EFFECT OF HYDROXYL CONCENTRATION ON CHEMICAL SENSITIVITY OF POLYVINYL ALCOHOL/CARBON-BLACK COMPOSITE CHEMIRESISTORS

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ABSTRACT

The sensitivity and selectivity of polyvinyl alcohol (PVA) / carbon black composite films have been found to vary depending upon the hydroxylation percentage ("-OH") of the polymer. These chemiresistors made from PVA films whose polymer backbone is 88% hydroxylated (PVA88) have a high sensitivity to water, while chemiresistors made from PVA75 have a higher sensitivity to methanol. The minor differences in polymer composition result in films with different Hildebrand solubility parameters. The relative responses of several different PVA-based chemiresistors to solvents with different solubility parameters are presented. In addition, polyvinyl acetate (PVAC) films with PVA88 are used in an array to distinguish the responses to methanol-water mixtures.

INTRODUCTION

Commercial humidity sensors are often imprecise especially at low concentrations of water vapor. Many polymer-based humidity sensors suffer from interference from other chemicals such as methanol or ethanol. Recently several research groups have studied different types of polyvinyl alcohol (PVA) based humidity sensors, ranging from capacitive or ionically conducting [1-3] to electronically conducting [4,5] films. Such a polymer is a good choice for humidity sensing due to its polar nature and ability to form strong hydrogen bonds to absorbed water [6]. Some of the previous work with PVA-based humidity sensors has shown poor sensitivity at low concentrations of H_2O [1,2], while other research, using a carbon-loaded polymer-composite, has shown high sensitivity, but very slow response [4]. Most of these studies have not addressed the problem of cross sensitivity or interference from other similar chemicals, such as methanol and ethanol. We have developed quick responding, highly sensitive PVA-based chemiresistors (carbon-loaded polymer-composites). In this paper we will explore the effect of hydroxyl content in polyvinyl alcohol chemiresistors and the relative sensitivity of these polymers to chemicals other than water. Furthermore, we will present a method for distinguishing water from mixtures of methanol or ethanol and water, using pattern recognition techniques.

EXPERIMENTAL

The polymer films used as chemiresistors were deposited on a platform consisting of platinum electrodes with a titanium adhesion layer, on a silicon wafer with a 100 nm

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silicon nitride layer. The platinum electrodes were arranged in a four-point-probe configuration, with two inner and two outer electrodes. Devices were made with an inner electrode spacing of either 100 or 50 microns, and the electrodes were 6 mm in length. The electrodes were connected to large pads for external electrical contact. This 4-terminal resistance measurement of the chemiresistor films is a method by which the bulk resistance can be separated from the contact resistance. Such contact resistance arises from poor adhesion of the polymer to the Pt electrodes.

The carbon-loaded polymers were made by dissolution of both the polymer and a particular weight percent (e.g., 40 wt. % is designated by "-40-C") of graphitized carbon particles (20 - 30 nm diameter, Polysciences, Inc.) in a solvent such as water or chlorobenzene. Typically, 0.1g of solids (polymer plus carbon particles) were dissolved in 5ml of solvent. The polymers used were polyethylene (PE, 125,000 MW), polyvinylacetate (PVAC, 500,000 MW), polyethylene vinylacetate co-polymer (PEVA, 82% ethylene), and polyvinyl alcohol (PVA) that was 75% (PVA75, 3,000 MW), 78% (PVA78, 2,000 MW), 88% (PVA88, 25,000 MW), 98% (PVA98, 25,000 MW) and 100% (PVA100, 115,000 MW) hydroxylated. All polymers were purchased from either Polysciences, Inc. or Scientific Polymer Products, Inc. Company. The carbon loading typically ranged from 25 to 60 wt. %. The composite films were deposited on substrates by either spin casting or pipetting the dissolved material directly onto the substrate. Spin-casting was performed at 3000 rpm for 30 seconds to yield approximately a 200 – 400 nm thick film. [5,7]

The sensors were placed in a test fixture that was attached to a gas manifold that had the capability of mixing several gases as well as two solvent vapor streams using nitrogen as the carrier gas through gas washing bottles ("bubblers"). A detailed description of the flow system and resistance measurements is presented elsewhere [5,7]. The analytes tested include water, methanol, ethanol, dimethylformamide, dimethylmethylphosphonate, diisopropylmethylphosphonate, acetone, trichloroethylene, toluene, m-xylene, cyclohexane, and isooctane.

Mass flowmeters were used to control the composition of the gas streams, and a constant total flow rate of 1000 cm^3/min was used for all experiments. The test fixture was placed in a constant temperature chamber, which could be controlled to ± 0.1°C and heated to 60°C. A digital multimeter (7.5 digit resolution) was used to measure the composite-film resistance. The flow stream was then split into six parallel branches, with each branch directing flow over a different sensor in the test fixture.

RESULTS AND DISCUSSION

A set of experiments performed with all sensors was the sequential exposure of the sensors to 10% P/P_{sat} of each of the twelve solvents listed above. The relative response of 4 different sensor films, to 12 solvents, is presented in Figure 1. The data is equalized such that each sensor's maximum response is equal to 1. The figure shows the responses in the order of increasing (left to right) Hildebrand solubility parameter. The more polar solvents such as ethanol, methanol, and H_2O appear on the right side of the plot. Two main results are made obvious by such a plot. First, the films with polar groups (acetate or alcohol) are significantly more sensitive to polar solvents than the PE

or PEVA films. Second, the different hydroxyl concentrations on the PVA polymers have different relative sensitivities to water, methanol, and ethanol. Figure 2 shows this result for the films with significant humidity sensitivity in greater detail. The relative responses of several different sensors to P/P_{sat} = 10% of ethanol, methanol, and water at 23°C are presented with all responses normalized to each sensor's water response. The PVA88 sensor has the greatest relative sensitivity to water over both ethanol and methanol, whereas a film such as PVA75 is somewhat more sensitive to methanol than water and much less sensitive to ethanol than either methanol or water. The high hydroxyl concentration films (PVA98 & PVA100) are less selective, in general, but still slightly more sensitive to water. This is perhaps due to the high hydrogen bonding character in these films. These films were very difficult to dissolve initially due to the strong internal hydrogen bonding between the polymer chains.

In comparison to the PVA films, the relative response of a commercial humidity sensor (Humicap from Vaisala) is also presented. The Vaisala humidity sensor is a polymer-based device that requires an AC impedance or capacitance measurement. The PVAC film and commercial humidity sensor are both more sensitive to methanol than water. Results such as these are important when considering the effects of interfering solvent species on the overall performance of any sensor.

The response of a PVA88-40-C sensor and a PVAC-25-C sensor to binary mixtures of water and methanol are presented in Figure 3. From the data in this plot, called a training data set, one can distinguish the concentrations of both the water and methanol in mixtures. The concentration levels of new or unknown mixtures of water and methanol may be correctly identified using interpolation from the known training data set. Data sets such as this may be collected for different mixtures of chemicals for use with pattern recognition algorithms. Other combinations of sensors can be used similarly to distinguish different solvent-water mixtures.

CONCLUSIONS

Polymer composite films containing carbon black and polyvinyl alcohol, with varied percentages of hydroxyl groups on the polymer backbone, have been found to have different relative sensitivities to ethanol, methanol, and water depending on the polymer composition. The differences in polymer composition are used to form arrays of sensors with different solubility parameters, which in turn can be used to sense a wide variety of chemicals. PVA88 and PVAC sensors were used to make a sensor array that could distinguish mixtures of methanol and water.

ACKNOWLEDGEMENTS

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

REFERENCES

[1] M. Yang and K. Chen, *Sensors and Actuators B*, **49**, 240 (1998).

[2] H. Wang, C. Feng, S. Sun, C. U. Segre, and J. R. Stetter, *Sensors and Actuators B*, **40**, 211 (1997).

[3] K. Ogura, M. Kokura, and M. Nakayama, *J. Electrochem. Soc.*, **142**, L152 (1995).

[4] J. Barkauskas, *Talanta*, **44**, 1107 (1997).

[5] R. C. Hughes, M. P. Eastman, W. G. Yelton, A. J. Ricco, S. V. Patel, and M. W. Jenkins, in *Tech. Digest of the 1998 Solid-State Sensor and Actuator Workshop*, Hilton Head Isl. p. 379, Transducers Research Foundation, (1998).

[6] J. Krzeminski and H. Molisak-Tolwinska, *J. Macromol. Sci.-Chem.*, **A28**, 413 (1991).

[7] S. V. Patel, M. W. Jenkins, R. C. Hughes, W. G. Yelton, and A. J. Ricco, "Differentiation of Chemical Components in a Binary Solvent Vapor Mixture Using Carbon/Polymer Composite-Based Chemiresistors," in preparation.

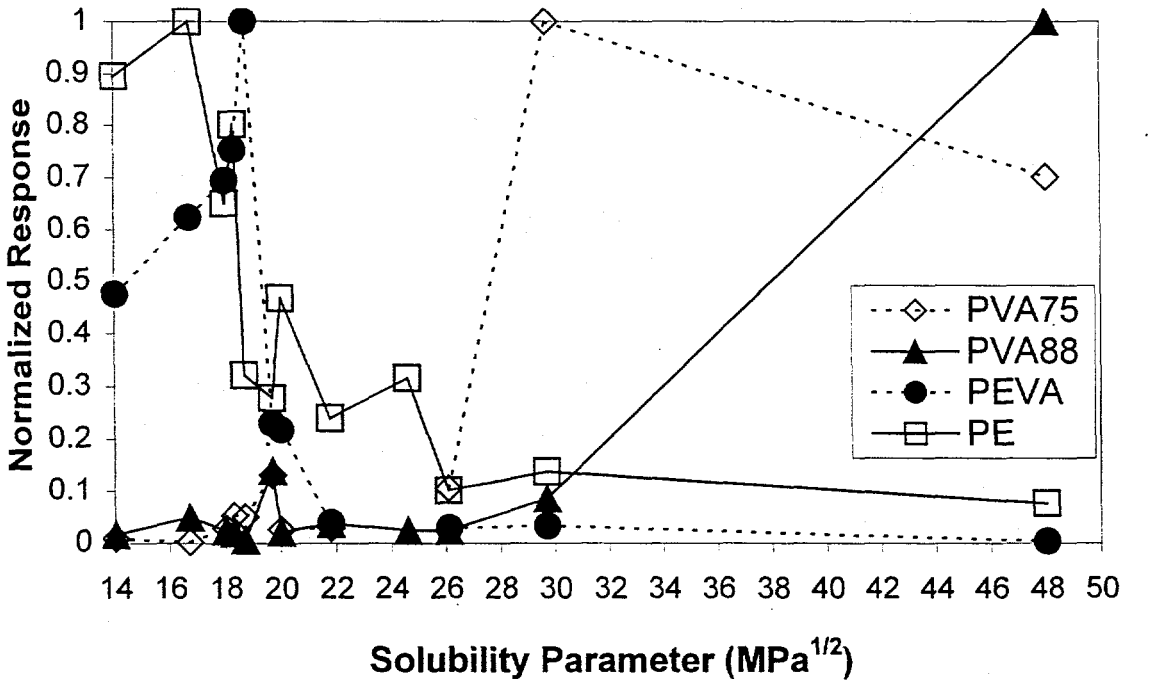

Figure 1: Response of PE, PVA75, PEVA, and PVA88 sensors to vapors from 12 solvents (P/P_{sat} = 10%) versus solubility parameter.

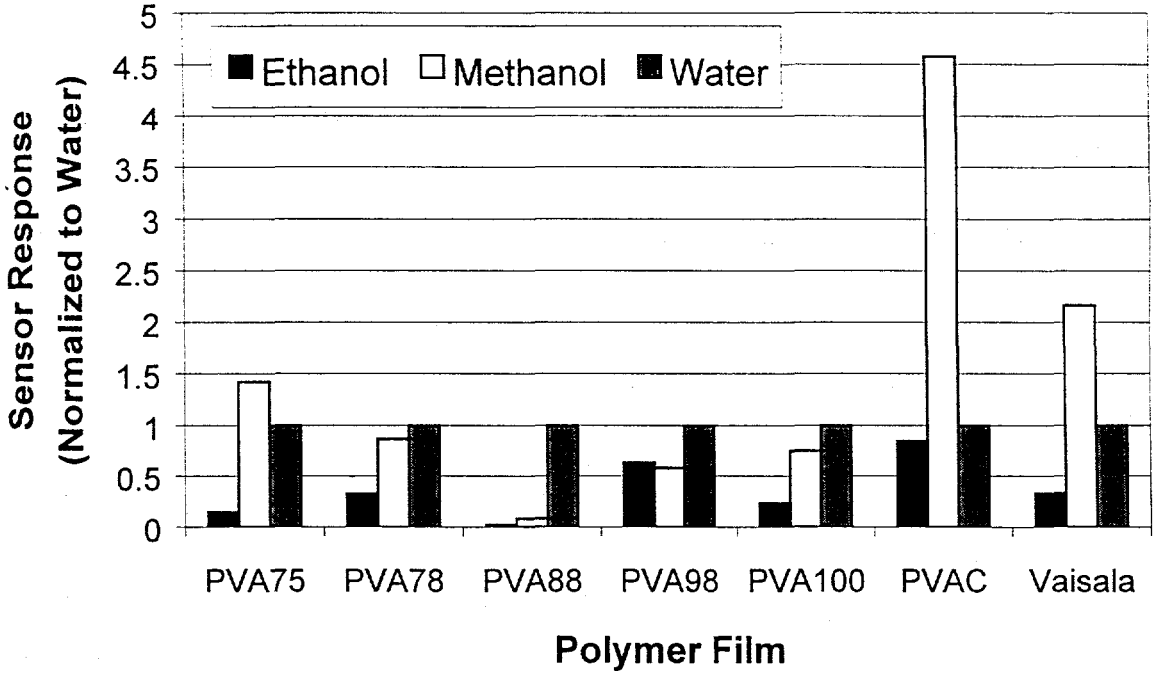

Figure 2: Response of several sensors to ethanol and methanol normalized to water response. The relative selectivity to water or methanol depends on the % hydroxylation of the PVA films. PVA88 has the highest selectivity to water, while the PVAC and Vaisala sensors have the highest selectivity to methanol.

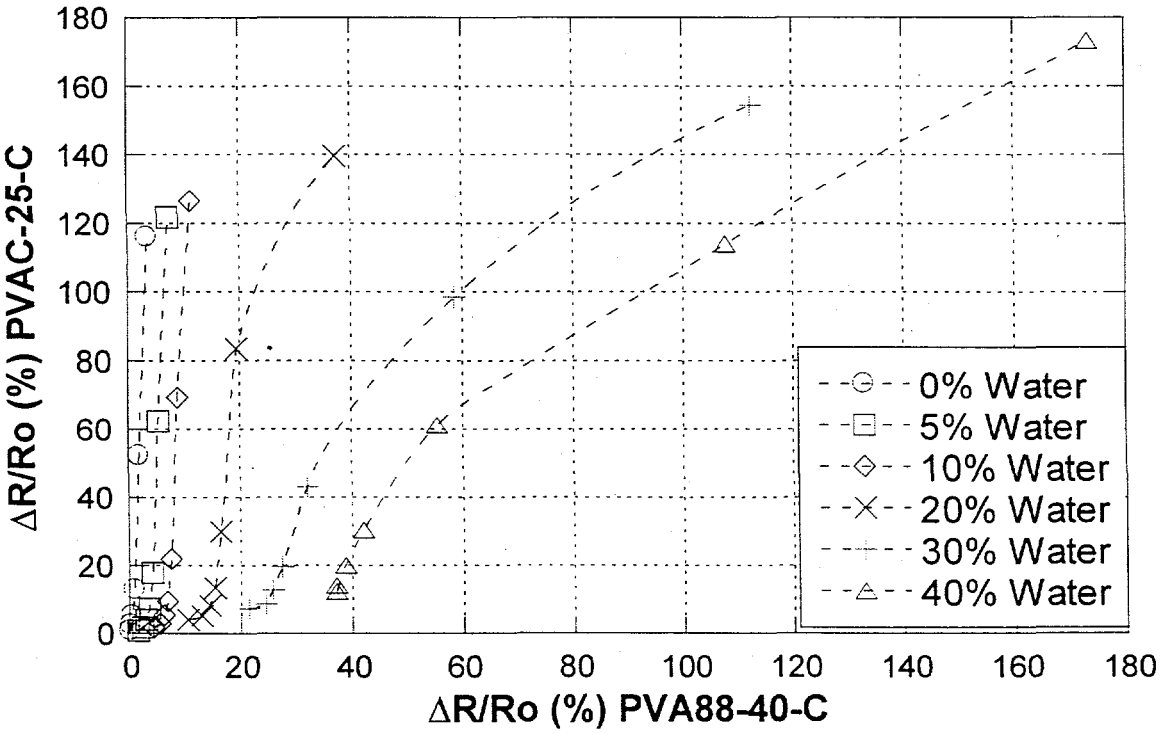

Figure 3: Binary plot of training set data for PVA88-40-C and PVAC-25-C sensors at 22°C. The solvents were H_2O {P/P_{sat} = 0, 5, 10, 20, 30, 40%} and methanol {P/P_{sat} = 0, 1, 3, 5, 10, 20, 30%}.

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Key words:

Hydroxyl
Chemical sensor arrays
Polyvinyl alcohol
Carbon-black polymer-composite
Chemiresistors
Solubility parameter
Humidity