Surface-Resistance-Type Humidity Sensor Based on Sulfonated Polyimide

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Sulfonated polyimide (SPI) was prepared from 1,4,5,8-naphthalenetetracarboxiylic dianhydride and 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid. Surface-resistance-type humidity sensors were prepared by coating the SPI solution onto comb-shaped electrodes on ceramic support plates, and their sensor properties were investigated. With increasing the relative humidity RH from 20% to 90 %, the resistance R of the SPI sensors decreased by three order in magnitude. The SPI sensors displayed excellent durability toward high temperature and high humidity and also toward water. The 90% response time was 1 min for humidification process and about 5 min for dehumidification. Hysteresis of R vs. *RH* relationship in humidification and dehumidification cycles was rather large because of slower molecular relaxation of polymer chains in the dehumidification process.
Key words: sulfonated polyimide, humidity sensor, water vapor sorption, polymer electrolyte membrane, ionic conductivity.

1. INTRODUCTION

Polymer electrolyte membranes have the strong dependency of the electrical conductivity on the water content and have been utilized as humidity sensors. Hydrophilic polymers bearing sulfonic acid salt or quaternary ammonium salt are used as the materials for electrical resistance type of humidity sensor. Their durability toward water is not high enough to be used under the severe conditions such as high temperature and/or high humidity [1]. Perfluorosulfonic acid membranes such as Nafion have excellent water stability and good performance for humidity sensor [2]. However, they can not be used high temperatures above 80 °C because of their low glass transition temperatures.

Recently, we developed novel sulfonated polyimides (SPIs) having high proton conductivity and high water-stability at relatively high temperatures, which are classified into main-chain-type and side-chain-type according to the substitution position of sulfonic acid groups [3-10]. In a previous paper, the fundamental properties of the SPI membranes for application to humidity sensor were investigated [11]. In this paper, surface-resistance-type humidity sensors are prepared using a SPI with reasonably high ionic conductivity, reasonably low water uptake and high water stability even at high temperatures and their sensor properties are investigated. The SPI used in this study is NTDA-BAPBDS derived from 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA) and 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS), of which the chemical structure is shown in Fig. 1.

Fig. 1 Chemical structure of NTDA-BAPBDS

2. EXPERIMENT

The SPI was obtained in triethylammonium salt form (Et_3NH^+) according to the literature method [5, 6, 10]. Surface-resistance-type SPI humidity sensors were prepared by coating the dilute m-cresol solution of the SPI onto comb-shaped electrodes on ceramic support plates (Fig. 2). Conventional humidity sensors made from poly(methylmethacrylate) bearing alkylammonium chloride groups were also used for comparison.

The resistance R of sensors was measured with a LCR meter (Agilent 4263B) at 1 kHz and 25 °C. The relative humidity *RH* and temperature of a measurement cell was controlled with a standard humidity generator (Shinei SRH-01).
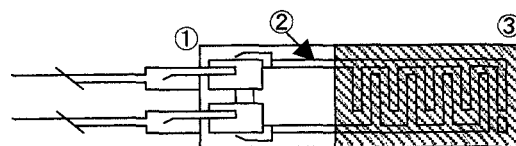
Fig. 2 Schematic diagram of humidity sensor
① ceramic support plate, ② comb-shaped electrodes,③coated polymer layer

3. RESULS AND DISCUSSION

3.1 Durability of the humidity sensors

The durability of the humidity sensors toward water was tested by measuring the R vs. *RH* relationship at 25 °C before and after immersing them in water at 25 °C. As shown in Fig. 3, after the one-time immersion for 10 h, the resistance hardly changed for the SPI sensor, but significantly increased for the conventional sensor. The aging results for the repeated immersion for a short time of 30 min are shown in Fig. 4. In the case of the conventional sensor, the resistance increased
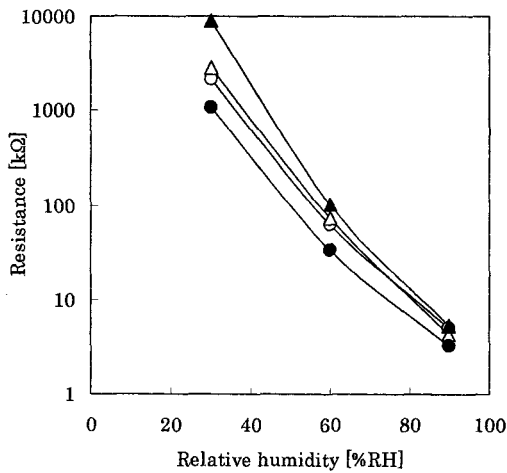
Fig. 3   Effect of immersion in water at 25 °C for 10 h on the characteristics of humidity sensors of NTDA-BSPBDS (○, △) and conventional polymer (●, ▲) at 25 °C. The circle and triangle keys refer to the data before and after the immersion, respectively.
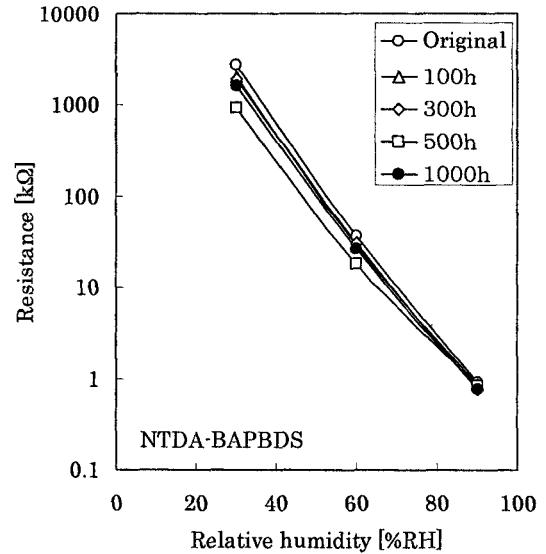

Fig. 5   Effect of exposure in dry air at 120 °C on the characteristics of humidity sensors of NTDA-BAPBDS at 25 °C.
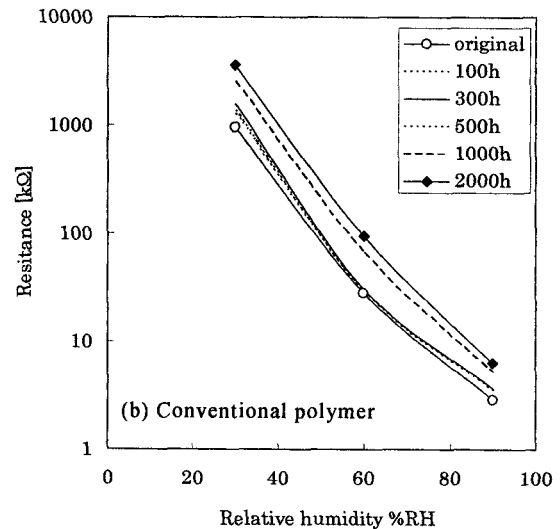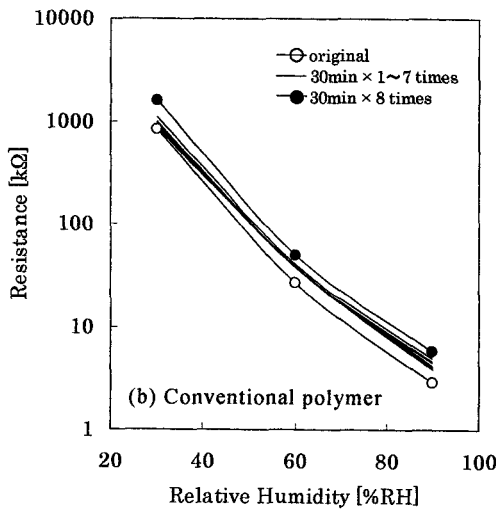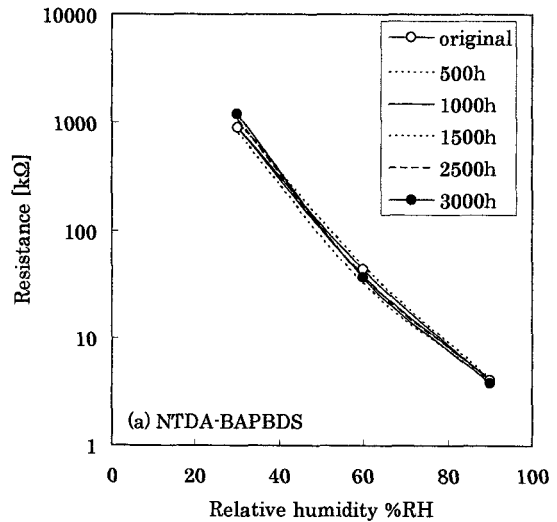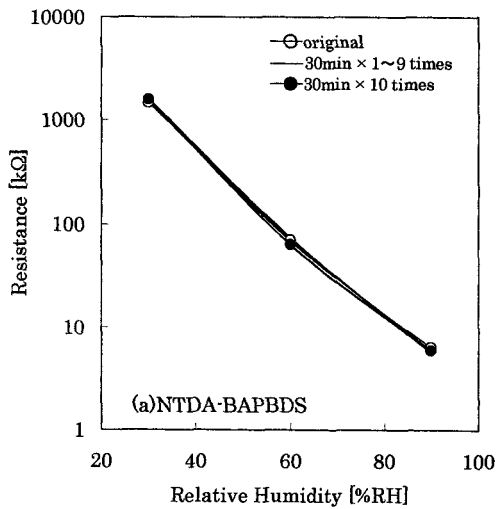

Fig. 4   Effect of ten-times repeated immersion in water at 25 °C for 30 min on the characteristics of humidity sensors of (a) NTDA-BAPBDS and (b) conventional polymer at 25 °C.

Fig. 6   Effect of aging at 65 °C and 100 %RH on the characteristics of humidity sensors of (a) NTDA-BAPBDS and (b) conventional polymer at 25 °C.

gradually with increasing immersion time and the polymer layer was peeled off after the 8-th immersion. On the other hand, the SPI sensor did not show any change in the R vs. RH relationship during the aging experiments. These results indicate the SPI sensors have excellent water durability but the conventional polymer sensors have rather poor water durability.

The durability of the humidity sensors toward hot dry air was tested by measuring the R vs. RH relationship after aging them in air at 120 °C. The conventional polymer sensors could not stand such a high temperature. As shown in Fig. 5, the SPI sensors did not show any systematic change in R during the exposure for 1000 h, although the R values measured at 30 and 60 %RH were somewhat scattered. The SPI sensors showed the fairly good heat resistance.

Figures 6 and 7 show the results of durability tests under the saturated water vapor at 65 °C and 85 °C, respectively. The conventional sensors had the durability of 500 h at 65 °C and 100 %RH. After the exposure of more than 500 h, the increases in R were observed, indicating some degradation. On the other hand, no appreciable change in the R vs. RH relationship was observed for the SPI sensors even after the exposure of 3000 h at 65 °C. In the case of the aging test at 85 °C and 100 %RH, the resistance initially decreased somewhat, but after that hardly changed. These results clearly indicate the much higher durability of the SPI sensors toward high temperature and high humidity.
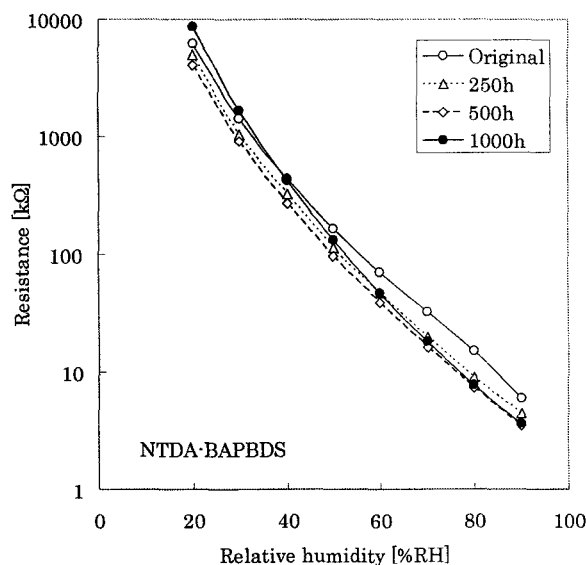

Fig. 7   Effect of aging at 85 °C and 100 %RH on the characteristics of humidity sensors of NTDA-BAPBDS at 25 °C.

3.2 Characteristics of the humidity sensors

Figure 8 shows the temperature dependence of R vs. RH relationship. With increasing RH from 30 % up to 90 %, the R decreased by about three order in magnitude. The R was much more sensitive on RH than on temperature. This behavior is suitable to humidity sensor. The sensitivity of R on RH for the SPI sensors was similar to that for the conventional ones.

Figure 9 shows response curves (change in the humidity output with elapsed time) for a stepwise change in RH between 30% and 90%. In the case of the SPI sensor, the 90% response time was about one min for the humidification process, whereas it was 5 min for the dehumidification process. The conventional polymer sensors showed the 90 % response time of about 2 min for both processes. The conventional polymer sensors had quick response against a humidity change because of the easy and quick molecular relaxation of rubbery polymer chains. On the other hand, the SPI sensors showed slower response for dehumidification process due to the slower molecular relaxation of rigid and glassy polymer chains from the more swollen state to the less swollen state.
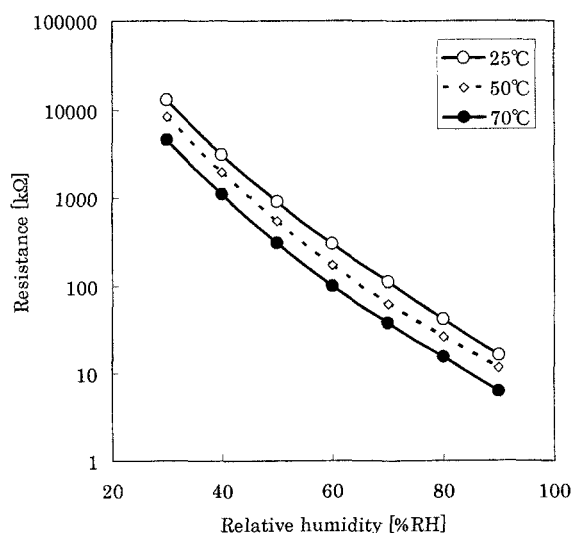

Fig. 8   Temperature dependence of R vs. RH relationship of humidity sensors of NTDA-BAPBDS.

The R was measured with increasing RH from 30% through 60 % to 90% at intervals of 15 min (humidification cycle) and then with decreasing RH in the similar manner (dehumidification cycle). The typical results are shown in Fig. 10. For the conventional polymer sensor, the R vs. RH curves in humidification and dehumidification cycles almost overlapped, that is, there was no hysterisis. On the other hand, for the SPI sensor, the R vs. RH curve in the dehumidification cycle was fairly below that in the humidification cycle, that is, a given R value leads to 10% lower RH value in the dehumidification cycle than in the humidification cycle. Thus, the SPI sensors showed a fairly large hysterisis because of the same reason mentioned above.

For the practical applications in wide fields, the 90% response time is desirable to be 2 min or less, and the hysterisis should be less than 5 %. Further study is in progress. At present, the SPI sensors have high potential of special applications where the high water durability is essentially required rather than the quick response.
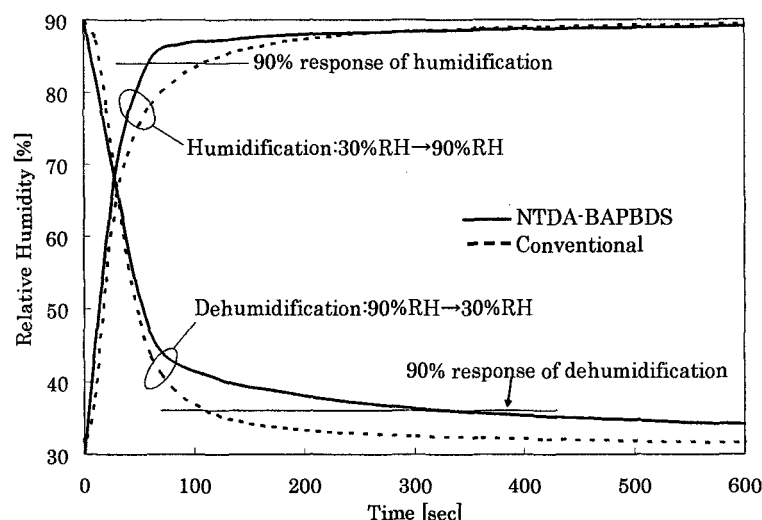
Fig. 9   Response curves with step-wise change in RH for humidity sensors of NTDA-BAPBDS and conventional polymer at 25 ℃ and at a velocity of 1.2cm/s.
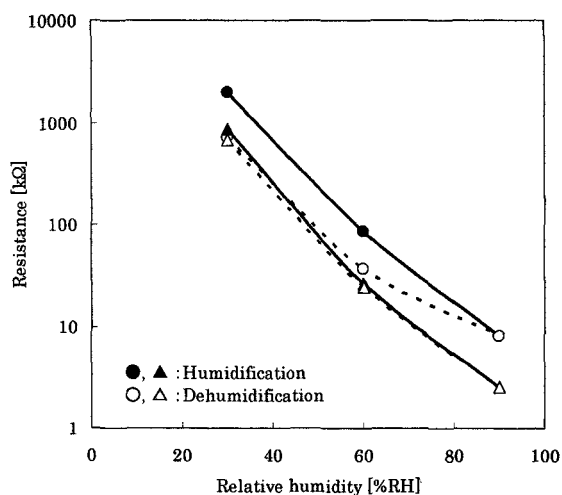

Fig.10   Effect of humidification and dehumidification cycles on R vs. RH relationship for humidity sensors of NTDA-BSPBDS (●, ○) and conventional polymer (▲, △) at 25 ℃.

4. CONCLUSIONS

The humidity sensors based on NTDA-BAPBDS displayed excellent durability toward high temperature and high humidity, for example at 85 ℃ and 100 %RH.

The R vs. RH relationship was stably reproduced after the severe aging tests. The 90 % response time was 1 min for humidification process but about 5min for the dehumidification. The SPI sensors showed fairly large hysterisis of R vs. RH relationship between humidification and dehumidification cycles, which should be reduced to a half.

5. ACKNOWLEDGEMENT

6.REFERENCES

1) Y. Sakai, M. Matsuguchi, N. Yonesato, *Electrochim. Acta*, **46**, 1509 (2001).
2) D. R. Morris and X. Sun, *J. Appl. Polym. Sci.*, **50**, 1445 (1992).
3) J. Fang, X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, and K. Okamoto, *Macromolecules*, **35**, 9022 (2002).
4) X. Guo, J. Fang, T. Watari, K. Tanaka, H. Kita, and K. Okamoto, *Macromolecules*, **35**, 6707 (2002).
5) T. Watari, J. Fang, X. Guo, K. Tanaka, H. Kita, K. Okamoto and K. Hirano, *Kagakukougaku Ronbunnshu*, **29**, 165 (2003).
6) T. Watari, J. Fang, K. Tanaka, H. Kita, K. Okamoto and T. Hirano, *J. Membr. Sci.*, **230**, 111 (2004).
7) Y. Yin, J. Fang, Y. Cui, K. Tanaka, H. Kita and K. Okamoto, *Polymer*, **44**, 4509 (2003).
8) Y. Yin, J. Fang, H. Kita and K. Okamoto, *Chem. Letters*, **32**, 328 (2003).
9) Y. Yin, J. Fang, T. Watari, K. Tanaka, H. Kita and K. Okamoto, *J. Mater. Chem.*, in press.
10) K. Okamoto, *J. Photopolymer Sci. & Technol.*, **16**, 247 (2003).
11) T. Nakayama, T. Watari, K. Tanaka, H. Kita and K. Okamoto, *Trans. Mater. Res. Soc. Jpn.*, **28**, 777 (2003).