

## Inkjet Printing of Polymeric Resistance Humidity Sensor Using UV-Curable Electrolyte Inks

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Received September 9, 2007, Revised December 20, 2007

**Abstract:** UV-curable electrolyte inks were prepared by dissolving [2-[(methacryloyloxy)ethyl]dimethyl]propylaminium bromide (MEPAB), 1,5-[bis(2-methacryloyloxyethyl)dimethyl ammonio]pentane dibromide (MDAPD), hexafunctional reactive oligomer (SP1013), trimethylolpropane triacrylate (TMPTA) and a photoinitiator in methanol/2-methoxyethanol. The compositions of the electrolyte inks were MEPAB/MDAPD/SP1013/TMPTA=6/24/17.2/12.8, 15/15/17.2/12.8 and 24/6/17.2/12.8. Humid-membranes were deposited on a gold electrode/alumina electrode using an ink-jet printer equipped with a UV lamp followed by immediate UV curing. The humidity-sensing characteristics including hysteresis, frequency and temperature dependence, response time and water durability were estimated.

**Keywords:** ink-jet printing, humidity sensor, UV-curable, reactive oligomer, electrolyte ink.

### Introduction

Polymeric resistive humidity sensors contain a polyelectrolyte, which contains a high molecular polymeric salt.<sup>1-10</sup> Such high molecular weight polyelectrolytes, which have a high viscosity, are limited to dip-coating and screen printing methods.<sup>11-15</sup> Conventional dip-coating methods produce humidity sensor samples  $\pm 5\%$  RH variations in the electrical characteristics, which are too large for measuring the humidity with precision under an ambient environment.<sup>16,17</sup> This is possibly because it is difficult to control the viscosity of high molecular weight polyelectrolytes, most of which are insoluble or are solutions that can easily cause clogging problems.

The ink-jet printing method is intrinsically compatible with flexible film electrodes, such as flexible printed circuit boards, and is expected to reduce the deflection of the characteristics of sensors. The ability of ink-jet printers to deliver a precise amount of material to a pre-determined location in a quick, reproducible manner under computer control is a desirable feature for many applications, such as the production of sensors and electronic applications.<sup>18-24</sup> There are few reports on polymeric humidity sensors by ink jet printing.<sup>25</sup> The development of the ink itself is the critical issue that needs to be addressed when extending ink-jet printing to other applications. The inks must be formulated to fit the physical and rheological requirements of fluid flow

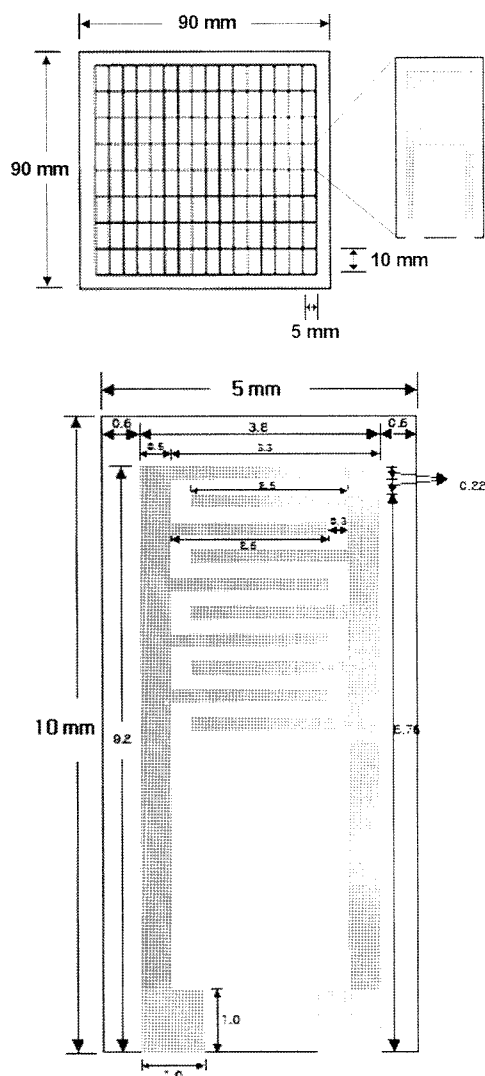
during the printing process, with viscosity being the key factor.<sup>26</sup>

This study used inkjet printing technology to deposit polymeric resistive humidity sensors on a gold electrode/alumina substrate using UV-curable electrolyte inks prepared from reactive ammonium salts-containing monomers and reactive oligomers.

### Experimental

**Materials and Measurements.** [2-[(methacryloyloxy)ethyl]dimethyl]propylaminium bromide (MEPAB) and 1,5-[bis(2-methacryloyloxyethyl)dimethyl ammonio]pentane dibromide (MDAPD) were prepared by reacting 2-(*N,N*-dimethylamino)ethyl methacrylate with propylbromide and 1,5-dibromopentane, respectively.<sup>22</sup> Pentaerythritol triacrylate dimer (SP1013) and trimethylolpropane triacrylate (TMPTA) were purchased from Miwon Co. LTD. The photoinitiator, DAROCUR 1173 (Ciba Specialty Chem. Inc.), was used as received. The leveling agent, Rad 2200N (Tego Co.), was used as received. A syringe filter was used a PTFE membrane filter (Advantec MFS, Inc, pore size 0.45  $\mu\text{m}$ ). The viscosity of the ink was measured using a Viscometer (DV-II+, Brookfield Inc.), and the surface tension was determined using a Surface Tensiomat 21 (Fisher Scientific Inc.). A flat bed inkjet printer (Hyperjet-UVF2513 Pilot, UV Plotter, Hypernics Co.) consisting of a piezoelectric head (Konica KM512 LN/LH, diameter 41  $\mu\text{m}$ , 42 pL/drop, viscosity 10 $\pm$ 0.5 cps at 20  $^{\circ}\text{C}$  and 20 $\pm$ 0.5 cps at 40  $^{\circ}\text{C}$ , surface tension

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**Figure 1.** Schematic view of electrodes.

28–34 dyn/cm) connected to a reservoir by a capillary tube was used to deposit the ink. The UV lamp (Mercury lamp, 1,000 mJ/cm<sup>2</sup>, Model Vzero 220, Integration Co.) was equipped by the printer head.

The humidity and temperature controller (Jeio-Tech Korea, TM-NFM-L; 30–90% RH) was used for the measurement of relative humidity at constant temperature. The resistance was measured with an LCR meter (EDC-1630, ED Lab. Co.).

One hundred and twenty eight tooth-comb gold electrodes (width: 0.15 mm; thickness of electrode: 8–10 μm) were silkscreen printed on the alumina substrate (10 mm × 5.08 mm × 0.635 mm) using a 280 mesh sieve as shown in Figure 1. A soldering pad and overcoat were formed using gold and glass paste, respectively. The surface resistance of the gold electrode was found to be less than 0.04 Ω using a 4-point probe measurement system.

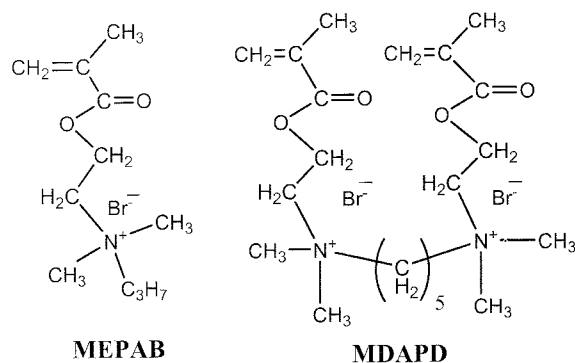
**Preparation of Photo-Curable Reactive Oligomer Ink and Fabrication of Humid Membranes.** MEPAB (6 g), MDAPD

(24 g), multifunctional oligomer (SP1013, 17.2 g), TMPTA (12.8 g) and UV-initiator DAROCURE 1173 (0.5 g) was dissolved in MeOH/2-methoxyethanol (1/3). The solution was stirred 30 °C for 12 h under nitrogen. Finally, the surfactant (D1113, 0.1 g) was added to the above solution, and the resulting solution was filtered using a syringe membrane filter. Immediately after the electrolyte solution had been printed by an ink-jet printer by double mode printing technology, the layer on the alumina gold-substrate was UV-cured at room temperature.

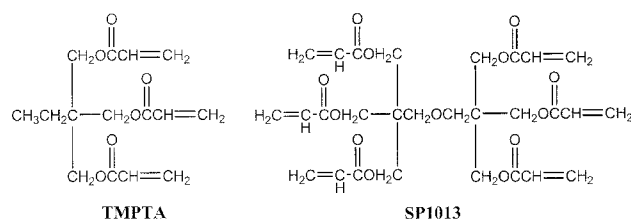
**Measurement of Resistance Characteristics.** Resistance versus relative humidity characteristics of the sensor were measured for an absorption process from 30 to 90% RH, and for a desorption process, from 90 to 30% RH at 1 V, 1 kHz and 25 °C. The measurement of the humidity detection output was performed 15 min after reaching the temperature and humidity setting. Durability of the sensors against water was examined by immersing them into water. The change of resistance of the sensors after immersion for 30 min measured as estimated.

## Results and Discussion

MEPAB and MDAPD, which contained quaternary ammonium bromide, were selected as the mono- and difunctional humidity-sensing monomers as shown in Scheme I. The hexafunctional oligomer, SP1013, and trifunctional oligomer, TMPTA, were used to control not only the degree of cross-linking of the electrolyte but also the humidity-sensing characteristics as shown in Scheme II. UV-curable reactive electrolyte inks were prepared by dissolving MEPAB,



**Scheme I**



**Scheme II**

**Table I. Components of Humidity-Sensitive Electrolyte Inks and Their Physical Properties**

Component	A	B	C	Ref.
MEPAB	24	15	6	Monofunctional Monomer
DMBAP	6	15	24	Difunctional Monomer
SP1013	17.2	17.2	17.2	Reactive Oligomer
TMPTA	12.8	12.8	12.8	Reactive Oligomer
D1173	0.2	0.2	0.2	Photo Initiator
Rad 2200N	5.0	5.0	5.0	Leveling Agent
Viscosity (cps)	18.8	17.6	17.0	-
Surface Tension (dyn/cm)	32.0	32.0	32.0	-
Conductivity (mS/cm)	3.37	3.28	4.35	-

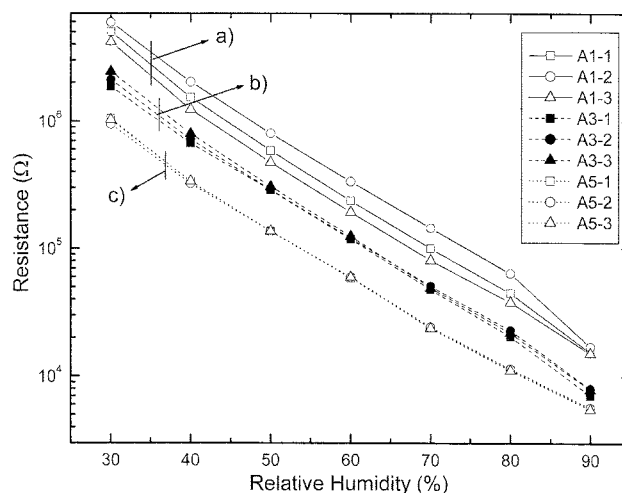
MDAPD, the multifunctional oligomers and UV initiators, as shown in Table I. The composition of the inks were MEPAB/MDAPD/SP1013/TMPTA = 6/24/17.2/12.8, 5/15/17.2/12.8 and 24/6/17.2/12.8.

The viscosity, surface tension and solvent volatility of the polyelectrolyte inks are essential parameters that govern the conditions for fabricating humid membranes. In particular, the film formation behavior can be affected by the surface of the substrate material. The surface tension of 32 dyne/cm was controlled by adding a surfactant, Rad 2200N. The experiments showed that a solution with a viscosity > 15 cps could be printed through a tiny nozzle. The UV-curable reactive electrolyte solution with a viscosity of 17-19 cps could be obtained using a mixture of methanol and 2-methoxyethanol so that it could be printed using a commercial printer without clogging the nozzle of the printer head. The mixed solution did not show any changes in viscosity even after being stored for several days at room temperature.

The films were printed 1-5 times on a comb-type gold electrode/alumina substrate using an ink-jet printer. As soon as the electrolyte ink had been printed on the substrate, the layer of UV-curable electrolyte was irradiated with UV light to produce an insoluble polyelectrolyte membrane through UV-initiated radical polymerization.

The typical resistance characteristics of the humidity sensor obtained from the UV-crosslinked polyelectrolyte were measured at 25 °C and 1 kHz. Since three humidity sensitive membranes were coated at the same time using a wide format inkjet printer equipped with a UV lamp, their resistance characteristics were in a close agreement with each other after ink-jet printing 5 times. The resistance decreased from 30 to 90%RH with increasing number of ink-jet printing steps from 1 to 5.

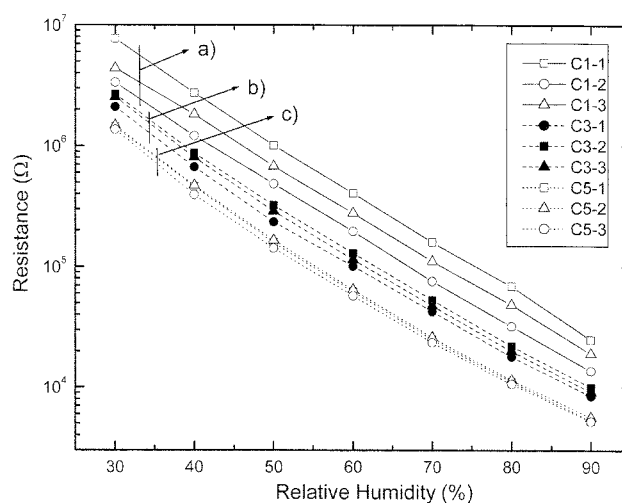
The resistance characteristics depend upon the film thickness because it affects the diffusion of water molecules inside the film and the absorption capacity of water in the film. The resistance versus relative humidity was measured



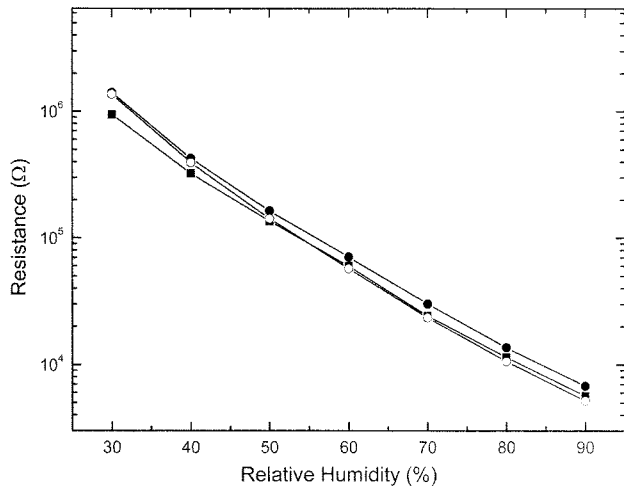
**Figure 2.** Dependence of resistance on the number of ink-jet printing using MEPAB/MDAPD/SP1013/TMPTA=6/24/17.2/12.8: (a) 1, (b) 3, and (c) 5 times.

using the humidity-sensors with different numbers of ink-jet printing steps. The higher number of ink-jet printing steps showed a lower resistance, while a lower number of ink-jet printing showed a higher resistance, as shown in Figure 2(a-c). When the solution was printed once, the thickness of the dry humidity membrane was approximately 1.8  $\mu\text{m}$ . The semi-logarithmic response curve showed moderate linearity over all humidity regions.

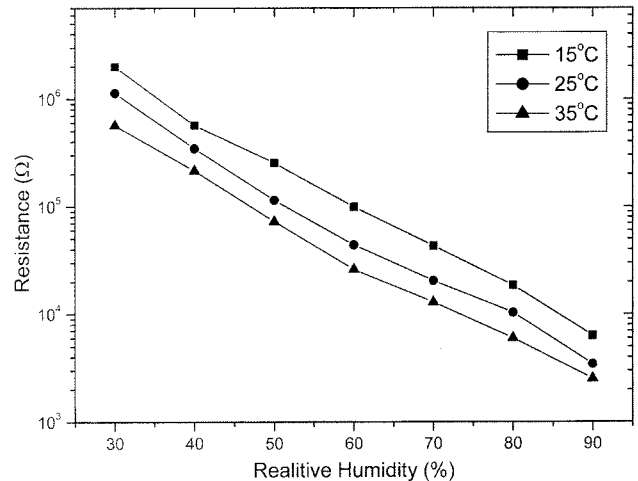
The surface of the electrode between the alumina substrate and the sintered gold electrode with a thickness 8-10  $\mu\text{m}$  was quite rough. Therefore, the thickness of the printed films showed large thickness variations in the humid membranes. The variation in the resistance of the samples



**Figure 3.** Dependence of resistance on the number of ink-jet printing using the humidity sensor obtained from photo-cured polyelectrolyte MEPAB/MDAPD/SP1013/TMPTA=24/6/17.2/12.8: (a) 1, (b) 3, and (c) 5 times.



**Figure 4.** Dependence of resistance for the humidity sensors obtained from MEPAB/MDAPD/SP1013/TMPTA=( $\blacksquare$ ) 24/6/17.2/12.8, ( $\bullet$ ) 15/15/17.2/12.8, ( $\circ$ ) 6/24/17.2/12.8 after 5 times ink-jet printing at 1 kHz and 1 V.



**Figure 6.** The resistance dependence on relative humidity of humidity sensor obtained from MEPAB/MDAPD/SP1013/TMPTA=24/6/17.2/12.8 at ( $\blacksquare$ ) 15 °C, ( $\bullet$ ) 25 °C, and ( $\blacktriangle$ ) 35 °C at 1 kHz and 1 V.

decreased with increasing number of ink-jet printing steps from 1 to 5 times, as shown in Figures 2(a)-(c) and 3(a)-(c).

In the case of the UV-crosslinked polyelectrolyte systems MEPAB/MDAPD/SP1013/TMPTA=6/24/17.2/12.8 and 24/6/17.2/12.8, the average resistance at 30, 60 and 90%RH was 945, 60 and 5.7 k $\Omega$ , and 1365, 57 and 5.2 k $\Omega$ , respectively, as shown in Figure 4.

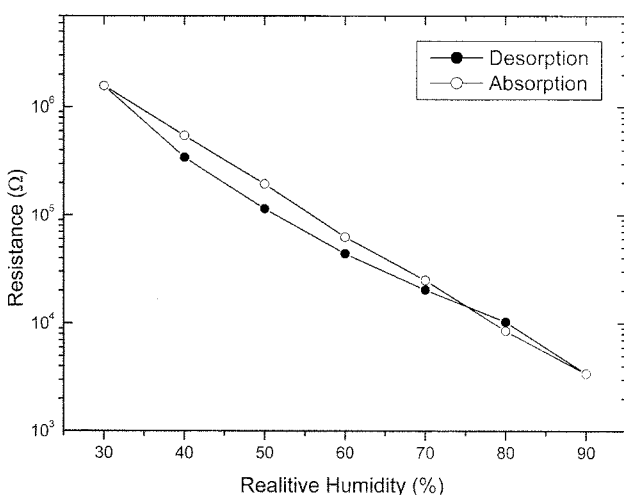
The hysteresis between the humidification and desiccation process was measured at humidity ranging from 30–90%RH. Large hysteresis was observed for the sensor using MEPAB/MDAPD/SP1013/TMPTA=6/24/17.2/12.8 electrolyte ink. At a lower relative humidity range, the desiccation process appeared at the bottom of the loop but changed to

the upper side of the loop at > 75%RH. The resistance upon desiccation was slightly lower than that upon humidification and the corresponding hysteresis was < -3%RH, as shown in Figure 5. The adsorbed water molecules have a much stronger interaction with the UV-cured polyelectrolyte membranes. Therefore, it is hard for a highly crosslinked film to remove moisture from the humidmembrane, resulting in a large hysteresis.

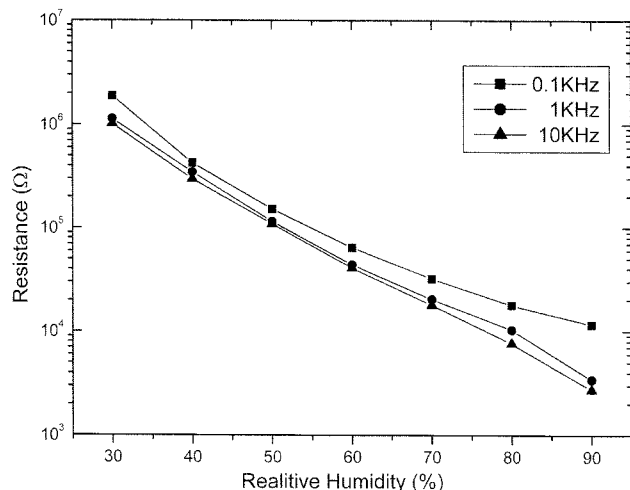
The ion transport in the polyelectrolyte depends strongly on the operating temperature. The resistance was lower at higher temperatures due to the improved mobility of the bromide ions. The resistance of the sensor was also dependent on the ambient temperature, with a negative coefficient, as shown in Figure 6.

The electrical characteristics of the polymeric film humidity sensor were measured under an a.c. field because as the sensor became unstable under a d.c. field due to the electrolysis of the polyelectrolyte. The resistance of the sensor is affected by the frequency of the applied a.c. voltage. The resistance dependence on the applied frequency was measured at frequencies ranging from 0.1 to 10 kHz, as shown in Figure 7. The sensor was estimated to be a typical polymeric resistive humidity sensor showing an increase in resistance at lower frequency.

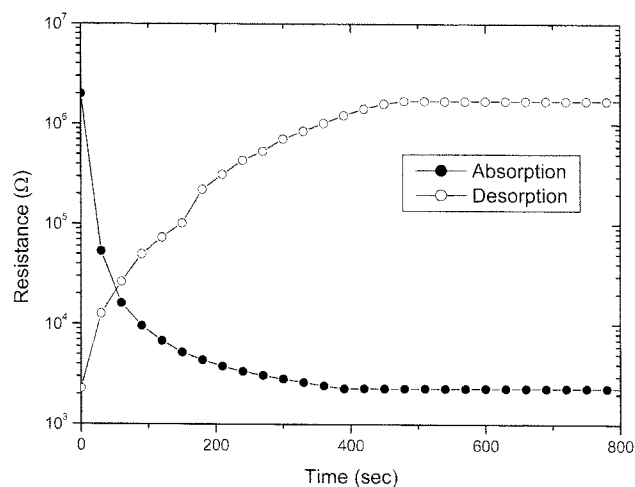
The response time is one of the most important features for estimating the performance of humidity sensors. Figure 8 shows the response time of the humidity sensor, in which the resistance is plotted against time in seconds. The response time from 33 to 94%RH was measured using a specially designed humidity chamber system. This system used moisture-saturated bottles at 33 and 94%RH. For the 33 and 94% environment, saturated KNO<sub>3</sub> and MgCl<sub>2</sub>·6H<sub>2</sub>O solutions at 25 °C were used. The response time between



**Figure 5.** Hysteresis characteristics of the humidity sensor obtained from MEPAB/MDAPD/SP1013/TMPTA=24/6/17.2/12.8 at 25 °C, 1 kHz and 1 V; ( $\circ$ ) humidification and ( $\bullet$ ) desiccation process.



**Figure 7.** The resistance dependence of the humidity sensor obtained from MEPAB/MDAPD/SP1013/TMPTA = 24/6/17.2/12.8 on the applied frequency ( $\blacksquare$ ) 0.1 kHz, ( $\bullet$ ) 1 kHz, and ( $\blacktriangle$ ) 10 kHz at 25 °C and 1 V.

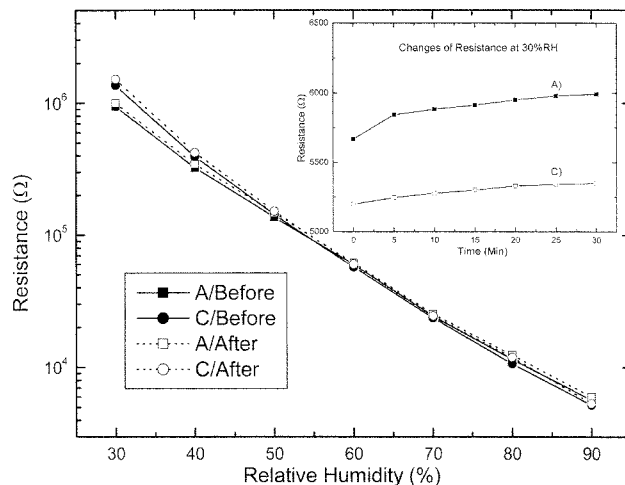


**Figure 8.** Response time of the humidity sensor obtained from the MEPAB/MDAPD/SP1013/TMPTA=24/6/17.2/12.8 polyelectrolyte at 25 °C.

33 and 94%RH was measured by transferring the humidity sensor from the chamber equilibrated at 33%RH to the other chamber in equilibrium at 94%RH. The response time of the devices was  $< 400$  sec in the case of an abrupt change in humidity from 33 to 94%RH. However, the response time was larger during the desiccation process ( $\sim 430$  sec) than in the humidification process, as shown in Figure 8.

The durability of the sensors against water was examined by immersing them in water. The resistance of the sensors after immersion for 30 min showed a detectable change in resistance, as shown in Figure 9.

A highly crosslinked humidity-sensitive membrane is believed to be durable against water because it is insoluble in water. The resistance leveled off after soaking in water at



**Figure 9.** Durability test of humidity sensor obtained from MEPAB/MDAPD/SP1013/TMPTA=24/6/17.2/12.8: ( $\blacksquare$ ,  $\bullet$ ) before and ( $\square$ ,  $\circ$ ) after soaking in water for 30 min.

the first stage. This initial change might be caused by the washing-away of the insufficiently crosslinked oligomers in water. The UV-crosslinked polyelectrolyte exhibited improved water durability. The three sensors with a different reactive monomers content showed good water durability with  $< +0.5\%$  RH variation after soaking in water 30 min.

## Conclusions

A drop-on-demand ink-jet process for fabricating the humidity-sensitive membranes on gold electrode/alumina can be performed successfully using a UV-curable electrolyte ink. Homogeneous humidity-sensitive films were formed after immediate UV-curing after ink-jet printing of an electrolyte ink on the substrate resulting in sensors with 1%RH variations in the characteristics of the sensor. From a processing point of view, the procedures described in this reported are expected to be attractive because it affords a precise sample.

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