

## Humidity Sensitivity of Hybrid Polyelectrolytes Prepared by the Sol-Gel Process

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**Abstract:** Thin-film humidity sensors were prepared using inorganic/organic hybrid polyelectrolytes, which were prepared from the sol-gel reaction of copolymers of [2-(methacryloyloxy)ethyl]dimethylpropylammonium bromide (MEPAB), *n*-butyl methacrylate (BMA), and 3-(trimethoxysilyl)propyl methacrylate (TSPM) with tetraethyl orthosilicate (TEOS). The humidity-sensitive polyelectrolytes were composed of the copolymers having the following mole ratios of MEPAB, BMA, and TSPM: 60/30/10, 55/30/15, and 50/30/20. We found that the impedance varied with the content of MEPAB or TEOS; it ranged from  $10^7$  to  $10^3\Omega$  between 20 and 95% relative humidity, which is the range required for a humidity sensor operating at ambient humidity. In addition we investigated a number of characteristics of these humidity sensors, such as their hysteresis, response time, temperature dependence, frequency dependence, water durability, and long-term stability.

**Keywords:** humidity sensor, TEOS, polyelectrolyte, organic/inorganic hybrid, cross-linking, copolymer.

### Introduction

Many kinds of methods have been used to solve the problem of resistance to high humidity atmosphere using polymeric sensing material.<sup>1-4</sup> Cross-linking and copolymerization with hydrophobic monomer have been frequently employed for the preparation of water-durable polymer membrane.<sup>5-17</sup>

Surface treatments that enable strong covalent bonding at the interface would maximize long-term hydrolytic stability. One approach to such interface bonding is through the application of sol-gel coating. This can provide inorganic functionality for bonding to the inorganic substrate and tailorable organic functionality for interaction with the subsequent polymer layer.<sup>18-21</sup> Conventional silane sol-gel chemistry relies on hydrolysis and condensation reactions occurring on the substrate during film application.<sup>22</sup> The coupling agents, such as 3-(trimethoxysilyl)propyl methacrylate, are typically difunctional molecules having both a vinyl group to react with the resins and the alkoxy groups to interact with silica or alumina.<sup>17-19</sup> Treatment with these agents could form covalent bonding, and hence improve the adhesion between incompatible inorganic surface and/or organic polymers through intra- or intermolecular reaction. We have been researching in the synthesis of a new family of organic-inorganic hybrid materials in which

the vinyl polymer chains are uniformly distributed and covalently bonded to the inorganic networks at the molecular level via the sol-gel process.<sup>22</sup>

In this article we present a new class of organic/inorganic hybrid polyelectrolytes for humidity-sensitive materials. The polyelectrolytes are derived from the sol-gel reactions of trialkoxysilyl group-containing copolymers and tetraethyl orthosilicate. The humidity-sensitive films were coated onto the comb-shaped electrode for the humidity sensor. The impedance characteristics of the film as humidity sensor were examined and evaluated as a function of the relative humidity.

### Experimental

**Materials and Sample Preparations.** 3-(Trimethoxysilyl)propyl methacrylate (TSPM), butyl methacrylate (BMA) and TEOS (Aldrich Chem. Co.) were used as received. [2-(Methacryloyloxy)ethyl]dimethyl propyl ammonium bromide (MEPAB) were prepared by the method previously reported.<sup>23</sup> 2-Methoxyethanol was purified by conventional purification methods. FT-IR spectra were obtained with a Midac Model M-1200 spectrophotometer and <sup>1</sup>H NMR spectra were recorded on a Varian Gemini-2000 spectrometer. Gel-permeation chromatography (GPC) data were obtained with a Waters HPLC using three columns ( $\mu$ -Stryragel  $10^2$ ,  $10^3$  and  $10^4$  Å) in THF and calibrated with polystyrene standards at 20 °C. The humidity and temperature

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controller (Jeio Tech Korea, Model: TM-NFM-L; 20%~95% RH) was used to measure relative humidity at constant temperature. The impedance of the sensors was measured with an LCR meter (ED-Lab Korea, Model EDC-1630, 0.1  $\Omega$ ~100 M $\Omega$ ).

A tooth-comb gold electrode (width: 0.15 mm; thickness of electrode: 8~10  $\mu$ m) was silkscreen-printed on the alumina substrate (10 mm  $\times$  5.08 mm  $\times$  0.635 mm) using a 280-mesh sieve. A soldering pad and over-coat were formed using silver-palladium alloy and glass paste, respectively. The surface impedance of the gold electrode was found to be less than 0.04  $\Omega$ . The sensor chips were rinsed in 0.1 N HCl for 3 h and washed with distilled water before use.

**Representative Preparation of Copolymers Containing Trialkoxysilyl Groups.** A mixture of the humidity sensitive monomer MEPAB (16.81 g, 90 mmol), BMA (4.27 g, 30 mmol), TSPM (2.48 g, 10 mmol) and azobisisobutyronitrile (AIBN: 0.18 g, 0.108 mmol) dissolved in anhydrous 2-methoxyethanol (80 g) were placed in a glass ampoule. The solution was degassed by freeze-thaw method. The sealed glass ampoule was heated at 60  $^{\circ}$ C and maintained for 24 h. The polymerized mixture was precipitated into a large amount of anhydrous ethyl ether. The product was purified by dissolution in dry 2-methoxyethanol followed by reprecipitation in *n*-hexane. The copolymers were dried under vacuum at 50  $^{\circ}$ C for 12 h. Other copolymers of MEPAB and BMA with TSPM were prepared by the similar to those described above.

**MEPAB/BMA/TSPM: 50/30/20.** FT-IR (KBr) 2920-2880 (aliphatic C-H), 1720-1740 (C=O), 1400-1440 (C-N<sup>+</sup>), 1100-1235 (C-O and C-N) and 1086 (Si-O)  $\text{cm}^{-1}$ . <sup>1</sup>H NMR (CDCl<sub>3</sub>) 4.1-3.6 (m, -O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, -O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub> and -O-CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 3.4 (br, -O-CH<sub>2</sub>CH<sub>2</sub>N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.5-1.0 (m, 3 -CH<sub>2</sub>-C(CH<sub>3</sub>)-, -O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OCH<sub>3</sub>)<sub>3</sub> and -O-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

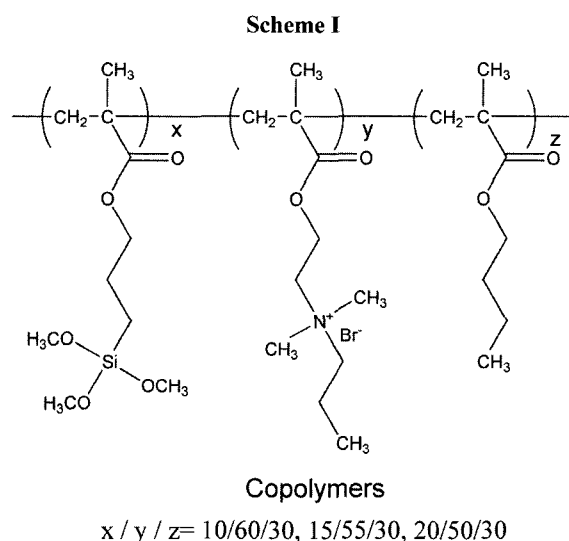
**Fabrication of Humid Membrane.** The copolymer (2.0 g), TEOS (1.0 g) and 0.1 N HCl (0.05 g) were dissolved in 2-methoxyethanol (30 g) at room temperature. The mixture was

fabricated on an alumina electrode by dip-coating method and then the sensor chips were heated to induce the cross-linking reaction at 60  $^{\circ}$ C for 2 h and 120  $^{\circ}$ C for 6 h. The sensor chips were finally rinsed with ethanol/water (90/10) at 50  $^{\circ}$ C for 5 h and dried under vacuum at 100  $^{\circ}$ C for 12 h.

**Measurements and Characterization.** Impedance *versus* relative humidity characteristics of the sensor was measured for an absorption process, at 20%RH $\rightarrow$ 95%RH, and for a desorption process, at 95%RH $\rightarrow$ 20%RH at 1 V, 1 kHz and 25  $^{\circ}$ C. The temperature dependence was measured at temperatures of 15, 25 and 35 at 1 V and 1 kHz. The frequency dependence was measured at frequencies of 100 Hz, 1 kHz and 10 kHz at 1 V and 25  $^{\circ}$ C. The response time was determined over a saturated salt solution of KNO<sub>3</sub> for 94%RH and MgCl<sub>2</sub>·6H<sub>2</sub>O for 33%RH at its equilibrium state.

## Results and Discussion

Polyelectrolyte copolymers containing trimethoxysilyl



**Table I. Components of Copolymers and Inorganic/Organic Hybrid Polyelectrolytes Derived from TEOS**

Entry No.	Mole Ratio			MW <sup>d</sup>	$\eta_{inh}^e$	Weight (g)	
	MEPAB <sup>a</sup>	BMA <sup>b</sup>	TSPM <sup>c</sup>			Copolymer	TEOS
1	60	30	10			0.2	0.1
2	60	30	10	43,200	0.45	0.2	0.2
3	60	30	10			0.2	0.3
4	55	30	15			0.2	0.1
5	55	30	15	52,480	0.48	0.2	0.2
6	55	30	15			0.2	0.3
7	50	30	20	62,000	0.53	0.2	0.1

<sup>a</sup>[2-(methacryloyloxy)ethyl]dimethyl propyl ammonium bromide. <sup>b</sup>*n*-butyl methacrylate.

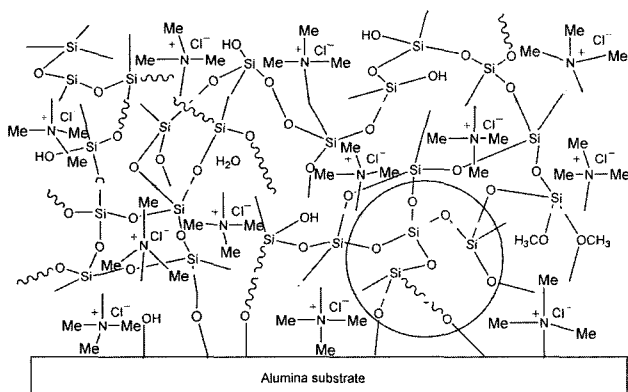
<sup>c</sup>3-trimethoxysilylpropyl methacrylate. <sup>d</sup>molecular weight. <sup>e</sup>Inherent viscosity was obtained at a concentration of 1  $\text{gdL}^{-1}$  in THF at 25  $^{\circ}$ C.

group were prepared by free radical copolymerization of MEPAB and BMA with TSPM using AIBN as an initiator in 2-methoxyethanol at 60 °C as shown in Scheme I. Table I summarizes the results of copolymerization and the components of the organic/inorganic hybrid materials.

BMA was adopted for the purpose of enhancing the flexibility of polyelectrolyte and adhesion of humid membrane to the electrode substrate. And also BMA was also used for the controlling of the humidity sensitive properties of polyelectrolyte.

To introduce strong covalent bond between organic and inorganic phases, vinyl monomers that have trialkoxysilyl groups have been widely used. Because these silane-coupling agents have three terminal alkoxy groups, those terminal groups can form covalent bonds with silanol groups on the inorganic phase in the sol-gel reaction. TSPM was adopted for not only the intermolecular or intramolecular cross-linking of polyelectrolyte but also anchoring of polyelectrolytes to the alumina substrate. The comonomer TSPM was used for both cross-linking and anchoring of the polyelectrolytes with TEOS to the alumina substrate as shown in Scheme II. The copolymer precursor could be hydrolyzed in the presence of HCl as catalyst to yield hybrid sol-gel materials. The reaction consists primarily of hydrolysis and condensation reactions of alkoxy silane precursor and TEOS as shown in Scheme II. The extent of hydrolysis that occurs before condensation is a function of the kinetic conditions, solvent and water content. As the condensation reaction proceeds, an inorganic network polyelectrolyte is produced by polysiloxane formation. The polycondensation reactions occur repeatedly until the active silanol sites have formed a high density of siloxane-bridge. When 10~20 mol% of TSPM and 50% of TEOS was used, the resulting polyelectrolyte was stable enough to endure in the water. Higher TSPM and TEOS content in the precursor should lead to greater extent of crosslinking of the polyelectrolyte chain. When the organic/inorganic precursor was fabricated on the electrode, the adhesion property to the alumina electrode was very efficient.

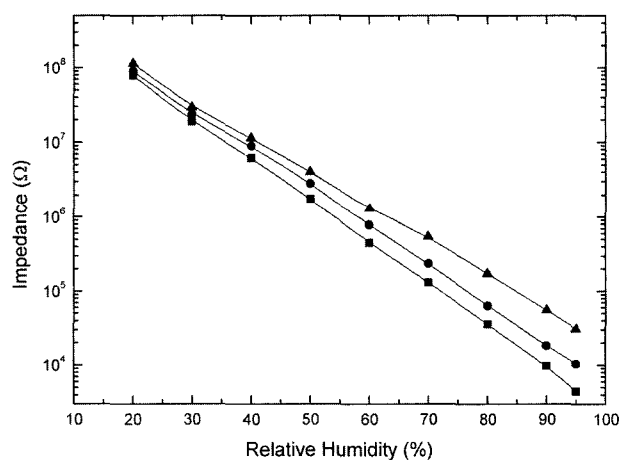
Scheme II



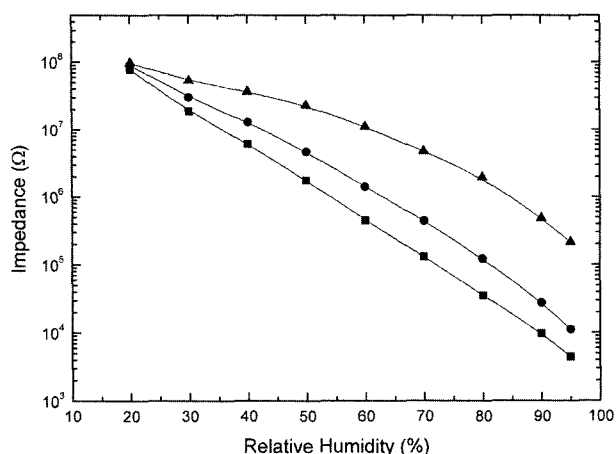
Impedance *versus* relative humidity characteristics of the sensors was measured at 1 V and 1 kHz. When the fifty sensor chips were fabricated on the gold electrode by dipping, their response characteristics were in a close agreement with each other. The accuracy of the response curve is within  $\pm 1.5\%$ RH. The typical impedance characteristic curves of the sensors obtained from the hybrid polyelectrolyte of copolymers and TEOS at 25 °C are shown in Figure 1. In the case of the hybrid polyelectrolyte of MEPAB/BMA/TSPM=60/30/10 and 50% TEOS, the average impedance at 30, 60 and 90%RH was 20.2 M $\Omega$ , 455.3 k $\Omega$  and 10.3 k $\Omega$  respectively. The impedance of the device decreased by 4 orders of magnitude from  $10^7$  to  $10^3$   $\Omega$  with the increase of humidity from 20 to 95%RH. The sensor responded with a high sensitivity over 20 up to 100%RH. The semi-logarithmic response curve had a moderate linearity over all humidity regions. The impedance of the copolymers increased gradually with an increase of the content of TMSM comonomer in the copolymer. The degree of crosslinking of the humid membrane had an effect on the ion transport by generally causing a drastic reduction in conductivity.

The impedance characteristics depended upon the amount of ionic species. The impedance of the hybrid polyelectrolytes also increased gradually with an increase of the TEOS content, as shown in Figure 2. When 50% (w/w) TEOS was added, the hybrid polyelectrolyte sensing material had a wide humidity working range, low hysteresis and satisfactory resistance to high humidity atmosphere.

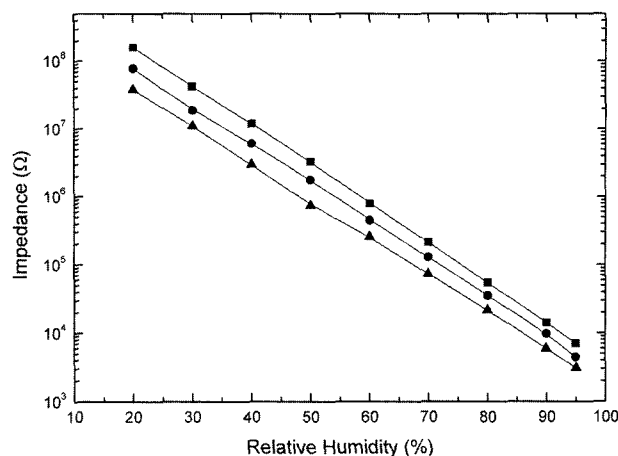
The hysteresis of humidity sensors obtained from MEPAB/BMA/TSPM= 60/30/10 (mole ratio) and TEOS for the absorption and desorption process was also measured between 20% RH and 95% RH as shown in Figure 3. The impedance on desiccation was somewhat lower than that on



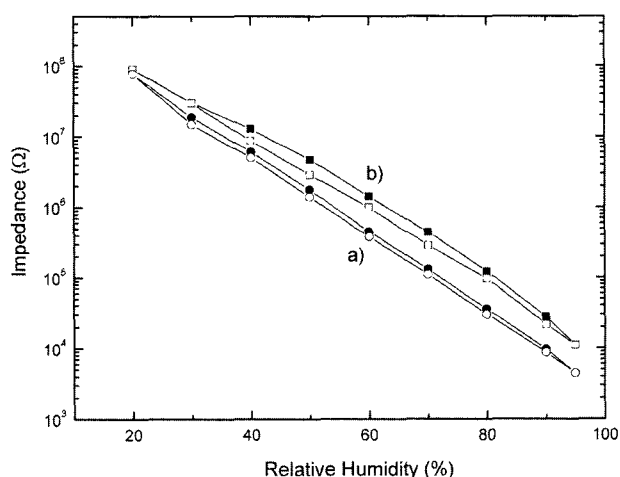
**Figure 1.** Dependence of impedance on the relative humidity for the humidity sensors using hybrid polyelectrolyte obtained from MEPAB/BMA/TSPM=(■) 60/30/10, (●) 55/30/15, and (▲) 50/30/20, and 50% colloidal silica at 25 °C, 1 kHz and 1 V.



**Figure 2.** Dependence of impedance on the relative humidity for the sensors using hybrid polyelectrolytes obtained from MEPAB/BMA/TSPM=60/30/10 and (■) 50%, (●) 100%, (▲) 150% colloidal silica at 25 °C, 1 kHz and 1 V.



**Figure 4.** The impedance dependence on the relative humidity for the humidity sensor obtained from MEPAB/BMA/TSPM=60/30/10 and 50% colloidal silica at (■) 15 °C, (●) 25 °C, and (▲) 35 °C at 1 kHz and 1 V.



**Figure 3.** Dependence of impedance on the relative humidity and hysteresis for the humidity sensors using MEPAB/BMA/TSPM=60/30/10 with 50% and 100% TEOS at 25 °C, 1 kHz and 1 V; (solid symbol) absorption and (hollow symbol) desorption.

humidification and the corresponding hysteresis fell within -2.9%RH. The inorganic/organic hybrid polyelectrolyte with higher TEOS content showed larger hysteresis, as shown in Figure 3(b). This fact demonstrates that the rate of humidification and desiccation during the desiccation process of the absorbed water was slower than that of the polyelectrolytes composed of MEPAB/BMA/TSPM=60/30/10 and 50% TEOS.

The impedance of the humidity sensors also depended on the ambient temperature with a negative coefficient. The data were plotted as the measured impedance of copolymer as a function of relative humidity at 15, 25 or 35 °C and an operating frequency of 1 kHz as shown in Figure 4. The

sensor resistance across the whole humidity range generally decreases with an increase of the ambient temperature. The sensor shows therefore consequently typical properties of a semiconductor. The ion transport in the polymer electrolyte was strongly dependent on the operating temperature. At higher temperature, the resistance was decreased because the mobility of the carrier ions was improved. The temperature dependence coefficient between 15-35 °C was -0.65% RH/°C, indicating that the temperature compensation is necessary for the application of a humidity sensor.

The temperature influence on the sensor impedance-humidity characteristics can be well compensated by integrating a NTC resistor for the application of a humidity sensor.

The electrical characteristics of the polymeric film humidity sensor were measured in AC fields, as the sensor became unstable under DC fields due to electrolysis of the polyelectrolyte. The conducting mechanism of this sensor is ionic with protons and bromide anion as the main charge carriers. The impedance of the sensor was affected by the frequency of the applied AC voltage. Figure 5 shows the frequency dependence of the impedance of the sensor at 100 Hz, 1 kHz and 10 kHz. The frequency characteristics of the sensor were also dependent on the humidity range; at low humidities the sensor impedance was more affected by the frequency.

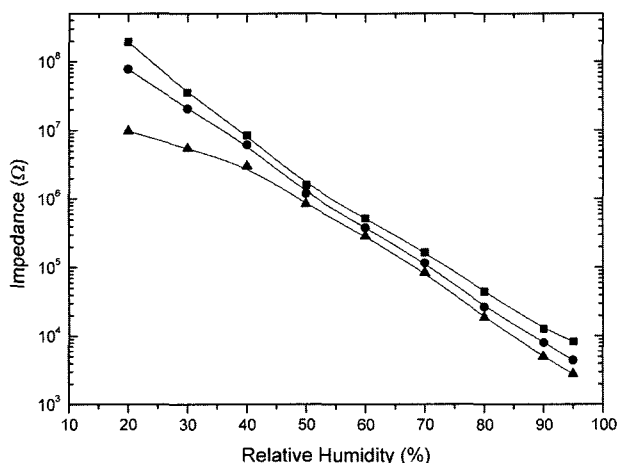
The response times of the sensor were measured when the sensor was connected with a current of 1 V at 1 kHz. This sensor was moved very quickly from a humidity level of 94%RH (when the sensor was kept in a closed bottle saturated with water vapor) to another bottle adjusted to a humidity level of 33%RH, and vice versa. Figure 6 is a graph showing the response time of the humidity sensor with relative humidity (percentage) plotted against time

(seconds). The response time from 33 to 94%RH was measured by using a specially designed humidity chamber system which employed two air conditions at 33 and 94%RH each equilibrated by using moisture-saturated bottles with a saturated solution of  $\text{KNO}_3$  and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  solution respectively at a temperature of 25 °C. A relatively long time seems to be required to absorb the water vapor. The typical response times were approximately 120 s for the absorption process and about 130 s for the desorption process.

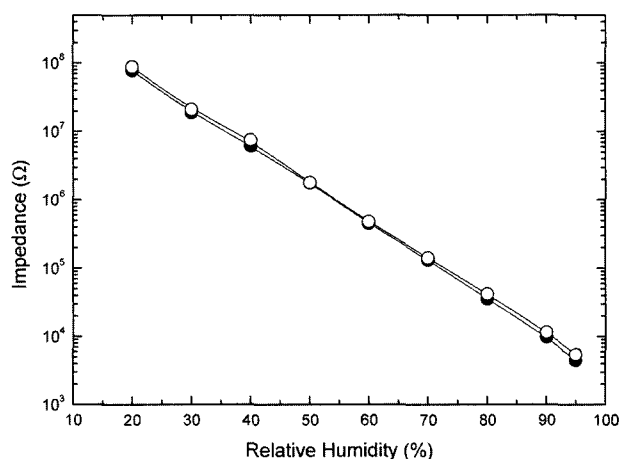
Humidity sensors should have high reliability in various environments as they are directly exposed to the atmosphere. Stability against dew is very important for humidity sensors as they are occasionally dewed during the measurement of ambient humidity. The durability of the sensors

against water was examined by immersing them into boiling water. The impedance of the sensors after immersing for 10 min showed little change in impedance as shown in Figure 7. The result indicated that the humidity-sensitive film has an excellent durability against water and dewdrops.

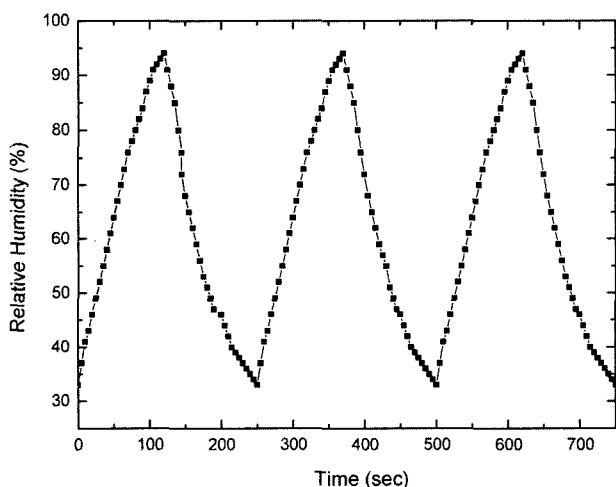
In general, humidity sensors tend to drift significantly when used at high temperature and high humidity. In order to analyze the drift of the samples, they were kept at 90%RH and 80 °C, and measured at 1 kHz at 1 V. The sensors obtained from MEPAB/BMA/TSPM=55/30/15 and TEOS appeared to be very stable over 720 h. When the device was kept at 90%RH and 80 °C, the resistances at 50 and 70%RH showed a little change, as shown in Figure 8. The variation of the humidity detection output should be within  $\pm 0.17\%$  RH against the initial value. The inorganic/



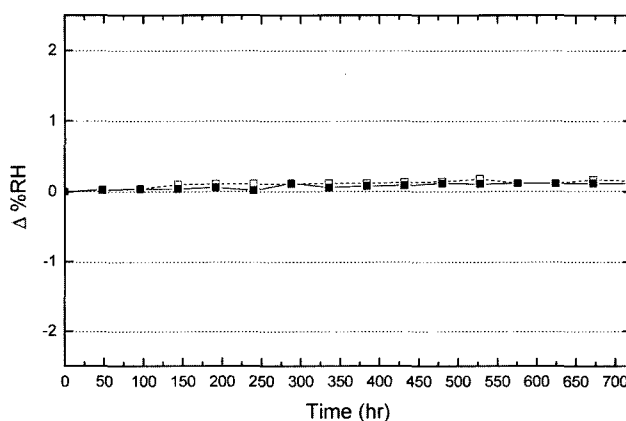
**Figure 5.** Impedance dependence on the applied frequency of (■) 100 Hz, (●) 1 kHz, and (▲) 10 kHz for the humidity sensor obtained from MEPAB/BMA/TSPM=60/30/10 and 50% colloidal silica at 25 °C and 1 V.



**Figure 7.** Durability test (measured at 70%RH) for the humidity sensor obtained from MEPAB/BMA/TSPM=60/30/10 and 50% colloidal silica; (●) before and (○) after soaking in boiling water for 10 min.



**Figure 6.** Response time for the humidity sensor obtained from MEPAB/BMA/TSPM=60/30/10 and 50% colloidal silica at 25 °C.



**Figure 8.** Long-term stability of the sensor under 90%RH at 80 °C measured at (■) 50%RH and (□) 70%RH for the humidity sensor obtained from MEPAB/BMA/TSPM=60/30/10 and 50% colloidal silica.

organic hybrid polyelectrolyte was stable when operated at high humidity and high temperature at the applied 1 kHz at 1 V.

## Conclusions

A new family of inorganic/organic hybrid polyelectrolytes, potentially useful in humidity sensitive materials, was prepared through the sol-gel reactions of trialkoxysilane-containing copolymer and TEOS. The humidity sensor demonstrated a resistance varying from 20.2 M $\Omega$  to 10.3 k $\Omega$  over the humidity range from 30 to 90%RH. The temperature coefficient between 15~35 °C was -0.65%RH/°C and the response time was 120-130 s between 33 and 94%RH. The inorganic/organic hybrid, cross-linking techniques proved to be very efficient in improving water durability and the constructed humidity sensor showed long-term stability at high temperature and high humidity. This type of humidity sensor is therefore recommended for practical applications.

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