Humidity Sensitive Property of Polymer Containing Viologen Moiety

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Abstract : A pair of comblike electrodes with intervals of 0.15mm are fabricated on the alumina substrate to measure the change in impedance of polymer electrolyte under ambient humidities. The silk screen printing technique was employed to form electrode, soldering pad and over-coat using Au, Ag-Pd and glass paste, respectively. The major ingredient of humid membrane is the copolymers of 1-(2-methacryloxy ethyl dimethyl ammonopropyl)-1'propyl-4,4'-bipyridinium tribromide(MEDAT) with MMA. The impedance of the copolymers varies from $1.0 \times 10^2$ to $1.0 \times 10^4 \Omega$ for the range of 30~90% RH. The copolymer of MEDAT/MMA=1/6 showed average impedance of 920, 29 and 3.3K$\Omega$ at 30, 60 and 90% RH, respectively. The temperature dependence at 10~40\degree C is $-0.5$% RH/\degree C and the hysteresis falls on the range of $\pm 3$% RH.

INTRODUCTION

Several kinds of polymer electrolytes have been used for humidity sensors.\textsuperscript{1~4} However, most of them are not sufficiently resistive to water and can not be used under high humidities for a long time. Crosslinking is one way to make a polymer electrolyte water-durable.\textsuperscript{5~6} Copolymerization of hyd-
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Aromatic monomer with hydrophobic monomer is another promising method to prepare a water-resistant humidity sensor.\textsuperscript{7-8} The preparation of poly-electrolytes with water durability and a highly humidity-dependent impedance has been extensively studied.

In this article, we designed a new type of polyelectrolyte material containing viologen moiety as a pendent group, and coated its copolymer with MMA onto the tooth-comb electrode. The impedance characteristics of the material for the application of a humidity sensor were measured and evaluated various ambient humidity.

**EXPERIMENTAL**

**Chemicals and Instrument**

All the chemicals were purchased from Aldrich Chem. Co. and used without further purification. Alumina(10.0×5.08×0.635mm, 96%) plate was used as an insulating substrate.

The adhesion strength was measured by wire peeling method using a tensile tester(Mecsin M100-ELC). The humidity and the temperature were controlled by Tabai Espec Model PL-2G (30~90% RH, -49~150°C).

The impedance of the device was measured with LCR meter(Booton Model 5110, 0.1~20MΩ). Electron microscope(SEM. Jeol-820) was used to obtain the information of the morphology and thickness of the electrode.

**Preparation of Electrode**

A conducting gold electrode of 0.15mm wide tooth-comb was fabricated on the surface of alumina(10.0×5.08×0.635mm) by silk screen printing techniques. Soldering pad of lead wire and over-coat were formed by using silver-palladium alloy and glass paste, respectively. After printing these materials onto the substrate, the electrode was dried at 125°C for 10minutes to remove the remaining solvent in the paste, followed by firing at 850°C for 10 minutes to burn out the non-volatile paste ingredient.

**Preparation of 1-Propyl-4-(4'-Pyridyl) Pyridinium Bromide**

A solution of 2.0g(12mmole) of 4,4'-bipyridyl and 1.4g(12mmole) of propyl bromide in 40ml of anhydrous acetonitrile was refluxed for 40hrs with exclusion of moisture. The resulting yellow precipitate was removed by filtration and the filtrate was evaporated. The solid product was recrystallized from anhydrous acetonitrile to give the pale yellow hygroscopic crystals in 59% yield.

Spectroscopic evidences are as follows : IR(KBr, cm\textsuperscript{-1}) : 1400~1440(C-N\textsuperscript{+}), 2830~2930(alkyl, C-H), 3030(aromatic, C-H), \textsuperscript{1}H-NMR(D\textsubscript{2}O, ppm) : δ=1.0(t, 3H, CH\textsubscript{3}), 2.1(m, 2H, -CH\textsubscript{2}-), 4.7(m, 2H, \textsubscript{N}-CH\textsubscript{2}-), 7.7~9.0(m, 8H, 2-\textsuperscript{15}N).

**Preparation of Dimethyl-(2-Methacryloxy Ethyl)-3-(Bromomethyl) Ammonium Bromide**

5.0g(0.03mole) of 2-(dimethylamino)ethyl methacrylate and 0.1g of hydroquinone was mixed with 100 ml of anhydrous acetonitrile, then 10g(0.039 mole) of 1,3-dibromo propane was added dropwise with vigorous stirring for 5hrs. The solvent was removed by evaporation. The solid residue was washed with anhydrous ether then recrystallized from acetonitrile/ether(1/1) to give hygroscopic white crystal in 78% yield.

Spectroscopic evidences are as follows : IR(KBr, cm\textsuperscript{-1}) : 1000~1200(-C-O-), 1400~1440(-C-N\textsuperscript{+}), 1600(C=C), 1700(-C=O), 2900~3000(alkyl, C-H), \textsuperscript{1}H-NMR(D\textsubscript{2}O, ppm) : δ=0.8(t, 2H, -CH\textsubscript{2}Br), 1.9(s, 3H, -C=C), 2.2(m, 2H, -C=CH\textsubscript{2}C-), 3.1(s, 6H, -N\textsuperscript{-}), 3.4(m, 4H, -CH\textsubscript{2}-N=CH\textsubscript{2}), 4.5(s, 6H, -OCH\textsubscript{2}C-), 5.9, 6.0(d, 2H, H\textsubscript{2}C=C=).
ammonium bromide in 20ml of acetonitrile was added dropwise with vigorous stirring for 5hrs. The resulting dark yellow precipitate was filtered, and washed with ether. The pale yellow solid product was obtained in 73% yield.

Spectroscopic evidences are as follows: IR(KBr, cm\(^{-1}\)) : 1000~1200(-C=O\(-\)), 1400~1440(-C-N\(^+\)), 1600(C=C), 1700(-C=O), 2880~2970(alkyl C-H), \(^1\)H-NMR(D\(_2\)O, ppm) : δ=0.9(t, 3H, CH\(_3\)C-\(-\)), CH\(_3\)
1.8(s, 3H, -C=\(-\)), 2.3(m, 4H, 2\(N\)-C-CH\(_2\)-),
CH\(_3\)
3.1(s, 6H, -N\(-\)), 3.4(t, 2H, \(+\)N\(-\)\(\text{C-CH}_2\)-), 3.7(m, CH\(_3\))
4H, \(-\text{CH}_2\)-\(+\)N\(-\)-\(\text{C-CH}_2\)-), 4.5(m, 4H, 2\(N\)-C-CH\(_2\)-),
5.8, 6.0(d, 2H, H\(_2\)N=C-\(-\)), 7.8~8.9(m, 8H, 2\(N\)-C-\(-\))

Fabrication of Thin Film Resistance Humidity Sensor

The mixed aqueous solution of monomer(MEDAT), MMA, initiator(AIBN) and DMF was coated on the electrode by injecting 5\(\mu\)l of solution with micro-syringe. MEDAT is copolymerized with MMA by radical initiated polymerization at 65°C for 2hrs. After the humidity sensitive film is fabricated and then dried in vacuum at 50°C for 5hrs.

Measurement of Response Characteristics

Impedance-versus-relative humidity characteristics of the sensor were measured for an absorption process, 30% RH\(\rightarrow\)40% RH\(\rightarrow\)50% RH\(\rightarrow\)60% RH\(\rightarrow\)70% RH\(\rightarrow\)80% RH\(\rightarrow\)90% RH, and for a desorption process, 90% RH\(\rightarrow\)80% RH\(\rightarrow\)70% RH\(\rightarrow\)60% RH\(\rightarrow\)50% RH\(\rightarrow\)40% RH\(\rightarrow\)30% RH, in their equilibrium state, respectively.

RESULTS AND DISCUSSION

A schematic view of the tooth-comb electrode is shown in Fig. 1.

The surface resistivity of gold electrode was less than 0.04Ω/\(\square\). The adhesion strength between gold electrode and alumina substrate is determined to be 10~13 lb/cm\(^2\) which is high enough for humidity sensor chip. It was also found that the final thickness was 8~13μm for gold electrode.

The humidity sensitive film was composed of copolymers of MMA and methacyrylate containing viologen as a pendant group. The ionic methacrylate monomer, 1-(2-methacryloxy ethyl dimethyl ammonopropyl)-1’-propyl-4,4’-bipyridinium tribromide(MEDAT), was prepared by quaternization reaction of 1-propyl-4-(4’-pyridyl) pyridinium bromide with dimethyl-(2-methacryloxy ethyl)-(3-bromopropyl) ammonium bromide in acetonitrile as shown in scheme 1.

The monomer, MEDAT, was very hygroscopic solid crystal and readily polymerized with radical initiator. The copolymerization of MEDAT with MMA was carried out by AIBN at 65°C on the surface of the gold electrode. All the humidity sensors derived from various composition of copolymer showed a good linearity in their semi-logarithmic response curve of impedance vs. relative humidity.
The typical impedance characteristics of the copolymers with various MMA content at 25°C, 1KHz are shown in Fig. 2(a~d). Impedance changed as the ratio of the copolymer composition varied from MEDAT/MMA=1/1 to 1/6. The impedance of copolymer increases gradually with an increase of the content of hydrophobic MMA in feed.

In the case of MEDAT/MMA=1/6, the average impedance at 30, 60 and 90% RH are 920, 29 and 3.3\(k\Omega\), respectively. This copolymer has moderate values required for the humidity sensor, although it contains low content of MEDAT. It is mainly due to the high ionic density of MEDAT unit. As the salt density of polyelectrolyte increased, the impedance decreased because of increasing the concentration of the carrier ion such as proton.

The durability of the sensor in water was tested by immersing in water for 1 minute and drying in air. A comparison of dried samples at various humidities shows that the impedance of copolymer with higher content of MEDAT gives increased values. The homopolymer of MEDAT is not durable against water because of being soluble in water. The water durability of copolymer was enhanced as the component of MMA unit in copolymer increased from MEDAT/MMA=1/1 to 1/6.

Since the humidity sensitive membrane is coated on the sensor chips by micro-syringe, their response characteristics have a close agreement with each other. The accuracy of the response curve is better than ±2% RH.

The impedance of the sensor also depends on the ambient temperature with negative coefficient. The impedance properties at 10, 25 and 40°C are shown in Fig. 3 and the temperature coefficient between 10 and 40°C is −0.5% RH/°C, therefore the compensation of temperature is necessary for the application as a humidity sensor.

**Fig. 2.** The relative humidity dependence of impedance for the copolymer of MEDAT/MMA=1/6(●), 1/4(■), 1/2(○), 1/1(□) at 25°C, 1 volt and 1 KHz.

**Fig. 3.** The impedance dependence on the temperature for the copolymer(MEDAT/MMA=1/6) at 10°C (□), 25°C(○), and 40°C(△), 1KHz and 1 volt.
Fig. 4. The impedance dependence on the applied frequency at 100 Hz (△) and 1 KHz (○) for the copolymer (MEDAT/MMA=1/6) at 25°C and 1 volt.

The impedance dependence on the applied frequency was measured at the frequency of 100Hz and 1KHz as shown in Fig. 4. The impedance change of the sensor is almost independence of the applied frequency from 100Hz to 1KHz above 30% RH. Direct-current operation of the sensor must be avoided because of degradation of polyelectrolyte by electrolysis.

The hysteresis between adsorption process (30% RH → 90% RH) and desorption process (90% RH → 30% RH) was measured between 30% RH and 90% RH, the deviation falls on the range of ±3% RH for the copolymers with various composition of MEDAT and MMA (Fig. 5).

Fig. 5. The hysteresis of impedance for the copolymer (MEDAT/MMA=1/6) between adsorption and desorption process at 25°C, 1 KHz and 1 volt.

CONCLUSION

1. A new type of polyelectrolyte humid membrane containing viologen moiety as a pendant group was synthesized for the humidity sensor.
2. The response characteristics of the copolymers of MEDAT and MMA have an accuracy of ±2% at 25°C, 1V between 30 and 90% RH.
3. The semi-logarithmic plot shows a good linearity between 30 and 90% RH.
4. The copolymer of MEDAT/MMA=1/6 shows an appreciable durability against water.

REFERENCES