

## A Humidity Sensor Using an Electrochemically Prepared Poly(1,5-Diaminonaphthalene) Film

Deong-Su Park and Yoon-Bo Shim

### Abstract

An electrochemical humidity sensor was fabricated with poly(1,5-diaminonaphthalene) film coated on a gap of two splitted gold electrodes, which were made by vacuum deposition. Response currents according to humidity were measured by the potential sweep method and chronoamperometry. The stability of the polymer film was improved by double step chronoamperometry using the applied voltage of  $\pm 0.5$  Vdc. The response time determined by the pulse technique was about  $\sim 50$  msec and the relative standard deviation of current response was within  $\pm 5.0$  %. The response current of the film was intrinsically humidity dependent. The film exhibited a non-linear but reproducible response in ordinary range of relative humidity. The linear equations were  $I(\text{nA}) = 0.28 \times \%RH - 1.01$  between 10 to 70 %RH and  $I(\text{nA}) = 6.05 \times \%RH - 403.21$  between 70 to 90 %RH.

**key words** : humidity, 1,5-diaminonaphthalene, conducting polymers

### 1. Introduction

Much attentions have been received for the development of sensors using organic and inorganic materials, which of them were made by metal oxide semiconducting materials<sup>[1,2]</sup>. Although sensors made of metal oxides are cheap and straightforward in application, they suffer from certain shortcomings against their wider applications. Some gas sensors made from metal oxides have a lack of sensitivity and high operating temperature.

To overcome these disadvantages, one can use organic semiconducting gas-sensing materials. Of these,

studying of conducting polymers have considerably increased both technological and scientific interest, especially for the gas sensors<sup>[3-5]</sup>.

Electrical properties including conductivity are regulated by chemical or electrochemical preparation with specific monomers. Furthermore, the conductivity of several doped polymers can be modified on treatment with strong acids and bases. These properties suggest that conducting polymers can be used as sensing materials for chemical sensors to detect humidity and other gases. Humidity sensors have been widely used in various electronics and process control systems. Of these, integrated polymer-humidity sensors<sup>[6-11]</sup> have some advantages compared to the conventional ones, which are expensive and need the extra electronic circuits. They provide fast response time because of a thin moisture absorption

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layer of only a few microns. In addition, they give enhanced sensor performance by the combination of sensor and signal processing circuitry on the same chip. The humidity sensors based on the change in electrical properties of materials due to the adsorption of water vapor are divided into an electrical resistance and a capacitance type sensors. Hydrophilic polymers are used for a resistance-type humidity sensor, while hydrophobic ones are preferable for a capacitance-type sensor. Since electrical conducting polymers are typically hydrophilic, they can be applied to a humidity sensor of a resistance type.

In the present study, the poly(1,5-diaminonaphthalene) (poly(1,5-DAN)) film was electrochemically coated on a gap between two separated gold electrodes and applied to an amperometric humidity sensor. In addition, the experimental parameters affecting the sensitivity of the humidity sensor were optimized.

## 2. Experimental

**Reagents and apparatus.** 1,5-Diaminonaphthalene (Aldrich Co.) was recrystallized twice in an aqueous ethanol solution under nitrogen atmosphere, then dried over  $P_2O_5$  for 48 hours under vacuum at room temperature. Water purified by a Milli-Q system (Millipore Co.) was used to prepare all aqueous solutions. An EG & G 273A potentiostat/galvanostat was used for DC and pulse voltammetric measurements. The IR spectra were obtained with FTIR spectrophotometer of Mattson Co. (Model Polaris). The standard humidity measurements were carried out with a hygrometer (SATO Thermohygrometer Model R-704) in the room and in the chamber containing various saturated-salt solutions to

regulate humidity<sup>[12]</sup>. A saturated salt solution in a sealed chamber establishes a constant RH that has only  $\pm 0.5\%$  variation at constant temperature. Relative humidity values in the chamber containing standard saturated solutions<sup>[12]</sup> were as follows: 12% ( $LiCl \cdot H_2O$ ), 33% ( $MgCl_2 \cdot 6H_2O$ ), 55% ( $Mg(NO_3)_2 \cdot 6H_2O$ ), 76% ( $NaCl$ ), 85% ( $KCl$ ), 93% ( $KNO_3$ ). Sensors were preconditioned by placing them in the chamber containing the saturated salt solutions. The measuring temperature for the standard salt solutions was  $20 \pm 0.1^\circ C$ .

**Sensor fabrication.** The microelectrochemical sensor substrate was fabricated by vacuum deposition. Fig. 1 shows cross-sectional and top view of the micro electrochemical humidity sensor. A gap width between two splitted gold electrodes was ca.  $20 \mu m$ . A gap between splitted gold electrodes was bridged with electrochemically prepared poly(1,5-DAN). A poly(1,5-diaminonaphthalene) film was grown on a gap between splitted gold electrodes by the potential cyclic in a 0.1 M HCl solution containing 0.01 M 1,5-DAN. Film-coated splitted electrodes were dried under vacuum at  $100^\circ C$  for 6 hrs, then stored in nitrogen atmosphere. The thickness of the deposited film was about  $60 \mu m$  when determined by SEM (not shown).

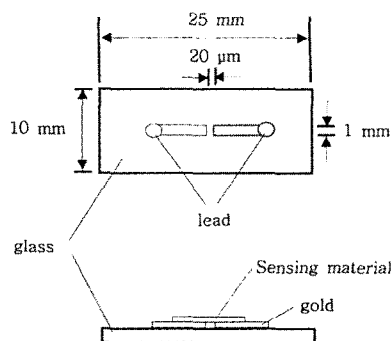


Fig. 1. Cross-sectional and top view of the micro fabricated humidity sensor.

### 3. Results and discussion

Fig. 2 shows cyclic voltammograms recorded during the growth of the poly(1,5-DAN) film on micro fabricated gold electrodes. The potential was cycled between +1.0 and -0.1 V vs. Ag/AgCl (sat'd KCl) at a scan rate of 50 mV/sec. The first scan (from 0.0 V to +1.0 V) led to the oxidation of the monomer at +0.8 V. The oxidation peak current of the monomer decreases as the cycle number increases indicating the growth of the polymer film on the electrode surface. New redox peaks appeared at +0.25/+0.31 and +0.38/+0.43 V, respectively. The peaks in the cyclic voltammogram recorded after the oxidation of monomer might correspond to the redox chemistry of diverse species generated by the oxidation of monomer, dimer, oligomer, and polymer including the generation of radical cations. Redox peaks of the polymer were well-defined and peak potentials were not changed during film growth. Two splitted gold electrodes were not bridged with poly (1,5-DAN) when growing time was below 30 min.

To confirm the structure of electrochemically synthesized poly(1,5-DAN), we obtained the FTIR spectrum of the polymer.

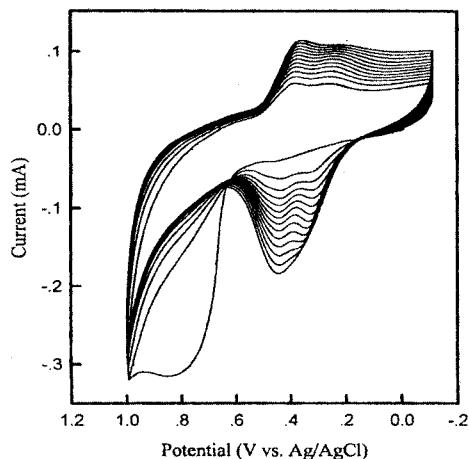


Fig. 2. Cyclic voltammograms recorded during the polymerization of poly (1,5-DAN) in a 0.1 M solution containing 0.01 M 1,5-DAN.

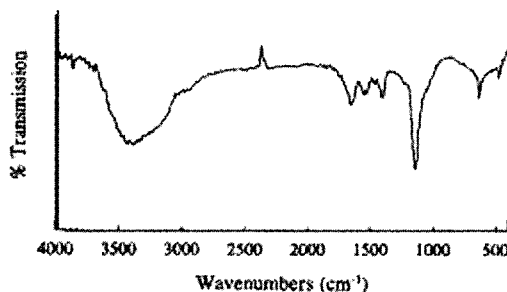


Fig. 3. The IR spectrum of electrochemically prepared poly(1,5-DAN) grown in a 0.1 M HCl solution containing  $1 \times 10^{-3}$  M monomer for 30 min.

Table 1. Wavenumbers ( $\text{cm}^{-1}$ ) of absorption bands in a FTIR spectrum of poly(1,5-DAN) grown in a 0.1 M HCl solution containing  $10 \times 10^{-3}$  M 1,5-DAN

Poly(1,5-DAN)	Assignment
3600~3100 $\text{cm}^{-1}$ (broad, strong)	N-H
3015 $\text{cm}^{-1}$ (very weak)	aromatic C-H
1646 (medium)	C=N
1632, 1624 $\text{cm}^{-1}$ (medium)	C=C
1574~1397 $\text{cm}^{-1}$ (medium)	ring vibration, N-H deformation
1339, 1285 $\text{cm}^{-1}$ (weak)	C-N
1217, 1123 $\text{cm}^{-1}$	aromatic C-H in plane
900~600 $\text{cm}^{-1}$ (very weak,weak)	aromatic C-H out-of plane bending

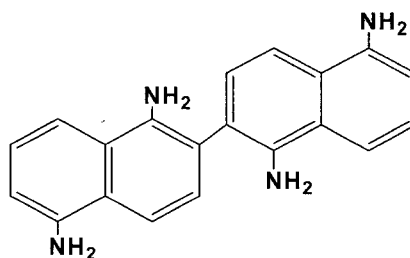


Fig. 4. Tentative structure of electrochemically synthesized poly (1,5-DAN).

Fig. 3 shows an IR spectrum and Table 1 summarized assignment of the IR spectrum of electrochemically prepared poly(1,5-DAN) grown in a 0.1 M

HCl solution containing  $1 \times 10^{-3}$  M monomer for 30 min. Although the band-broadening in IR spectra of polymer films makes it difficult to interpret the weak bands, the absorption peaks in the out-of-plane bending region (900~700  $\text{cm}^{-1}$ ) are very useful in diagnosing the assignment of substitution on the aromatic ring. This band can be assigned as C-H out-of-plane bending vibrations of three adjacent C-H groups as seen in the monomer spectrum. An absorption band at 811  $\text{cm}^{-1}$  can be assigned to  $\nu$ C-H vibrations of two adjacent C-H groups. These observations show that the polymer contain naphthalene rings with three adjacent C-H groups in the polymer backbone grown in early stage of the polymerization and with two adjacent C-H groups in the other polymer backbone. Therefore, it can be thought that the polymerization proceeds with coupling of the monomer to the 2- or 4- position of the naphthalene ring. From the assignment, the electrochemically synthesized polymer structure could be tentatively suggested as shown in Fig. 4.

The humidity measurement was performed using a flow-system with a saturated salts chamber. The response time of the sensor to the humidity change was determined by rapidly transferring the sensor out of the hermetic chamber containing a saturated salt solution. In this procedure, the sensor was first brought to equilibrium with the humidity in the hermetic chamber regulated by a saturated salt solution. Then, the sensor was expose to the humidity in the room by transferring it out of the hermetic chamber. During that time, pulse measurements were done at the voltage of  $\pm 5$  Vdc. In the following step, the sensor was reinstated and allowed to equilibrate in the chamber, which maintained its specified humidity.

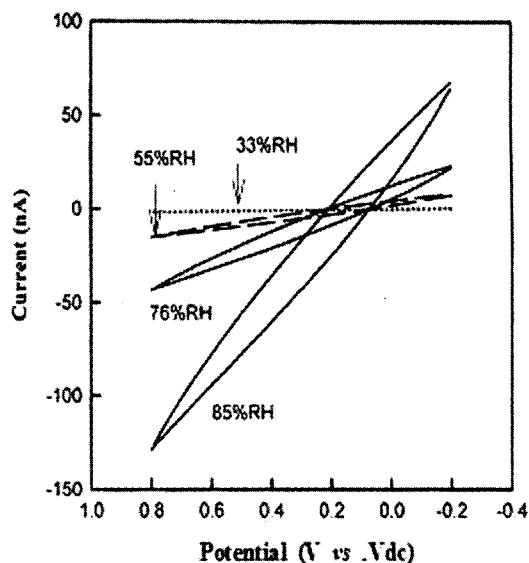


Fig. 5. Cyclic voltammograms of poly(1,5-DAN) according to %RH.

Fig. 5 shows cyclic voltammograms of poly(1,5-DAN) at various RHs. The response current range of the sensor was quite small because the active site volume of bridged polymer was ca.  $1 \times 10^{-3} \text{ cm}^3$ . The poly(1,5-DAN) film was stable when the potential was applied from +1.0 to -0.8 Vdc at the low humidity. The response current decreased when the applying voltage was above +1.2 Vdc. Poly(1,5-DAN) partially oxidized at 1.0 V and fully oxidized when the potential went over +1.2 Vdc. These results were consistent that the conductivity of fully oxidized polyaniline was lower than the partially oxidized polyaniline<sup>(13)</sup>. The stability of poly(1,5-DAN) is declined on times going at the single step chronoamperometric humidity measurement, owing to the oxidation of poly(1,5-DAN) and the larger leakage current at a higher content of humidity than lower that of humidity. To avoid of the instability of the polymer film due to the oxidation of the film at high measuring potential, the applied potential reduced to +0.5 V for the single step chronoamperometric humidity deter-

mination. Even the potential of +0.5 V was applied, the current response of poly(1,5-DAN) was gradually decreased as time passed at a given RH. The resistance of oxidized polyaniline between two polyaniline-connected microelectrodes was not changed as a function of RH as previously reported<sup>(14)</sup>. The oxidized polyaniline remains a good conductor with and without humidity. But, the resistance of partially oxidized poly(1,5-DAN) was changed as a function of RH in single step chronoamperometry. Thus, double potential step chronoamperometry was undertaken to minimize the instability of the polymer film.

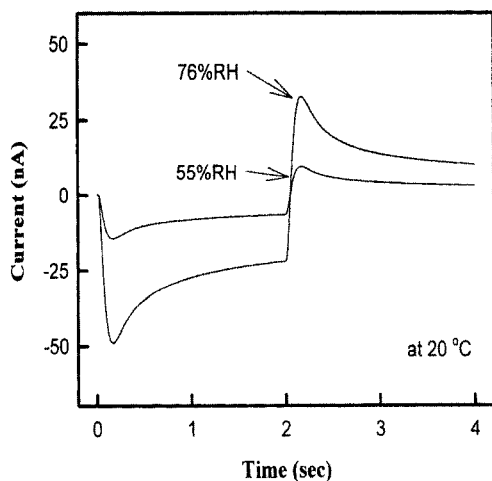


Fig. 6. The current response in double step chronoamperometry according to %RH.

To overcome the low stability of the sensor in single step chronoamperometry, we tested the double potential step method. The stability was improved by this method that applied voltage was  $\pm 0.5$  Vdc. Fig. 6. shows the current response of the humidity sensor in double-step chronoamperometry corresponding to the %RH. The poly(1,5-DAN) coated electrode was stabilized by the oxidation and reduction alternatively due to the alternative application of the cathodic

and anodic potential. This procedure prohibits the over oxidation of the poly(1,5-DAN) of the sensor, and it provided reproducible results for humidity measurements.

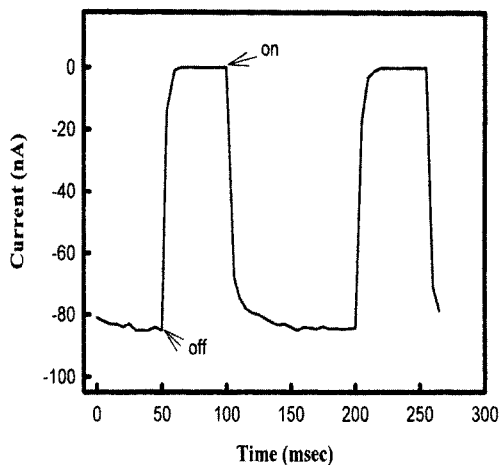


Fig. 7. Response characteristics of a humidity sensor.

The response time of a sensor to sudden changes in humidity was determined by rapidly changing humidity of the hermetic chamber using chronoamperometry. Fig. 7 illustrates the response time of the poly(1,5-DAN) electrode grown in a 0.1 M HCl solution. In this procedure, the sensor was first brought to the equilibrium state in humidity in the hermetic chamber followed by the atmospheric humidity in room, during that time response measurements were done at the voltage of  $\pm 0.5$  Vdc. Then, the sensor was rapidly exposed to the vacuum environment by opening T-valve. At this point, current measurements were taken until the current change became small within  $\pm 5$  %. The response time determined by pulse technique was about  $\sim 50$  msec. This response time was very fast compared with one of ceramic materials used as a humidity sensor. The reversibility was maintained with ex-

posure at every relative humidity value. The reversibility for this humidity sensor was examined by measuring the current with and without the humidified nitrogen gas. The hysteresis for a cycle 33 → 93 → 33 % RH was less than  $\pm 1\%$ .

Fig. 8 shows a plot of the response current vs. %RH obtained with the poly(1,5-DAN) sensor. The non-linearity with two different slopes was observed over this measurement region. The linear equations in different slopes were  $I(\text{nA}) = 0.28 \times \%RH - 1.01$  between 10 to 70 %RH and  $I(\text{nA}) = 6.05 \times \%RH - 403.21$  between 70 to 90 %RH. As the percentage of relative humidity increased, more water was partitioned into the film due to the hydrophilicity of poly(1,5-DAN), which led to the polymer film in a increasing hydrated state. This results in swelling of the film and greater mobility of the proton, which increased the electrolysis currents due to increasing the film conductivity.

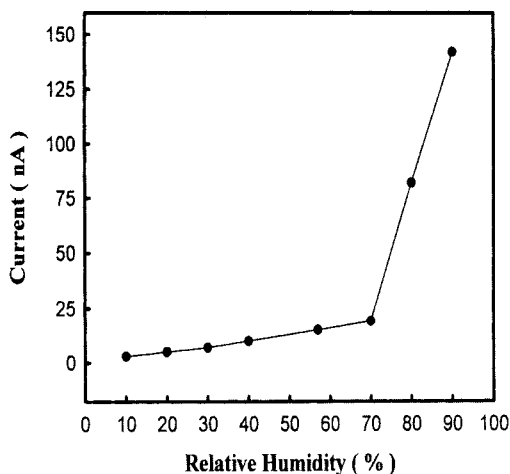


Fig. 8. The current response according to %RH using a poly(1,5-DAN) humidity sensor.

To test the stability of humidity sensor, the following experiment was carried out. Monitoring the output

current fluctuation was undertaken according to the measuring times. The current response against %RH was measured during 2 weeks as shown Fig. 9, which shows the output current changes. Measurements were done in a hermetic chamber controlled 76 and 85 %RH at 20 °C. The sensor, when not in use, was stored in an opened bottle of the laboratory bench at ambient RH, which varied from 30 to 70 % during this period.

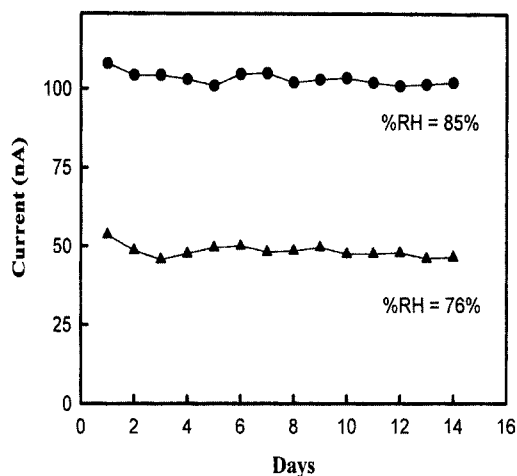


Fig. 9. Stability curves of a poly(1,5-DAN) humidity sensor.

#### 4. Conclusion

In the present work, we studied the electrical behavior of the electrochemically prepared poly(1,5-DAN) according to ambient humidity. The poly(1,5-DAN) film was electrochemically coated on splitted gold electrodes to be bridged with polymer. A reproducible humidity-induced electrical behavior of polymer layers was characterized by a fast response after humidity changes. The conductivity of a thin film of poly(1,5-DAN) is humidity sensitive, so that it can be the basis for a relative humidity sensor. The response time, sensor size, sensor signal, and the RH range of the poly(1,5-DAN)

sensor were comparable to those of other polymer-based sensors that have been developed. An advantageous characteristic of the poly(1,5-DAN) coated sensor is the rapid reversible response to changes in RH at higher humidity. The stability was improved by a double pulse method that applied voltage is  $\pm 0.5$  Vdc. The response time determined by the pulse technique was about  $\sim 50$  msec. The non-linearity with two different slopes was observed, in which linear equations were  $I(nA) = 0.28 \times \%RH - 1.01$  between 10 to 70 %RH and  $I(nA) = 6.05 \times \%RH - 403.21$  between 70 to 90 %RH.

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