Polyaniline–maleicacid–dodecylhydrogensulfate Salt as Sensor Material for Toxic Gases

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ABSTRACT: This article reports the results of novel polyaniline material as gas sensor, capable of operating at room temperature for toxic gases. Polyaniline–maleicacid–dodecylhydrogensulfate salt (PANI-MA-DHS) was prepared by emulsion polymerization pathway, which is soluble in N,N-dimethyl formamide. PANI-MA-DHS was coated on a ceramic bead by simple brush coating method and used as sensor material. The resistance change of PANI-MA-DHS material for NH_3, CO_2, SO_2, and H_2S gases at different concentrations (10, 100, 1000, and 10,000 ppm level) was monitored for sensor characteristics. The stability of the polyaniline material under continuous exposure of gas level from 10 to 10,000 ppm was also studied. This novel gas sensor material has advantages such as excellent sensing ability, low cost, fast regeneration time ($\sim$ 1–2 min), simple experimental setup, and operable at room temperature. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 518–524, 2010

Key words: sensors; conducting polymers; emulsion polymerization

INTRODUCTION

During the last 25 years, global research and development (R&D) in the field of sensors has expanded exponentially in terms of financial investment, the published literature, and the number of active researchers.[1,2] Legislation has fostered a huge demand for the sensors necessary in environmental monitoring, e.g. monitoring toxic gases and vapors in the workplace or contaminants in natural waters by industrial effluents and runoff from agriculture fields. Thus, a near revolution is apparent in sensor research, giving birth to a large number of sensor devices for medical and environmental technology.

Sensor devices have been made from classical semiconductors,[3–5] solid electrodes and electrolytes,[6,7] insulators based,[8,9] metals,[10–12] and catalytic materials.[13–16] As the chemical and physical properties of polymers may be tailored by the chemist for particular needs, they gained importance in the construction of sensor devices. Recently, there has been much more interest in exploiting intrinsically conducting organic polymers such as polypyrrole, polyaniline, and polythiophene.[17–22] Of all the conducting polymers, polyaniline has been extensively studied for its environmental stability in the conducting form, easiness in synthesis, low cost synthesis, unique redox properties,[23] and reasonable conductivity.[24] Agbor et al.[25] have studied the importance of layer sensitivity of nondoped PANI layers deposited either by spin-coating, thermal evaporation, or by Langmuir–Blodgett technique for several gases, such as NOx, H_2S, SO_2, CO, CH_4. Kukla et al.[26] showed a decrease of the polyaniline based sensor sensitivity in the temperature range from 27 to 78°C, proving that desorption was favored compared to adsorption. Collins and Buckley[27] have deposited PANI onto poly(ethylene terephthalate) or nylon threads and they have studied the gas sensing properties to NH_3 and NO_2 gases. Syu and Liu[28] have used blends of PANI and Nafion to improve the response time and the selectivity of SO_2 gas. Koul and Chandra[29] reported the conducting polyaniline-poly(acrylonitrile–butadiene–styrene) blend films as a sensor material for aqueous ammonia. Recently, Deshpande et al.[30] prepared the thin films of tin oxide-intercalated polyaniline nanocomposite through solution route technique and they evaluated the NH_3 sensing property. Yoo et al.[31] synthesized multiwall carbon nanotube/polyaniline composite films by plasma treatment for NH_3 sensor. Chang et al.[32] prepared gold/polyaniline/multiwall carbon nanotube nanocomposites and studied the ammonia gas sensing properties. However, apart from the many attractive properties of polyaniline based gas sensors, there are some fundamental problems are still existing, such as cost of production, solubility problems, long-term mechanical and

MA= Maleic acid, DHS=Dodecylhydrogensulfate
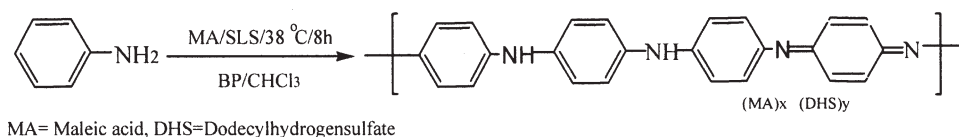
Scheme 1 Reaction scheme of PANI-MA-DHS.

chemical stability of the polymeric materials, sensing ability and reversibility are not always satisfactory at room temperature and detection limits to various pollutants, etc. Moreover, there are only few reports are available on application of polyaniline material as sensor for toxic gases such as CO_2, SO_2, and H_2S.[25,33–35]

Polyaniline, which results from oxidative polymerization of aniline, is one of the most promising conducting polymers for chemical sensor application.[25,33–38] Generally, polyaniline materials synthesized by aqueous polymerization pathway were insoluble in organic solvents, therefore processing of polyaniline has remained a difficult problem. Recently, our group has prepared industrially important novel soluble polyaniline–maleicacid–dodecylhydrogensulfate salt (PANI-MA-DHS) containing dual dopants and patented the work.[39] Polyaniline powder prepared using maleic acid was soluble in polar solvents like DMF (N,N-dimethylformamide), NMP (N-Methyl-2-pyrrolidone), DMSO (Dimethyl sulfoxide) and maximum solubility was found to be 6% w/v.[39]

Inspite of the various advantages of conducting polymer based gas sensors, some fundamental problems still persist. The fabrication of good material is often hampered by solubility problem. Long-term mechanical and chemical stability of the polymeric materials are points of concern in many instances. Sensing ability and reversibility are not always satisfactory. To overcome the above-mentioned problems, in this work, polyaniline salt was dissolved in DMF solvent and coated on ceramic material by simple brush coating process using novel soluble PANI-MA-DHS and used as sensing material. The resistance change of the resultant polyaniline material on exposure to different levels of various gases (NH_3, CO_2, SO_2, and H_2S) at room temperature was monitored. To prepare particular concentration of gas, each gas was diluted with nitrogen gas. The stability of the polyaniline material under continuous exposure of gas level from 10 to 10,000 ppm was also studied.

EXPERIMENTAL

Synthesis of PANI-MA-DHS salt

Synthesis of PANI-MA-DHS (Scheme 1) was carried out by the procedure as reported earlier.[39] A total of

3.0 g of benzoyl peroxide was dissolved in 30 mL chloroform taken in 250-mL round bottom flask. A total of 1.0 g of sodium lauryl sulfate was dissolved in 20 mL distilled water and added to the above solution. The reaction mixture was stirred at 37–38°C. A total of 30 mL aqueous solution containing 2.9 g of maleic acid and 1.0 mL of aniline was added drop wise into the initiator-surfactant mixture for 15 min duration. After addition, the reaction was continued for 8 h at 37–38°C. After 8 h, the whole reaction mixture was transferred to 250-mL separating funnel and kept under room temperature until the separation of organic and aqueous layer. The entire organic phase was filled homogeneously with dark-green polyaniline, whereas the aqueous layer appeared colorless. The organic layer was separated from the aqueous layer, and the polymerization was terminated by pouring the organic layer into 300 mL of acetone whereupon polyaniline precipitated. Precipitate of polyaniline salt was separated by filtration, washed with water followed by acetone and the powder was dried at 70°C for 24 h.

The properties of PANI-MA-DHS are given in Table I.

Preparation of polyaniline coated ceramic material

A total of 0.1 g of PANI-MA-DHS was dissolved in 2 mL of N,N-dimethyl formamide in 5-mL round bottom flask for 15 min, under constant stirring, then 1 mL of m-cresol was added to the mixture and stirred for 4 h at ambient temperature. The resultant solubilised PANI-MA-DHS material was coated on precleaned ceramic bead using a brush coating technique (coating has been done by manually using

TABLE I
The Properties of Polyaniline Salt Prepared by Emulsion Polymerization Technique

Properties	PANI-MA-DHS
Colour	Dark-green powder
Yield[a]	117%
Conductivity	0.1 S/cm
Pellet Density	1.25 g/cm^3
Amount of dopant	46 wt %
Solubility of powdered PANI	Soluble in DMF, NMP, DMSO 6% W/V
Viscosity	0.3 cPs

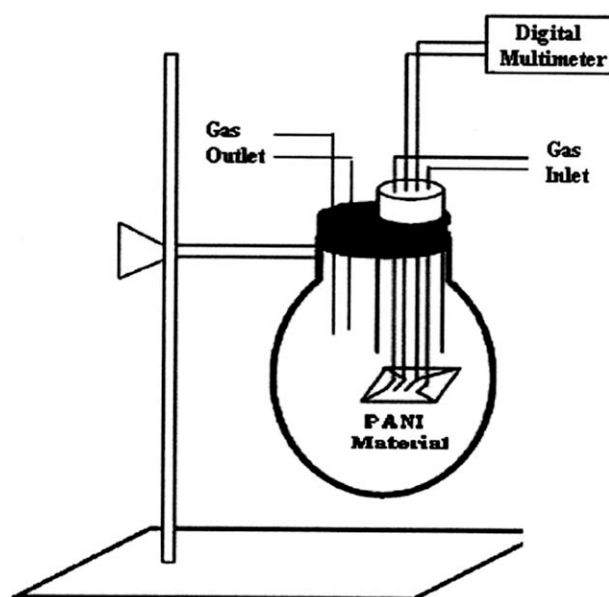[a] The yield of the polyaniline salt was calculated based on the amount of aniline used.

Figure 1   Polyaniline coated ceramic material.

ordinary paint brush) and dried in an oven. The dried material (Fig. 1) was directly used for gas sensing analysis.

Experimental setup for gas sensor

A schematic view of simple experimental setup to monitor the toxic gases sensing by the polyaniline material at ambient temperature; is shown in Figure 2. To make good contact for resistance measurement, silver paint was coated at the two edges on polyaniline coated bead. Two copper wires were tied on the silver paint coated edges of the polyaniline bead and the bead was kept inside the closed chamber, other end of the copper wires were connected to Keithley digital multimeter (MODEL-2010). Nitrogen gas was filled in balloon and mixed with target gas of particular concentration and passed inside the chamber, the resistance value was collected from the digital multimeter for plotting the repetitive response behavior graph. Reproducibility of

the sensing behavior of polyaniline material was checked three times for all the four different gases, such as NH_3, CO_2, SO_2, and H_2S at 10, 100, 1000, and 10,000 ppm level.

RESULTS AND DISCUSSION

Gas sensing response of PANI-MA-DHS material

Response behavior of PANI-MA-DHS material was studied for ammonia gas at 100 ppm level (Fig. 3). Resistance value was monitored under ammonia gas for 5 min and the resistance value was found to be increased. Stopped the ammonia gas and passed nitrogen gas for 2 min. The resistance value decreased back to very close to the original value.
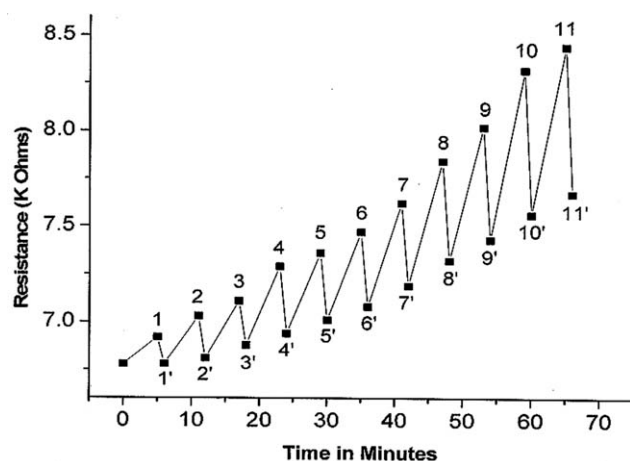
Repetitive response behavior of polyaniline salt (PANI-MA-DHS) was carried out in a similar manner for four different gases, such as NH_3, CO_2, SO_2, and H_2S at 10, 100, 1000, and 10,000-ppm level and the results are presented here.

Ammonia gas

As a representative system, response behavior of PANI-MA-DHS for ammonia gas at 10 ppm level is shown in Figure 4. On exposing the PANI-MA-DHS material under NH_3 gas for 5 min, it showed increase in the resistance value from 6.78 to 6.92 KΩ and on passing the N_2 gas for 1 min, it showed a decrease in resistance value back to 6.78 KΩ. Exposing the same material again to ammonia gas for duration of 5 min, showed increase in resistance value from 6.78 to 7.03 KΩ and on passing the N_2 gas for 1 min, showed a decrease in resistance value back to 6.81 KΩ. Similarly, the changes in resistance for third to eleventh cycles were observed as shown by the
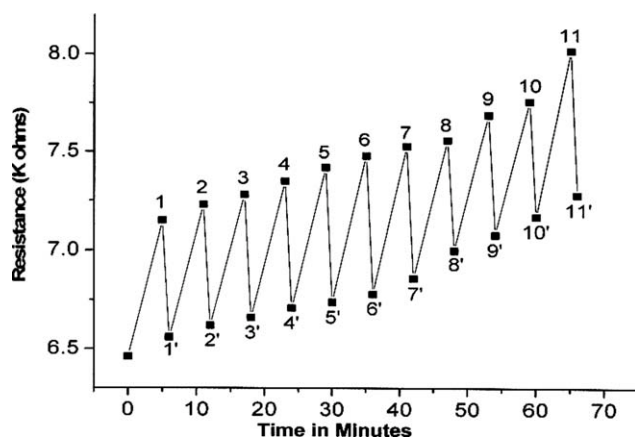

Figure 2   Experimental setup for gas sensor.
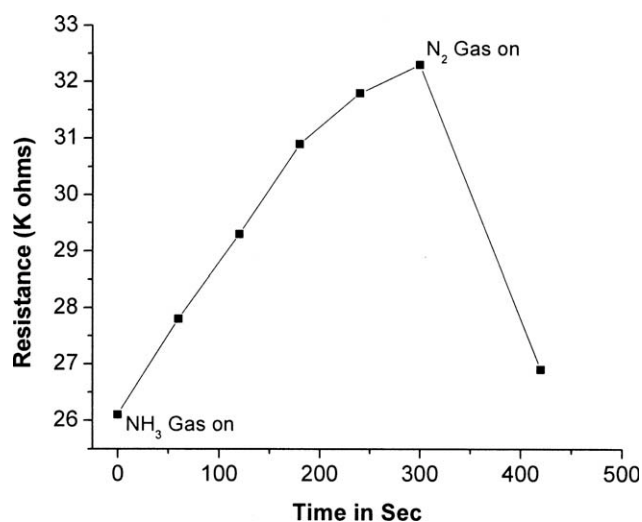
Figure 3   Response characteristics of PANI-MA-DHS to 100 ppm NH_3 at room temperature for 5 min and 2 min in N_2-atmoshphere.
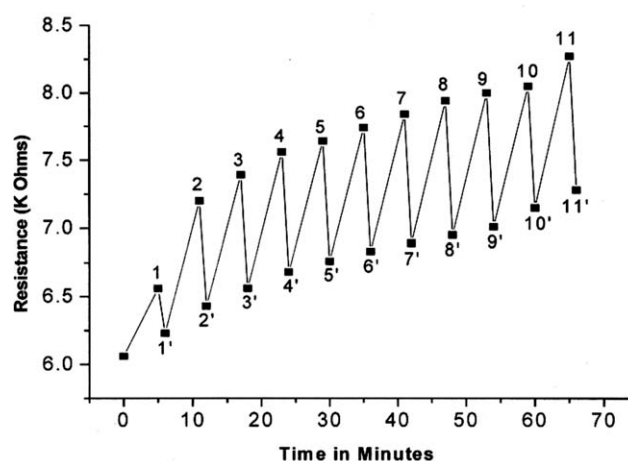
Figure 4 Repetitive response behavior of polyaniline material with 10 ppm ammonia gas. Where the points 1–11 corresponds to resistance changes of material after exposure to ammonia gas and 1′–11′ corresponds to resistance of material in presence of N_2 gas.

response cycle curve in Figure 4. It should be noted that after each cycle, the resistance value never came back to its original value and attained very slightly higher than the original one, however, the resistance value is very much under the detectable window. A similar response behavior was observed for 100, 1000, and 10,000 ppm level of ammonia gas concentration (Figs. 5–7).

On exposing the PANI-MA-DHS material to ammonia gas in different concentration, there is an increase in resistance value. The increase in resistance of the sensor material is attributed to the consumption of charge carriers from the polymeric backbone. PANI-MA-DHS contains dual dopants (maleic acid and dodecylhydrogensulfate), which on exposure to ammonia gas forms HOOC—CH=CH
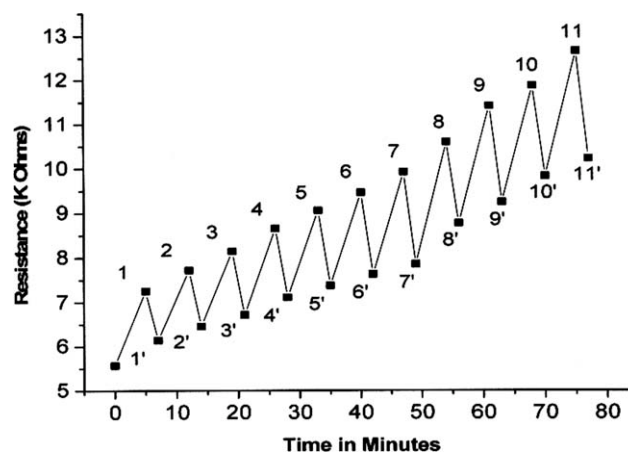

Figure 6 Repetitive response behavior of polyaniline material with 1000 ppm ammonia gas. Where the points 1–11 corresponds to resistance changes of material after exposure to ammonia gas and 1′–11′ corresponds to resistance of material in presence of N_2 gas.

—COO^- NH_4^+ and $CH_3 (CH_2)_{11}OSO_3NH_4^+$ due to the interaction of proton from the dopants and ammonia gas. Hence, the emeraldine salt state has been converted to the emeraldine base state, which accompanies an increase in resistance value. However, as the feeding of NH_3 is stopped and as soon the sensor material is kept under N_2 atmosphere, the NH_4^+ decomposes to NH_3 and H^+. The later adhere to the emeraldine base state to emeraldine salt and restore very close to the initial level of resistance value. This result shows the reversible nature of ammonia gas on polyaniline sensor material. This result is in good agreement with the literature reports.[40,41] After each cycle, the resistance value never came back to its original value and attained very slightly higher than the original one. This effect may be contributed to
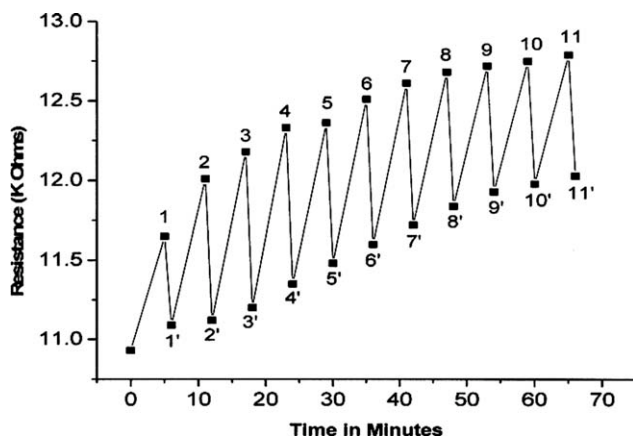

Figure 5 Repetitive response behavior of polyaniline material with 100 ppm ammonia gas. Where the points 1–11 corresponds to resistance changes of material after exposure to ammonia gas and 1′–11′ corresponds to resistance of material in presence of N_2 gas.

Figure 7 Repetitive response behavior of polyaniline material with 10,000 ppm ammonia gas. Where the points 1–11 corresponds to resistance changes of material after exposure to ammonia gas and 1′–11′ corresponds to resistance of material in presence of N_2 gas.

Figure 8 Repetitive response behavior of polyaniline material with 10 ppm carbon dioxide gas. Where the points 1–11 corresponds to resistance changes of material after exposure to carbon dioxide gas and 1'–11' corresponds to resistance of material in presence of N_2 gas.

the constant removal of ammonium salt of maleic acid and dodecylhydrogensulfate from the polymer chain by ammonia gas. Koul et al. also observed the similar result with polyaniline containing dual dopants such as dodecylbenzenesulphonic acid and *p*-toluenesulphonic acid system.[42] In some of the literature reports,[25,43,44] increase of resistance was attributed to removal of water from the polyaniline chain. In this work, as the polyaniline material was dried in oven and used for gas sensing analysis, the increase of resistance due to water molecule may be ruled out.

Carbon dioxide gas

Generally, a similar repetitive response behavior of polyaniline salt was observed for 10, 100, 1000, and 10,000 ppm of carbon dioxide gas. As a representative system, response behavior for carbon dioxide gas at 10 ppm level is shown in Figure 8. It was observed that under carbon dioxide atmosphere, the resistance of PANI-MA-DHS increases with time. As soon as the sensor material is kept under N_2 atmosphere, the resistance value decreased very close to its original resistance value and this may be because of the CO_2 dissociate from the PANI and restore very close to the initial doping level of PANI. However, after each cycle, the resistance value never came back to its original value and attained slightly higher than the original one. This result indicates that some amount of CO_2 is attached to polyaniline system.
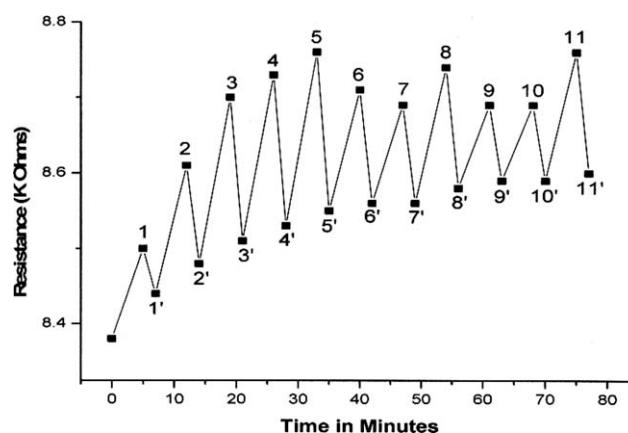
Sulfur dioxide gas

Repetitive response behavior of polyaniline salt was also carried out for 10, 100, 1000, and 10,000 ppm of sulfur dioxide gas. As a representative system,
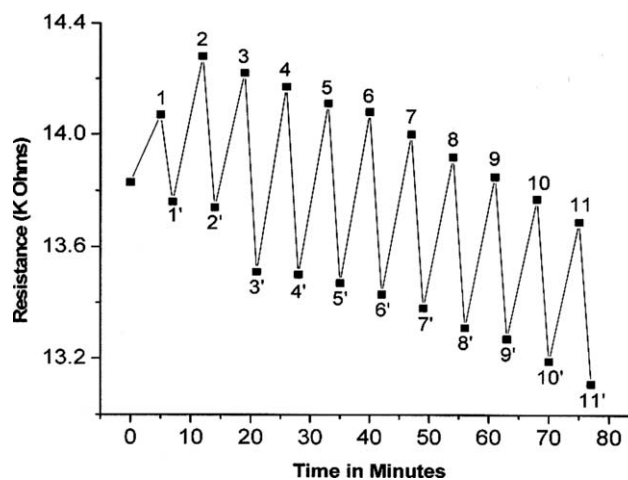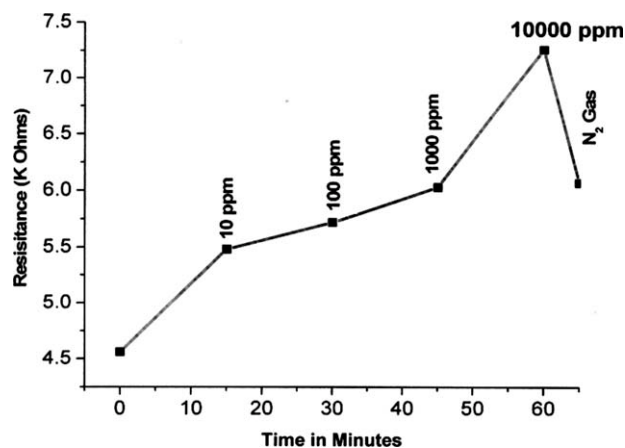
Figure 9 Repetitive response behavior of polyaniline material with 10 ppm sulfur dioxide gas. Where the points 1–11 corresponds to resistance changes of material after exposure to sulfur dioxide gas and 1'–11' corresponds to resistance of material in presence of N_2 gas.

response behavior observed for 10 ppm level is shown in Figure 9.

It was observed that under sulfur dioxide atmosphere, the resistance of PANI-MA-DHS increases with time. However, in N_2 atmosphere, the SO_2 dissociates slowly from the PANI and restore to the initial doping level of PANI. After each cycle, the resistance value never came back to its original value and attains slightly lower than the original one. Resistance of PANI decreases with SO_2 gas may be due to the constant addition of SO_2 on polyaniline backbone. A similar effect was observed for 100, 1000, and 10,000 ppm of SO_2 gas concentration.

Figure 10 Repetitive response behavior of polyaniline material with 10 ppm hydrogen sulfide gas. Where the points 1–11 corresponds to resistance changes of material after exposure to hydrogen sulfide gas and 1'–11' corresponds to resistance of material in presence of N_2 gas.

Figure 11 Response behavior of polyaniline material with different ppm level (10, 100, 1000, and 10,000 ppm) of ammonia gas.

Hydrogen sulfide gas

Generally, a similar repetitive response behavior of polyaniline salt was observed for 10, 100, 1000, and 10,000 ppm of H_2S gas. As a representative system, response behavior of hydrogen sulfide gas at 10 ppm level is shown in Figure 10.

PANI-MA-DHS material showed well-defined response behavior when exposed to 10 ppm H_2S gas (Fig. 10). The response curve was slightly disturbed due to the presence of some impurity in H_2S gas. On exposing the PANI material for 5 min, it showed increase in resistance value. On passing the N_2 gas for 2 min, the resistance value came back to close to the original value. However, after each cycle, the resistance value never came back to its original value and attained slightly higher than the original one. The redox state of polymers, the degree of protonation, and the amount of undissociated acid polymer are interrelated parameters.[45] So, the undissociated H_2S may play an important role in an increase in the resistance value of PANI.

Stability of PANI material under continuous exposure

To find out the stability of PANI-MA-DHS material under continuous exposure, PANI-MA-DHS material was first exposed to 10 ppm level of NH_3 for 15 min and then increased the concentration of ammonia gas from 10 to 100, 1000, and 10,000 ppm level for 15 min each. (Fig. 11). The observation indicates that polyaniline material can detect gas even at continuous exposure of high concentration level also. A similar behavior was observed for CO_2 and H_2S gases.

The mechanism of the intrinsic conducting polyaniline response is unknown but many theories have been suggested.[46,47] In this article we have proposed sensor mechanism of PANI-MA-DHS material on exposure to different gases based on general acid-base interaction concepts. With respect to sensing applications, the interaction between the target gases and polyaniline can be divided into two types: either the conductivity increases or decreases depending on both the undoped/doped state of the polyaniline and the electrophilic/nucleophilic behavior of the target gases. When PANI is treated with an electron rich molecule such as NH_3, H_2S an electron transfer interaction occurs. As PANI is a *p*-type doped conductive polymer and NH_3 or H_2S is a strong nucleophilic gas, NH_3 or H_2S tends to give electrons to PANI causing a decrease in the number of charge carriers, polarons and bipolarons, and the decrease in electrical conductivity; therefore, the negative response is expected and observed. On the other hand, the electron acceptor gas like SO_2 increases the number of charge carriers in PANI thus decreasing the resistance. However, it is difficult to find out the clear mechanism from this study. The systematic and quantitative studies on the mechanism of gas sensing property of PANI-MA-DHS material are now under progress.

CONCLUSIONS

Soluble polyaniline salt containing dual dopants such as maleic acid and dodecylhydrogen sulfate was successfully coated on ceramic bead and demonstrated as sensor material for NH_3, CO_2, SO_2, and H_2S gases from 10 to 10,000 ppm level. This novel gas sensor has advantages, such as excellent sensing ability, low cost, fast regeneration time ($\sim$ 1–2 min), easy processibility, simple experimental setup, and operable at room temperature.

References

1. Adhikari, B.; Majumdar, S. Prog Polym Sci 2004, 29, 699.
2. Kocache, R. Sens Rev 1994, 14, 8.
3. Sberveglieri, G. Sens Actuators B 1995, 23, 103.
4. Lee, A. P.; Reedy, B. J. Sens Actuators B 1999, 60, 35.
5. Korotcenkov, G. Sens Actuators B 2007, 121, 664.
6. Knake, R.; Jacquinot, P.; Hodgson, A. W. E.; Hauser, P. C. Anal Chim Acta 2005, 549, 1.
7. Shuk, P.; Wiemhofer, H.-D.; Guth, U.; Gopel, W.; Greenblatt, M. Solid State Ionics 1996, 89, 179.
8. Zamani, C.; Shimanoe, K.; Yamazoe, N. Sens Actuators B 2005, 109, 216.
9. Mowery, M. D.; Hutchins, R. S.; Molina, P.; Alajarin, M.; Vidal, A.; Bachas, L. G. Anal Chem 1999, 71, 201.

10. Ruiz, A. M.; Cornet, A.; Shimanoe, K.; Morante, J. R.; Yamazoe, N. Sens Actuators B 2005, 109, 7.
11. Raj, E. S.; Pratt, K. F. E.; Skinner, S. J.; Parkin, I. P.; Kilner, J. A. Chem Mater 2006, 18, 3351.
12. Maskell, W. C. Solid State Ionics 2000, 134, 43.
13. Penza, M.; Cassano, G.; Tortorella, F. Sens Actuators B 2001, 81, 115.
14. Niranjan, R. S.; Sainkar, S. R.; Vijayamohanan, K.; Mulla, I. S. Sens Actuators B 2002, 82, 82.
15. Tsang, S. C.; Bulpitt, C. D. A.; Mitchell, P. C. H.; Ramirez-Cuesta, A. J. J Phys Chem B 2001, 105, 5737.
16. Dusastre, V.; Williams, D. E. J Phys Chem B 1998, 102, 6732.
17. Lin, C. W.; Hwang, B. J.; Lee, C. R. Mater Chem Phys 1999, 58, 114.
18. N-Debarnot, D.; P-Epaillard, F. Anal Chim Acta 2003, 475, 1.
19. Arshak, E.; Moore, E.; Lyons, G. M.; Harris, J.; Clifford, S. Sens Rev 2004, 24, 181.
20. Hodgins, D. Sens Rev 1994, 14, 28.
21. Munoz, B. C.; Steinthal, G.; Sunshine, S. Sens Rev 1999, 19, 300.
22. Ameer, Q.; Adeloju, S. B. Sens Actuators B 2005, 106, 541.
23. Focke, W. W.; Wnek, G. E.; Wei, Y. J Phys Chem 1987, 91, 5813.
24. Kingsborough, R. P.; Swager, T. M. Adv Mater 1998, 10, 1100.
25. Agbor, N. E.; Petty, M. C.; Monkman, A. P. Sens Actuators B 1995, 28, 173.
26. Kukla, A. L.; Shirshov, Y. M.; Piletsky, S. A. Sens Actuators B 1996, 37, 135.
27. Collins, G. E.; Buckley, L. J. Synth Met 1996, 78, 93.
28. Syu, M.-J.; Liu, J.-Y. Sens Actuators B 1998, 49, 186.
29. Koul, S.; Chandra, R. Sens Actuators B 2005, 104, 57.
30. Deshpande, N. G.; Gudage, Y. G.; Sharma, R.; Vyas, J. C.; Kim, J. B.; Lee, Y. P. Sens Actuators B 2009, 138, 76.
31. Yoo, K.-P.; Kwon, K.-H.; Min, N.-K.; Lee, M. J.; Lee, C. J. Sens Actuators B 2009, 143, 333.
32. Chang, Q.; Zhao, K.; Chen, X.; Li, M.; Liu, J. J Mater Sci 2008, 43, 5861.
33. Virji, S.; Fowler, J. D.; Baker, C. O.; Huang, J.; Kaner, R. B.; Weiller, B. H. Small 2005, 1, 624.
34. Oho, T.; Tonosaki, T.; Isomura, K.; Ogura, K. J Electroanal Chem 2002, 522, 173.
35. Takeda, S. Thin Solid Films 1999, 343, 313.
36. Jin, Z.; Su, Y.; Duan, Y. Sens Actuators B 2001, 72, 75.
37. De Marcos, S.; Alcubierre, N.; Galban, J.; Castillo, J. R. Anal Chim Acta 2004, 502, 7.
38. Prasad, G. K.; Radhakrishnan, T. P.; Sravan Kumar, D.; Ghanashyam Krishna, M. Sens Actuators B 2005, 106, 626.
39. Palaniappan, S.; Amarnath, C. A. U.S. Pat. 6,942,822 (2005).
40. Chabukswar, V. V.; Pethkar, S.; Athawale, A. A. Sens Actuators B 2001, 77, 657.
41. Hu, H.; Trejo, M.; Nicho, M. E.; Saniger, J. M.; Garcia-Valenzuela, A. Sens Actuators B 2002, 82, 14.
42. Koul, S.; Chandra, R.; Dhawan, S. K. Sens Actuators B 2001, 75, 151.
43. Taka, T. Synth Met 1993, 57, 5014.
44. Yang, L. Y.; Liau, W. B. Mater Chem Phys 2009, 115, 28.
45. Hatchett, D. W.; Josowicz, M.; Janata, J. J Phys Chem B 1999, 103, 10992.
46. Blackwood, D.; Josowicz, J. J Phys Chem 1991, 95, 493.
47. Janata, J. Principles of chemical Sensors; Plenum publishing corporation: New York, 1989.