s, -$CH_2$-C*H*(Py)- and -$CH_2$-*CH*-COO-), 1.5–1.1 (m, -$\mathit{CH_2}$-CH(Py)-, -$\mathit{CH_2}$-C($\mathit{CH_3}$)-, -$\mathit{CH_2}$-CH-COO- and -$OCH_2\mathit{CH_2CH_2CH_3}$).

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Preparation of copolymers of 2-chloroethyl acrylate, (methacryloxyethyl)trimethylammonium chloride and *n*-butyl acrylate

A mixture of CEA (1.350 g, 10 mmol), METAC (2.081 g, 10 mmol), BA (0.642 g, 5 mmol) and AIBN (0.041 g, 0.25 mmol) dissolved in 2-methoxyethanol (20 ml) in a glass ampoule was degassed by the freeze–thaw method. The glass ampoule was sealed, and maintained at 65 °C for 24 h. The polymerized mixture was precipitated into a large amount of diethyl ether. The white precipitate was filtered and redissolved in 2-methoxyethanol, and precipitated into *n*-hexane. The solid powdery product was dried at 50 °C for 12 h under vacuum. Copolymers with different content, CEA–METAC–BA = 1 : 2 : 1, 2 : 3 : 1 and 3 : 2 : 1 were prepared by a similar method to that described above.

FT-IR (KBr) 2920 (aliphatic C–H), 1720–1740 (C=O), 1470, 1380 (alkyl, bending), 1235–1100 (C–O and C–N) cm^{-1}. ^{1}H NMR (CDCl$_3$) δ 4.1–3.6 (m, -O-CH_2CH$_2$CH$_2$CH$_3$, -O-CH_2CH_2Cl and -O-CH_2CH$_2$N$^+$(CH$_3$)$_3$), 3.2 (br, -O-CH$_2$-CH_2N$^+$(CH_3)$_3$), 2.6–2.3 (s, -CH$_2$-CH-COO-), 1.5–1.1 (m, -CH_2-C(CH_3)-, -CH_2-CH-COO- and -OCH$_2$$CH_2CH_2CH_3$).

Fabrication of humid membrane

The precursor solution of VP–METAC–BA = 2 : 2 : 1 (2.0 g) dissolved in DMSO (8.0 g) and CEA–METAC–BA = 2 : 2 : 1 (2.0 g) dissolved in DMSO (8.0 g) were mixed immediately. The mixture was adsorbed onto the gold–alumina electrode by the dip-coating method. After the sensor chips were heated to induce the cross-linking reaction at 25 °C for 2 h and 80 °C for 5 h, the temperature was raised to 120 °C for an hour. The samples were further reacted with 0.1 M benzyl chloride in ethanol for 6 h at 60 °C. The sensor chips were finally rinsed in ethanol and dried under vacuum at 50 °C for 12 h.

Other humidity sensors with different contents of copolymers were prepared by similar procedures to that described above.

Measurement of impedance characteristics

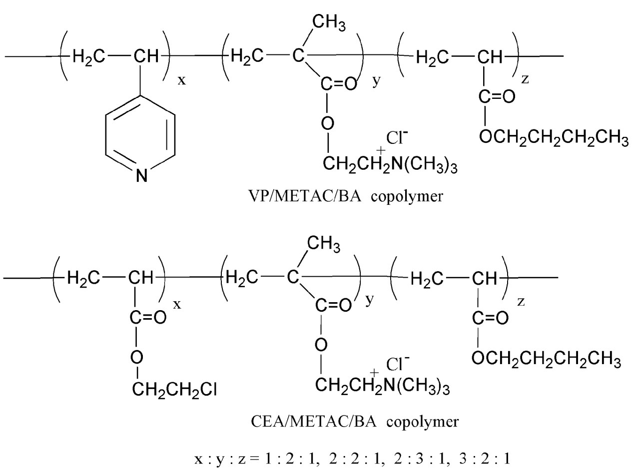
Impedance *versus* relative humidity characteristics of the sensor were measured for an humidification process from 20% RH to 95% RH, and for a desiccation process from 95% RH to 20% RH, at 1 V, 1 kHz and 25 °C. The temperature dependence was measured at temperatures of between 5 °C and 35 °C at 1 V and 1 kHz. Frequency dependence was obtained by measuring impedances with input frequencies to 100 Hz, 1 kHz and 10 kHz at 1 V and 25 °C. Response time was determined over a saturated salt solution of KNO$_3$ for 94% RH and MgCl$_2$·6H$_2$O for 33% RH at its equilibrium state.

Results and discussion

Copolymers, VP–METAC–BA and CEA–METAC–BA = 1 : 2 : 1, 2 : 2 : 1, 2 : 3 : 1 and 3 : 2 : 1 were prepared by copolymerization of the corresponding monomers as shown in Scheme 1. Table 1 summarizes the results of copolymerization.

The copolymers were characterized by IR and ^{1}H NMR spectroscopies and the results were consistent with the expected chemical structures. The copolymers were hygroscopic and soluble in common organic solvents such as ethanol, 2-methoxyethanol, dimethyl sulfoxide and *N*-methylpyrrolidinone. *n*-Butyl acrylate was used to enhance the flexibility and adhesion of the humid membrane to the electrode substrate. The humidity sensitive film was composed of cross-linked polyelectrolytes prepared by the cross-linking reaction of two mutually reactive copolymers as shown in Scheme 2.

When the copolymers VP–METAC–BA and CEA–METAC–BA were reacted, the resulting cross-linked polyelectrolyte was stable enough to endure high humidity or a dew point. The cross-linking sites are the pyridyl group in the copolymer VP–METAC–BAC and the chloroethyl group in the copolymer CEA–METAC–BA. The humid membrane adhered tightly to the electrode and alumina substrate, and no cracks were observed in the film.



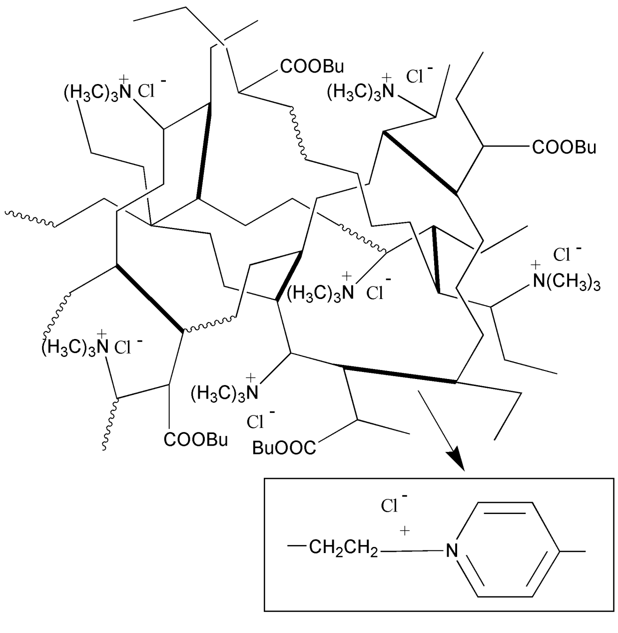
Scheme 1 Chemical structure of mutually reactive copolymers.

Table 1 Results of radical copolymerizations of VP–METAC–BA and CEA–METAC–BA with AIBN at 65 °C for 24 h

Copolymer entry no.	VP[a]	METAC[b]	CEA[c]	BA[d]	η_{inh}[e]	Yield (%)
	Mole ratio					
1	2	1	—	1	0.42	90
2	2	2	—	1	0.36	86
3	2	3	—	1	0.38	89
4	3	2	—	1	0.29	82
5	—	1	2	1	0.34	85
6	—	1	2	1	0.38	83
7	—	3	2	1	0.33	82
8	—	2	3	1	0.44	87

[a] VP, 4-vinylpyridine. [b] METAC, (methacryloxyethyl)trimethylammonium chloride. [c] CEA, 2-chloroethyl acrylate. [d] BA, *n*-butyl acrylate. [e] Inherent viscosities were measured in 2-methoxyethanol at 1 g dL^{-1} at 25 °C.

It is expected that as both the cross-linking and the density of the quaternary ammonium salt increased, the amount of



Scheme 2 Chemical structure of the cross-linked polyelectrolyte.

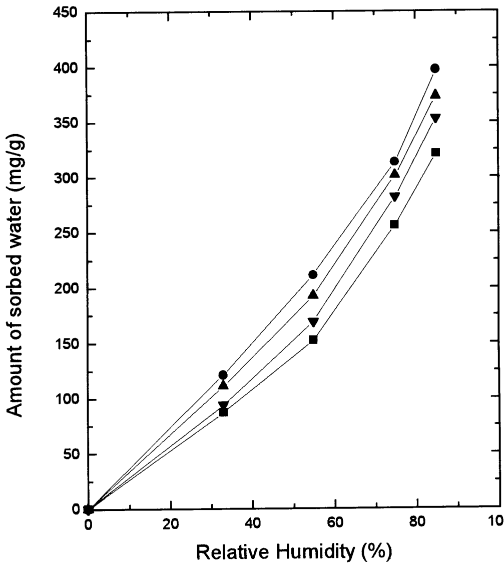


Fig. 1 Aborption isotherm curves for the cross-linked polyelectrolyte obtained from the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = (●) 2 : 3 : 1, (▲) 3 : 2 : 1, (▼) 2 : 2 : 1 and (■) 1 : 2 : 1.

absorbed water will change. An example is plotted in Fig. 1, showing that the amount of absorbed water decreases with an increase in the content of hydrophobic *n*-butyl acrylate. The sorption isotherm curves were obtained using the quartz crystal microbalance method for the samples with different compositions of cross-linked polyelectrolytes.[18,19]

The AC impedance dependence on humidity for the humidity sensors using cross-linked polyelectrolyte consisting of VP–METAC–BAC and CEA–METAC–BA over the range of 20–95% RH at 25 °C is shown in Fig. 2. The humidity sensors show a good linearity in their semi-logarithmic response curve of impedance *versus* relative humidity. The impedance increases with an increase in the content of METAC, however, it also increases with an increase of the *n*-butyl acrylate unit.[16]

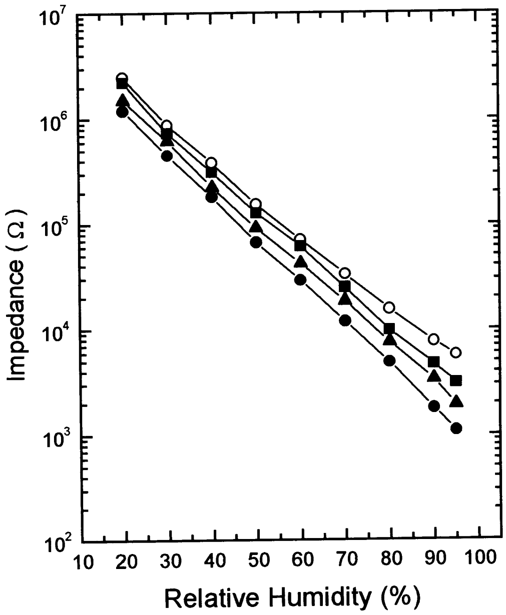


Fig. 2 Dependence of impedance on the relative humidity of the humidity sensor using the cross-linked polyelectrolyte obtained from the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = (●) 2 : 3 : 1, (▲) 3 : 2 : 1, (■) 2 : 2 : 1 and (○) 1 : 2 : 1 at 25°C, 1 kHz and 1 V.

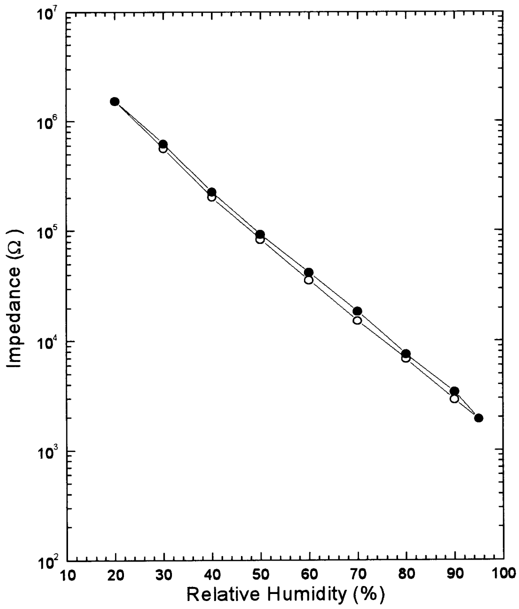


Fig. 3 Dependence of impedance on the relative humidity sensor using the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = 3 : 2 : 1; (○) humidification process and (●) desiccation process at 25 °C, 1 kHz and 1 V.

In the case of VP–METAC–BAC and CEA–METAC–BA = 3 : 2 : 1, the average impedance at 30, 60 and 90% RH are 620, 41.9 and 3.38 kΩ, respectively.

Since the humidity sensitive membranes were coated on several sensor chips at the same time by dipping, their resistance characteristics are similar. The accuracy of the response curve is better than ±2% RH. Notably, the impedance is very sensitive to the humidity by over three orders of magnitude between 20 and 95% RH.

The hysteresis between the humidification and desiccation processes was measured in the range of 20–95% RH. The two plots display the range of ±2.0% RH in Fig. 3. The impedance on desiccation is slightly lower than that on humidification and the corresponding hysteresis falls within −2% RH. This fact demonstrates that the rate of humidification and desiccation during the desiccation process of the absorbed water was slower than that during the humidification process.

The impedance characteristics were affected by the thickness of the fabricated film. The impedance decreased with an increase in the concentration of the humidity-sensitive copolymer as shown in Fig. 4. However, it was generally found that the sensitivities of the humidity sensor towards factors such as hysteresis and the response time decreased with an increase in the thickness of the humid-membrane.

Impedance of the sensor was also dependent on ambient temperature with a negative coefficient. Measurement of resistance was performed at 5, 15, 25 and 35 °C as shown in Fig. 5. When the temperature increased, the impedance characteristic shifted to a lower impedance. The temperature coefficient between 5 and 35 °C was about −0.62 to −0.67% RH $^{\circ}C^{-1}$ and, therefore, it is considered to be necessary to compensate for temperature prior to its application as a humidity sensor. The impedance of the sensor follows the Arrehenius equation, with straight line plots for the semi-log of the resistance against $1/T$. It was also observed that the slopes of these straight lines increased as the relative humidity decreased.

The impedance dependence on the applied frequency was measured at frequencies of 100 Hz, 1 kHz and 10 kHz as shown in Fig. 6. The variation of impedance with the applied frequency was different over the range of relative humidity, being larger at low humidity as shown in Fig. 6. A better linearity in

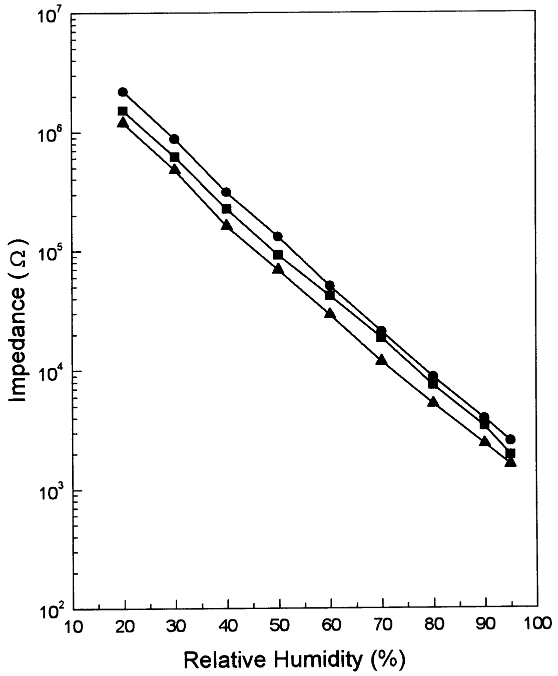


Fig. 4 Dependence of impedance on the relative humidity for the humidity sensor using the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = 3 : 2 : 1; (●) 10 wt%, (■) 13.5 wt% and (▲) 17 wt% in DMSO at 25 °C, 1 kHz and 1 V.

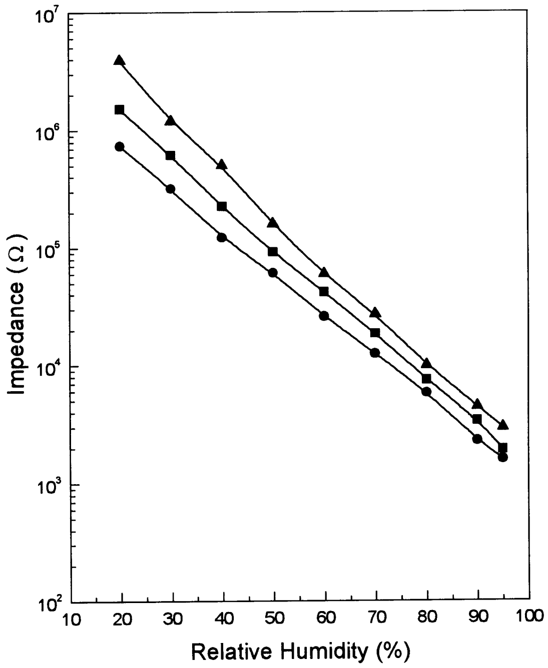


Fig. 6 The impedance dependence on the applied frequency of (▲) 100 Hz, (■) 1 kHz and (●) 10 kHz for the humidity sensor obtained from the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = 3 : 2 : 1 at 25 °C and 1 V.

the Arrehenius plot of the sensor was otained at higher frequency.

The response time is one of the significant features for the evaluating the efficacy of the humidity sensors. Constant humidity bottles were used for the measurement of response time. Fig. 7 shows a response time for the humidity sensor, in which the relative humidity is plotted against time in seconds. For 33% RH and 94% RH, a saturated solution of $MgCl_2 \cdot 6H_2O$ and KNO_3 solutions at a temperature of 25 °C were adopted, respectively. The response time between 33% RH and 94% RH was measured by transferring the humidity sensor from the chamber in equilibrium at 33% RH to the other chamber in equilibrium at 94% RH. The response time was measured to be approximately 70 seconds from 33% RH to 94% RH for the absorption process. The response time is larger in the desiccation process than in the humidification process. The response time significantly depends on the film thickness, degree of cross-linking and density of ionic species used. The most important factor governing the response time is the hydrophobicity of the ionic group.

The durability of the humidity sensor in water was tested. The sensor was immersed in water for a certain period and then dried in air. After the impedance of a dried sensor was measured, then the same sensor was immersed in water again and dried, and then the impedance was measured again. These procedures were repeated several times. The plot against total soaking time in water at 70% RH for the humidity sensor is shown in Fig. 8. The copolymers are considered to be quite durable against water because of their insolubility in water. The water durability of a copolymer was enhanced as the

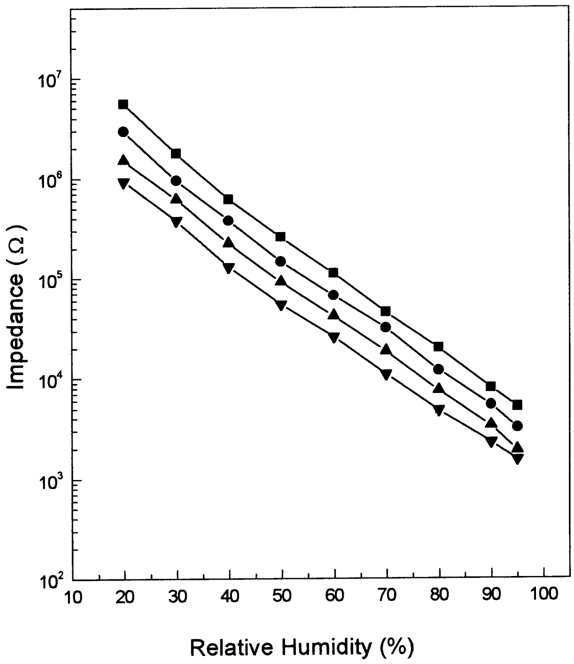


Fig. 5 The impedance dependence on relative humidity of the humidity sensor using the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = 3 : 2 : 1 at (▼) 35 °C, (▲) 25 °C, (●) 15 °C and (■) 5 °C at 1 kHz and 1 V.

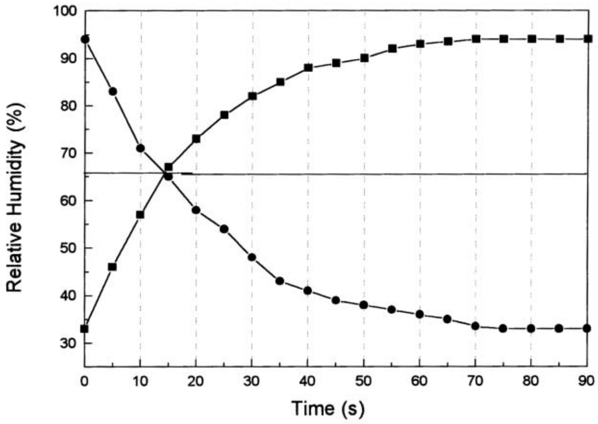


Fig. 7 Response time of the humidity sensor obtained from the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = 3 : 2 : 1; (■) humidification and (●) desiccation process at 25 °C.

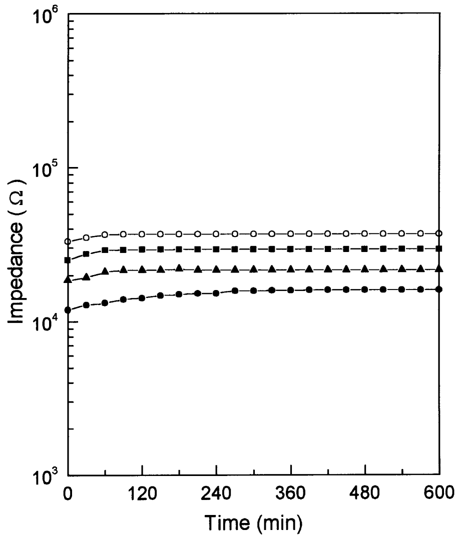


Fig. 8 Durability test at 70% RH of humidity sensor obtained from the cross-linked copolymers VP–METAC–BA and CEA–METAC–BA = (●) 2 : 3 : 1, (▲) 3 : 2 : 1, (■) 2 : 2 : 1 and (○) 2 : 1 : 1 after soaking in water at 25 °C, 1 kHz and 1 V.

cross-linking of a copolymer increased in VP–METAC–BA and CEA–METAC–BA. In the initial short period, the impedance of the cross-linked copolymer sensor increased by a factor of +0.15% RH. The impedance leveled off after further soaking in water. This initial change may be caused by the washing-away of the insufficiently cross-linked copolymer in water. Based on these results, it is found that the cross-linking techniques are very efficient to improve water durability.

Conclusion

New cross-linked polyelectrolytes consisting of cross-linked copolymers VP–METAC–BA and CEA–METAC–BA were prepared for the humidity sensor. The two copolymers were mutually reactive to form quaternary ammonium salts by cross-linking. The humid membrane adhered tightly to the electrode and alumina substrate. The impedance of copolymers decreased with an increase in the content of BA. In the case of gel polyelectrolyte with VP–METAC–BA and CEA–METAC–BA = 3 : 2 : 1, the resistance varied from 620 MΩ to 3.38 kΩ in the humidity range from 30% RH to 90% RH. The temperature coefficient between 5 and 35 °C is −0.62 to −0.67% RH °C^{-1} and the response time is 70 seconds between 33% RH and 94% RH. The cross-linking techniques improve the water durability very efficiently and this type of humidity sensor is considered to be applicable as a common humidity sensor.

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