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Application of Sulfonated Polyimides for Humidity Sensor

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Three types of sulfonated polyimides (SPIs) were prepared from 1,4,5,8-naphthalenetetracarboxiylic dianhydride (NTDA) with 2,2'-benzidinedisulfonic acid, 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid, 2,2'-bis(3-sulfopropoxy)benzidine (2,2'-BSPB). Surface-resistor type humidity sensors were prepared by coating dilute DMSO solutions of the SPIs in various cation forms on comb-shaped electrodes. Electrical conductivity, water vapor sorption isotherms and stability toward hot water of the membranes and the humidity sensor performance were investigated. With increasing the relative humidity from 30% up to 90 %, the resistance of the humidity sensors decreased by three order in magnitude. Hysteresis between humidification and dehumidification cycles was rather small for NTDA-2,2'-BSPB, but larger for the other SPIs. The 90% response time was about 1 min for the humidification process but longer for the dehumidification. The SPI humidity sensors displayed much better water durability even at high temperatures than conventional polymer one.

Key words: Sulfonated polyimide, Humidity sensor, Water vapor sorption, and polymer electrolyte membrane.

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 resistor type of humidity sensor. Their durability toward water is not high enough to be used under the severe conditions such as high temperature and high humidity. Perfluorosulfonic acid membranes such as Nafion have excellent water stability and good performance for humidity sensor [1]. However, they can not be used high temperatures above 90 ℃ because of their low glass transition temperatures.

Recently, we developed novel sulfonated polyimide (SPI) having high proton conductivity and high water-stability at high temperatures [2-6]. In this paper, the fundamental properties of the SPI membranes for application to humidity sensor are investigated.

2. EXPERIMENT

Three types of SPIs, NTDA-BDSA, NTDA-ODADS and NTDA-2,2'-BSPB, of which the chemical structures are shown in Fig. 1, were prepared according to the literature method [2, 3, 6]. These SPIs were obtained in triethylammonium salt form (Et_3NH^+) and the membranes were cast from their DMSO solutions onto glass plates and dried at 80 ℃. The as cast membranes were soaked in methanol at 60 ℃ for 1 h and then ion-exchanged into H^+, Na^+, NH_4^+ and Li^+ forms by immersing them in 1N HCl or the saturated aqueous solution (about 250 g/L) of the corresponding cation chloride. The membranes were washed with deionized water and then dried in vacuo at 150 ℃ for 20 h.

Thermogravimetry-mass spectroscopy (TG-MS) was measured with a JEOL MS-TG/DTA 220 in helium at a heating rate of 5 ℃/min.

Water vapor sorption and desorption measurements were carried by means of volumetric method using a vapor sorption apparatus (Nihon Bell, BEL-18SP). Water uptake (WU) was calculated from

$$WU = (W_s - W_d)/W_d \times 100\ (\%) \qquad (1)$$

where W_d and W_s are the weights of the dry and corresponding water-swollen sheets, respectively.

Ion conductivity was measured by an ac impedance method over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [2,3].

Surface-type humidity sensors were prepared by coating the dilute polyimide DMSO solution onto comb-shaped electrodes on ceramic support plates (Fig. 2). The membrane thickness of the sensors was about 1 μm. The resistance of the sensors was measured with a LCR meter (Agilent 4263B) at 1 kHz. The humidity and

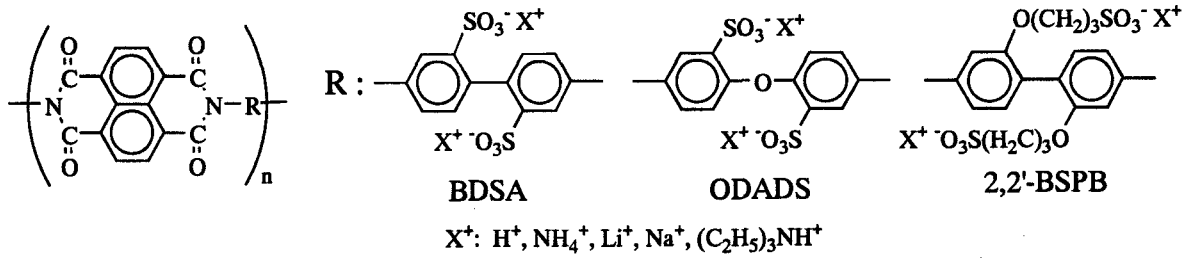

Fig. 1 Chemical structures of NTDA-based SPIs

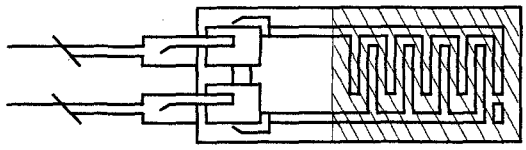

Fig. 2 Schematic diagram of humidity sensor with comb-shaped electrodes

temperature of the measurement cell was controlled with a standard humidity generator (Shinei SRH-01).

3. RESULS AND DISCUSSION

3.1 Fundamental properties

Thermal stability of the SPIs was investigated by TG-MS measurements. The weight loss attributed to the decomposition of sulfonic acid groups started from 250-290 ℃, indicating the SPIs had fairly good thermal

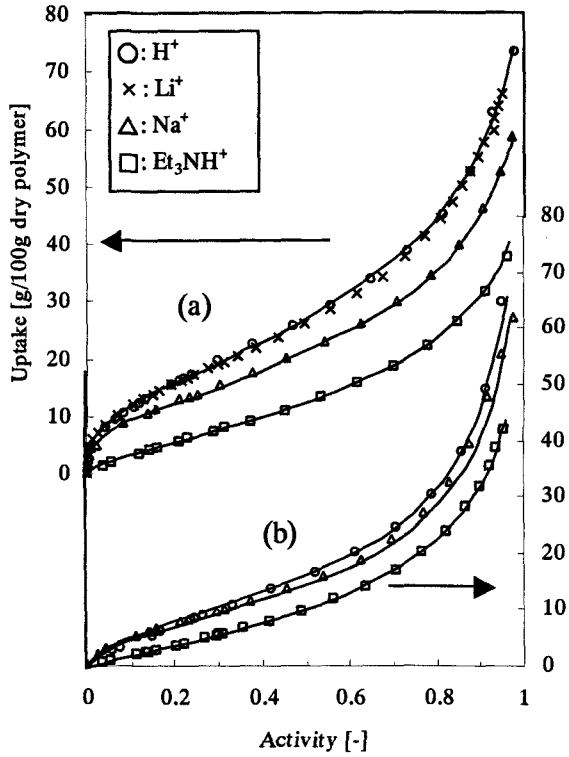

Fig. 3 Water vapour sorption isotherms of (a) NTDA-ODADS and (b) NTDA-2,2'-BSPB at 50℃

stability.

The calculated values of ion exchange capacity (IEC) of NTDA-BDSA, NTDA-ODADS and NTDA-2,2'-BSPB in H^+ form are 3.46, 3.37 and 2.89 meq/g, respectively. Water vapor sorption isotherms of NTDA-ODADS and NTDA-2,2'-BSPB in H^+ and salt forms at 50℃ are shown in Fig. 3. These sorption isotherms were measured by successive differential sorption experiments with increasing the water vapor activity a_w. All the sorption isotherms were sigmoidal and the WUs were largely dependent on the cation species, namely in the order of H^+> NH_4^+, Li^+ > Na^+ > Et_3NH^+. Both the sorption isotherms and the WUs of NTDA-BDSA and NTDA-ODADS were similar, but different from those of NTDA-2,2'-BSPB. NTDA-2,2'-BSPB showed the lower WUs than the others at the lower activities. This might be due mainly to the different morphology. Figure 4 shows the sorption isotherms obtained for the desorption experimental runs after the sorption ones. Distinct sorption-desorption hysteresis was observed. This is because the desorption process extremely slowed down with an increase in the desorption level, indicating non-Fickian diffusion behavior. The hysteresis was smaller for NTDA-2,2'-BSPB than for the others and also smaller for the Et_3NH^+form than for that of H^+ form.

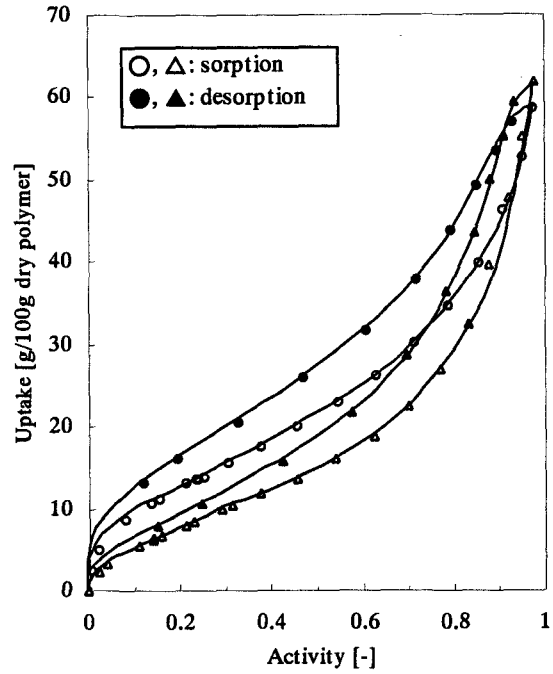

Fig. 4 Water vapour sorption isotherms obtained for sorption and desorption experimental runs of NTDA-ODADS (O, ●) and NTDA-2,2'-BSPB (△, ▲) in Na^+ form at 50℃

Figure 5 shows relative humidity dependence of conductivity for NTDA-ODADS and NTDA-2,2'-BSPB. With increasing the relative humidity (RH) from 30 to 95 %, the conductivity σ increased by about 2 orders in magnitude with a roughly linear relationship between $\ln \sigma$ and *RH*. The σ values were significantly dependent on the cation species; namely they were in the order of H^+> NH_4^+, Li^+ > Na^+ > Et_3NH^+. This was attributed to both the WU and the size of the cation. NTDA-2,2'-BSPB displayed a little larger σ values than NTDA-ODADS, in spite of the lower WU values in the lower RH range.

The temperature dependence of σ was rather small. This is suitable for the application to humidity sensor.

The membrane stability to hot water was tested by measuring variation in σ before and after the NTDA-2,2'-BSPB membranes were immersed in liquid water at 80 ℃. The σ values hardly changed after the

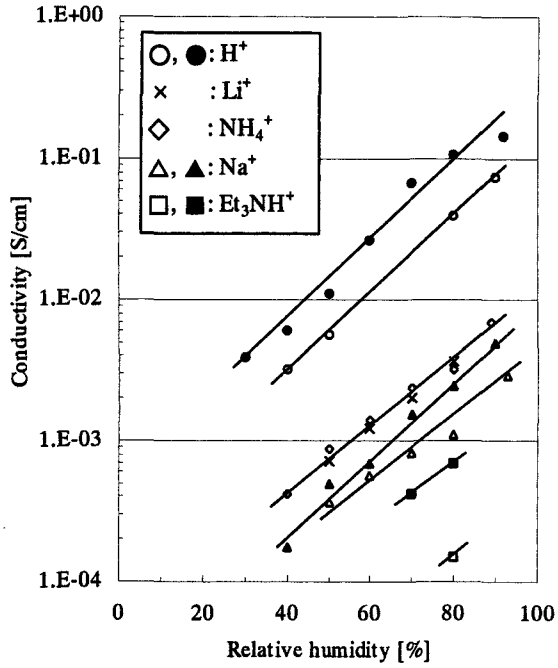

Fig. 5 Relative humidity dependence of conductivity for NTDA-ODADS (open keys, ×) and NTDA-2,2'-BSPB (closed keys) at 50°C

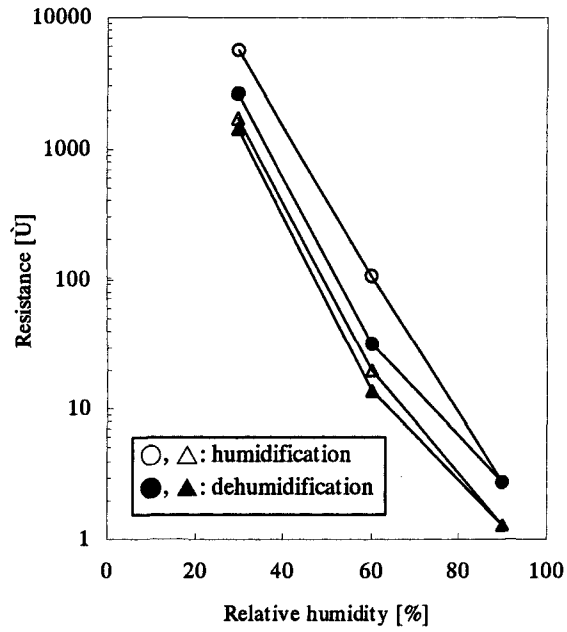

Fig. 6 Effect of humidificatin and dehumidification cycles on R vs. RH relationship for humidity sensors of NTDA-BDSA (○, ●) and NTDA-2,2'-BSPB (△, ▲) in Et_3NH^+ form at 25°C

immersion for 200 h even for the membrane in H^+ form, indicating the excellent membrane stability toward hot water.

The SPI bearing sulfonic acid groups in the flexible side chains might make it possible to form a microphase-separated structure. The small angle X-ray scattering spectrum of NTDA-2,2'-BSPB showed a small peak at 2θ = 2.4 deg, suggesting the presence of domains of 4 nm in size, whereas NTDA-ODADS did not show such a peak. Although the presence of the ion-rich domains isolated from the hydrophobic polymer backbones is not clearly confirmed, it seems probable that the ion-rich domains lead to the high proton conductivity of NTDA-2,2'-BSPB even in the low *WU* and the other characteristics different from those of NTDA-ODADS and NTDA-BDSA.

3.2 Characteristics of humidity sensor

The electric resistance R of surface-type humidity sensors 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. 6. The hysteresis between the humidification and dehumidification cycles was observed largely for NTDA-BDSA(Et_3NH^+) but only slightly for NTDA-2,2'-BSPB(Et_3NH^+). This is similar to the results in Fig. 4. It is noted that with increasing RH from 30% to 90%, the R decreased by about three orders in magnitude. Thus, the variation in R or σ was about ten times larger for the humidity sensors than for the

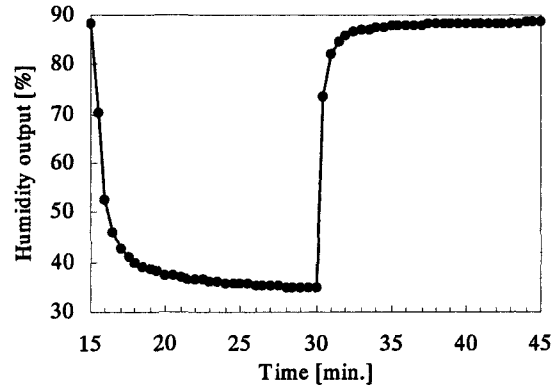

Fig. 7 Response curves for humidity sensor of NTDA-BDSA in Et_3NH^+ form at 25°C

thick membranes. This is preferable for a humidity sensor, although the reason is not clear.

Figure 7 shows response curve (change in the humidity output with elapsed time) for a stepwise change of RH between 30% and 90% for NTDA-BDSA (Et_3NH^+). The 90% response time was about three min for the dehumidification process, whereas it was one min for the humidification processes. For the practical application, the 90% response time is desirable to be 1 min or less. The response time for the dehumidification process must be shorten down to one min. This might be achieved for NTDA-2,2'-BSPB, judging from the smaller hysteresis between sorption and desorption as mentioned above.

The stability of the humidity sensors toward water was tested by measuring variations in R before and after the sensors were immersed in liquid water at room temperature for 24 h. The typical results are shown in

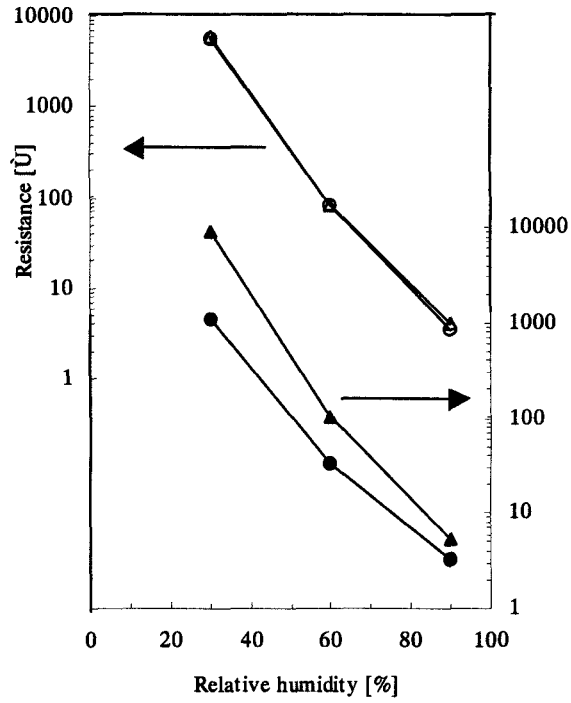

Fig. 8 Water stability of humidity sensors of NTDA-BDSA (Et_3NH^+) (○, △) and conventional polymer (●, ▲) at 25℃. (The circle and triangle keys refer to the data before and after the water immersion at room temperature for 24h respectively.)

Fig. 8 together with the result for a conventional humidity sensor made of poly(methylmethacrylate) bearing alkylammonium chloride groups. The humidity sensors of SPIs displayed very good water stability. On the other hand, the *R* values of the conventional sensor significantly increased after the immersion, indicating very poor water stability.

Judging from the high conductivity and excellent membrane stability and rather small hysteresis of sorption-desorption isotherms for NTDA-2,2'-BSPB as mentioned above, the humidity sensors made of NTDA-2,2'-BSPB in different cation species are expected to have excellent performance.

4. CONCLUSIONS

1) Sorption and desorption hysteresis of water vapor sorption isotherm and output response of humidity sensor was observed for SPIs, of which the level depended on the type of both SPI and cation species.

2) With increasing *RH* from 30% to 90 %, the conductivity of the SPI membranes and their humidity sensors increased by factors of 100 and 1000, respectively, with a roughly linear relationship between $\ln \sigma$ and *RH*.

3) The 90% response time was about 1 min for the humidification process but longer for the dehumidification one.

4) The SPI humidity sensors displayed much better water durability than a conventional polymer one.

5) NTDA-2,2'-BSPB was the most promising for humidity sensor application.

5. ACKNOWLEDGEMENT

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