Effect of NH₃ gas on the electrical conductivity of polyaniline blend films

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Abstract

The effect of NH₃ gas on the electrical conductivity of four kinds of polyaniline-insulating matrix polymer blend films was investigated for the purpose of preparing a practical NH₃ gas sensor operable near or at room temperature. The electrical conductivity of all blend films measured in N₂ was enhanced above a 2 wt.% of composition of polyaniline. The electrical conductivity decreased by exposure of the blend films to NH₃ gas. It was found that the sensing characteristics depended on the kind of dopant species, measuring temperature, matrix polymers, and the solvent used for film preparation. Among the considered sensors, the polyaniline–poly(methyl methacrylate) blend film prepared with toluene as the solvent showed the fastest response and good reversibility, because the porous film was obtained only by this combination. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: NH₃ gas sensor; Polyaniline blends

1. Introduction

Conducting polymers such as polypyrrole, polyaniline, and polythiophene have been widely investigated as materials for chemical sensors [1–9]. Previous reports revealed that the conducting polymers have great advantages of higher sensitivity towards toxic gases such as NH₃, a lower detectable limit in the range of a few tens of parts per millions, and the potential to operate at or near room temperature. Conducting polymers are prepared either by electrochemical oxidative polymerization or by the chemical oxidative polymerization method. So far, direct electrochemical synthesis of the conducting polymers on the electrode has generally been used for the preparation of gas sensing elements. However, quantitative production of thin films is limited by this method due to the complexity of current-density control and the process of selection of an electrolyte. Further, the film prepared electrochemically is often brittle and not processable. The alternative chemical polymerization method is simple compared with the electrochemical method, though, the former produces an insoluble powder that leads to poor processability and poor mechanical properties. Preparation of a stable thin film through a simple method is essential for the preparation of a practical sensor.

Efforts have been made to improve the processability of conducting polymers. Chemical synthesis of soluble conducting materials has been investigated [10–13]. Composite films, consisting of conducting polymers and various insulating films, have been used in attempts to produce a gas-sensitive device. Chemically polymerized polypyrrole was finely ground and dip-coated with a binder and attached to a paper to produce a gas-sensitive resistor [6]. The composite film, composed of microporous polyethylene–polypyrrole, was prepared by chemical oxidation of the pyrrole monomer inside the pores of porous polyethylene film [7].

Other useful approach for the improvement of the processability and the mechanical properties of insoluble polymers is the blending with soluble matrix polymers. Recently, blending of chemically polymerized polyaniline (PANI) with other soluble insulating polymers has received great attention for its potential application in a wide variety of electrical and electronic devices [14–16], since those blend films show high electrical conductivity and good mechanical properties. However, there are few reports on application of those blend films for gas sensors. PANI, which results from oxidative polymerization of aniline, is one of the most promising conducting polymers for chemical sensor application. It is an environmentally stable, and can exhibit high electrical conductivity. In this study, the effect of NH₃ gas on the electrical conductivity of PANI-insulating matrix polymer blend films was examined for the purpose of preparing a practical NH₃ gas sensor operable at or near room temperature.
2. Experimental

2.1. Preparation of blend films

Four kinds of blend films were prepared according to the procedures illustrated in Fig. 1. The polymerization of aniline proceeded by the well-known process of oxidative polymerization in the presence of 1 N HCl with ammonium persulphate as an oxidizing agent. The reaction mixture was stirred for about 4 h at \(-5^\circ\text{C}\) then the formed polymer was filtered. The polymer was washed with HCl and distilled water, then dried in the vacuum oven. Various amounts of HCl-doped PANI powder prepared in this way were added slowly to 15 wt.% of polystyrene (PSt)–toluene solution while stirring vigorously, and suspended solution containing various compositions of HCl-doped PANI was obtained (solution 1). Alternatively, the HCl-doped PANI powder was leached with 0.1 N aqueous ammonia and deprotonated, which resulted in the formation of polyemeraldine base PANI. The filtered polyemeraldine base PANI was protonated with \(\text{DiOHP}\) in a toluene solution (a half molecule of \(\text{DiOHP}\) was used per phenyl \(\text{N}\) repeat unit). The \(\text{DiOHP}\)-doped PANI solution in toluene was added slowly to 15 wt.% toluene solution of PSt (solution 2) or 15 wt.% toluene solution of poly(methyl methacrylate) (PMMA) (solution 3) of various compositions. The polyemeraldine base PANI was also protonated with \(\text{DiOHP}\) in a 2-butanone solution, and added to 15 wt.% 2-butanone solution of PMMA (solution 4). Chemical structures of \(\text{DiOHP}\), PSt, and PMMA are shown in Fig. 2.

2.2. Fabrication of the sensor device

The obtained PANI-matrix polymer blend solutions were spin-coated on an alumina substrate having a pair of interdigitated gold electrodes. These films were dried in the vacuum oven at 60 °C for 1 h. It was confirmed that all films had sufficient mechanical properties. The sensors fabricated are denoted as sensor 1–4 shown in Table 1.

2.3. Measurements

Each sensor thus prepared was set in a vessel into which dry \(\text{N}_2\) and then \(\text{NH}_3\) gas at varying concentrations diluted with dry \(\text{N}_2\) were introduced. The current was measured.
using an electrometer under the applied voltage of dc 10 V. Pure N₂ was passed through the vessel until a steady current reading had been obtained. The NH₃ gas was then introduced in the vessel and the current was recorded for 240 min. The NH₃ gas was then turned off and the sensor was left to recover in N₂ for 120 min. Use of this isochronal approach was based on the fact that current saturation was not obtained in some of the sensors studied. The measurement was carried out at 30 °C and 50 °C.

The morphology of the blend films was observed under scanning electron microscopy (SEM).

3. Results and discussion

3.1. Electrical properties of blend films

The electrical conductivity in N₂ of the various PANI blends versus PANI composition is depicted in Fig. 3. A similarity among conductivity curves for all polymer blends is observed. The conductivity of the blend films depends strongly on the composition of PANI. The films with less than 2 wt.% composition show an insulating characteristic while the conductivity is enhanced steeply above this composition. This transition from insulator to conductor is explained by the well-known percolation theory, i.e. the conductivity of the blends is ascribed to the degree of connectivity of the conducting polymer in the blends.

3.2. Response behavior of sensors

Sensor response of all blend films was measured. The results showed that the sensors with the blend films having larger compositions of PANI had better NH₃ sensing properties. Consequently, subsequent discussion here is given only for the results using the blend films with the PANI composition of 7 wt.%. After the steady conductivity had been obtained in the N₂ atmosphere, the time-dependent electrical conductivity (log σ) was plotted (see Fig. 4) during exposure of the sensor for the concentration of 500 ppm of NH₃ gas for 240 min and subsequent exposure to N₂ for 120 min at 30 °C. The conductivity decreased by exposing the sensor to NH₃ gas, and recovered toward the original value after switching back to N₂ gas for all sensors. The sensing mechanism is explained by the compensation effect [17]. When the conductive emeraldine salt is exposed to NH₃ gas, the dopant is partially dedoped, which leads to the reduction of electrical conductivity. But in N₂, NH₃ gas volatilizes and protons restore the initial level of doping. Data obtained from Fig. 4 are summarized in Table 2, which shows the

Table 1
Detailed description of prepared sensors

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Dopant</th>
<th>Solvent</th>
<th>Matrix polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HCl</td>
<td>Toluene</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>2</td>
<td>DiOHP</td>
<td>Toluene</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>3</td>
<td>DiOHP</td>
<td>Toluene</td>
<td>Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>4</td>
<td>DiOHP</td>
<td>2-Butanone</td>
<td>Poly(methyl methacrylate)</td>
</tr>
</tbody>
</table>

Table 2
Comparison of sensing characteristics at 500 ppm of NH₃

<table>
<thead>
<tr>
<th>Sensor</th>
<th>Measured temperature (°C)</th>
<th>S</th>
<th>t₀ (min)</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30</td>
<td>1.16</td>
<td>25</td>
<td>0.23</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>1.56</td>
<td>37</td>
<td>0.67</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>0.56</td>
<td>18</td>
<td>1.14</td>
</tr>
<tr>
<td>4</td>
<td>30</td>
<td>1.84</td>
<td>11</td>
<td>0.74</td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>0.90</td>
<td>4</td>
<td>0.87</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>1.62</td>
<td>59</td>
<td>0.60</td>
</tr>
</tbody>
</table>
sensor response \( (S) \), 70% response time \( (t_{70}) \), and \( R \) as a value representing the reversibility of the sensor response:

\[
S = \log(\sigma_0) - \log(\sigma_{240})
\]

\[
R = \frac{\log(\sigma_{360}) - \log(\sigma_{240})}{\log(\sigma_0) - \log(\sigma_{240})}
\]

where \( \sigma_0, \sigma_{240}, \) and \( \sigma_{360} \) are the conductivities measured at 0, 240, and 360 min, respectively. It is found that doped acid influences the sensor response. The blend film doped with HCl (sensor 1) has the highest dc conductivity, but the reversibility of the sensor response is invariably poor. The lack of reversibility seems attributable to the difficulty of desorption of the adsorbed NH\(_3\) as well as to the loss of dopant (HCl). On the other hand, sensor 2, using DiOHP, has a higher sensitivity and better reversibility compared with those of sensor 1 at the same temperature \( (30^\circ \text{C}) \). This result suggests that the size and strength of the acid may affect the sensor response. However, the response time and the reversibility of sensor 2 are still insufficient for practical use. For purposes of further improving these characteristics, the measuring temperature was raised from 30 to 50 \( ^\circ \text{C} \) for sensor 2. While the sensitivity decreased to one-third, the response time is reduced by 50% compared with that measured at 30 \( ^\circ \text{C} \). The decrement in both sensitivity and response time with the raised measuring temperature is attributed to the exothermic adsorption of NH\(_3\). However, the increase in the measuring temperature caused a problem for sensor 2. As shown in Fig. 4(c), the data indicate a slightly undesirable drift in the base line, and the value of \( R \) exceeds unity (original value in N\(_2\)). The reason of the drift is unclear at present. On the other hand, the drift phenomenon is hardly observed for sensor 3 using PMMA as the matrix polymer, even at 50 \( ^\circ \text{C} \). The response time is the shortest \( (t_{70} = 4 \text{ min}) \) and the reversibility is close to unity. The response of sensor 3 to repeated exposure to NH\(_3\) gas for 50 min and then to N\(_2\) for 100 min is shown in Fig. 5. The reproducibility of the sensor is fairly good. These results confirmed that PMMA is more suitable as the matrix polymer among the considered polymers. Interestingly, the solvent used for the preparation of the sensor device dramatically affected sensor response. Despite the use of PMMA, sensor 4 which was prepared using 2-butanone as the solvent, showed a comparatively long response time and poor reversibility, as shown in Fig. 4(e) and Table 2.

\[ \text{Fig. 5.} \text{ Response of sensor 3 resulting from replicate cycling between 500 ppm of NH}_3\text{ and N}_2\text{ at 50 }^\circ \text{C}. \]

\[ \text{Fig. 6.} \text{ SEM photographs of the surface of the sensors: (a) PANI–DiOHP–PSt; (b) PANI–DiOHP–PMMA (toluene), and (c) PANI–DiOHP–PMMA (2-butanone).} \]
3.3. Morphology of the blend films

Fig. 6 shows SEM photos of the surface of the coating film for three kinds of sensors. These figures show that small PANI particles are distributed homogeneously in the blend films. In sensor 2 and sensor 4, the PANI particles are completely covered with the matrix polymer. On the other hand, there are many pores on the surface in sensor 3, the combination of DiOHP–PMMA–toluene. The PANI particles appear inside the pores. The formation of these pores for the coating of sensor 3 was reproducible. These pores seem to contribute to the short response time and good reversibility of sensor 3. This is due to the fact that gas diffusion occurs more easily in porous structures, and the reaction between gas molecules and dopant therefore occurs easily.

3.4. NH$_3$ concentration dependence of the sensor response

The effects of NH$_3$ gas concentration on the sensor characteristics were examined as shown in Fig. 7. The threshold (limited by the measuring equipment) concentration level was 10 ppm. The change in conductivity $\Delta \sigma$ ($\sigma$(N$_2$)−$\sigma$(NH$_3$)) of sensor 3 varies nonlinearly with the NH$_3$ concentration. Relatively small NH$_3$ concentrations give rise to marked decrease in conductivity, and conductivity approaches a plateau value at high concentrations. It was found from this figure that this sensor has large sensitivity in the low level NH$_3$ concentration and the detection limit is less than 10 ppm. On the other hand, the response time became longer with decrease in the NH$_3$ concentration ($t_{70} = 8$ min at 100 ppm).

4. Conclusions

A PANI blend film was proposed as an NH$_3$ sensor coating. Poor processability and poor physical properties of chemically prepared PANI were improved by blending PANI with soluble matrix polymers. The preparation method represented an easy-to-handle and inexpensive method compared with that of electrochemical deposition. The response behavior observed in the blend films revealed many interesting features that are not yet fully understood. It clearly appeared that components of the blend films influenced the morphology, which led to the variation of the sensor response behavior. Among the sensors prepared in this study, sensor 3, which was prepared with PANI, DiOHP as dopant, and PMMA as matrix polymer using toluene as solvent, had the best sensing properties. However, the reversibility and especially response time were not enough for practical use. Further studies are needed.

References