Conductive polymer-coated fabrics for chemical sensing

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Abstract

A novel sensing format for the detection of toxic vapors is presented. It uses thin films of conductive polymers, polypyrrole or polyaniline, coated onto poly(ethylene terephthalate) or nylon threads woven into a fabric mesh. Chemical sensing on fabrics offers the opportunity of using the large surface area for improved sensitivity and expanded dynamic range. The resistivity of these materials was monitored following exposure to several toxic gases. Detection limits in parts per million (ppm) were demonstrated for various pollutants and chemical warfare simulants, including dimethyl methylphosphonate (DMMP), ammonia, and nitrogen dioxide. The effect of humidity on the detection capabilities of these materials was also characterized. Polymeric overcoats including polyethylenimine and fluoropolyol were evaluated as a means of introducing selectivity and sensitivity with respect to the adsorption of particular classes of gas analytes.

Keywords: Fabric; Sensors; Dimethyl methylphosphonate; Polypyrrole

1. Introduction

Conductive polymers have made a significant impact upon a number of different technologies since their introduction over twenty years ago. Applications range from optical and electrical devices (photovoltaics, transistors, batteries, etc.) to antistatic packaging and various coating applications (membranes, shielding, etc.) [1]. More recently, conductive polymers have been utilized as an effective medium for chemical sensing. A variety of conductive polymers have been evaluated using microelectronic devices, such as chemiresistors (interdigitated array transducers), quartz crystal microbalances (QCMs) and field-effect transistors (FETs). Examples of these studies include that of Kunugi et al. who utilized a specially modified QCM for making electrical and microgravimetric measurements of the uptake of alcohols onto polypyrrole thin films [2], and of Josowicz and Janata who investigated the measurement of work function changes using a polypyrrole-coated FET for the detection of lower aliphatic alcohols [3]. Several companies, including Neotronics [4] and AromaScan [5], manufacture 'electronic noses' comprised of arrays of chemiresistor-based conductive polymer sensors. Conductive polymers are an effective medium for chemical sensing, based upon electronic changes arising in the polymeric films with the gas-phase adsorption

of electronically active vapors. The conductivity changes observed in these polymers are commonly attributed to the interaction of electronically active analytes with either the polymer backbone itself or the dopant molecules incorporated within the film, thereby modulating the mobility and/or the number of free charge carriers available.

We are currently investigating a novel sensing format for conductive polymers, utilizing poly(ethylene terephthalate) or nylon threads which are uniformly coated with conductive polymers, polypyrrole or polyaniline, and then woven into a fabric mesh. The polymers are coated onto the fiber filaments by an in situ solution polymerization process that is based on oxidative coupling of the monomer species and simultaneous incorporation of the dopant [6]. This permits the controlled growth of relatively thin films of conductive polymers on fabric with conductivities that (i) are uniform over the length of the material, (ii) can be varied over a wide range of values, (iii) are stable over long time periods, and (iv) combine the electrical properties of the polymer coating with the mechanical properties of the fabric. Applications reported for these materials range from radar absorbing and edge-card materials to antistatic and resistive heating applications [7].

Chemical sensing on fabric has the potential for providing the following advantages over the use of microelectronic devices: (i) potential low cost and low operating power; (ii) commercial availability of the coated fabric; (iii) expected wide dynamic range due to the large surface area of a con-

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ductive polymer-coated piece of fabric; (iv) ease of measurement; and (v) demonstrated stability of the conductivities of coated fabrics. The US Navy is interested in the development of sensitive detectors capable of detecting low ppm levels of toxic gases as a warning device for the protection and safety of personnel operating under hazardous conditions. In parallel with this need is the requirement that these devices be inexpensive, compact, and simple to operate, features which we hope to incorporate within a fabric-based sensor device.

2. Experimental

2.1. Conductive polymer-coated fabrics

Unless mentioned otherwise, all fabrics were used as received from the manufacturer. The conductive polymer-coated fabrics were acquired from Milliken Research Corporation and included (i) polypyrrole on a 150 denier poly-(ethylene terephthalate) (PET) doped with naphthalene-disulfonic acid (NDSA) – available resistivities included 211, 775, and 3000 Ω/cm^2; (ii) polypyrrole on a 150 denier PET doped with anthraquinone-2-sulfonic acid (AQSA) – resistivity 129 Ω/cm^2; (iii) polypyrrole on an 840 denier nylon doped with NDSA – resistivity 100 Ω/cm^2; and (iv) polyaniline on a 150 denier PET doped with Cl^- – resistivity 75 Ω/cm^2. For all chemical sensing experiments, a 12 cm square piece of fabric was cut from a sheet of the conductive polymer-coated fabric, and a thin line of silver paint (Alfa Aesar) was applied to opposite ends of the fabric and allowed to dry. An additional small amount of silver paint was then

utilized for making an electrical connection between a Teflon-coated wire and the opposing sides of the fabric. After drying overnight, the fabric swatches were placed within the testing apparatus and allowed to equilibrate in a stream of dry air.

2.2. Apparatus and instrumentation

A diagram of the experimental configuration employed for examining the chemical sensing characteristics of the coated fabric materials is shown in Fig. 1. Four fabric swatches could be examined simultaneously by positioning them within a Teflon (PTFE, Du Pont) support containing four exposure holes (2 cm in diameter). The Teflon support was contained within a 0.5 liter glass chamber which held a set of baffled Teflon discs at the front and back of the chamber in order to promote laminar flow across the fabric surface. Air flow within the testing chamber was maintained using Matheson model 8200 series mass flow controllers at a constant flow rate of either 1 or 10 l/min. Given a cross-sectional area of 23.8 cm^2, the face velocities were calculated to be between 42 and 420 cm/min (1.4–14 ft/min), velocities that closely approximate exchange rates in typical indoor environments. Gas standards containing 450 ppm NH_3 in N_2 and 1053 ppm NO_2 in N_2 were obtained from Matheson, Inc. and Potomac Airgas, Inc., respectively. Dimethyl methylphosphonate (DMMP) was acquired from Aldrich, Inc., and placed within a bubbler held at a constant temperature of 15 °C using a temperature-controlled water bath manufactured by GCA, Inc. Previous studies have calibrated the DMMP bubbler to generate about 2960 mg of DMMP per m^3 while being maintained at this temperature [8]. Humidity was controlled via the use of bubblers and line mixers, and measured using a
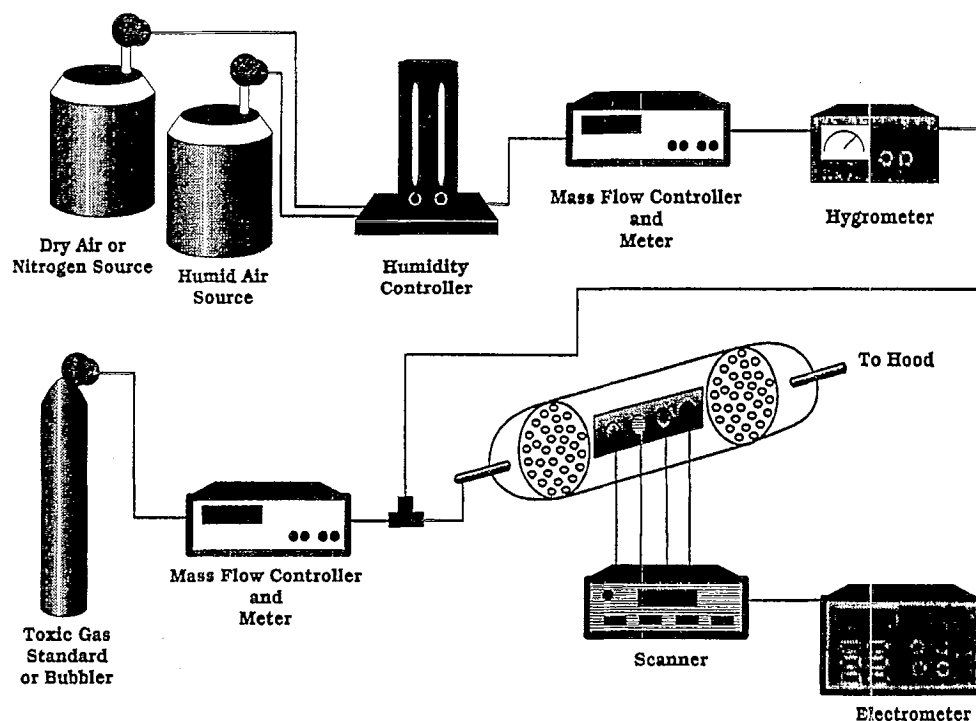

Fig. 1. Diagram of the flow cell chamber utilized for simultaneously characterizing the response of four different conductive polymer-coated fabrics to gas vapors.

Hygrodynamics hygrometer. All resistivity measurements were made using a Keithley 617 programmable electrometer (at an applied potential of 0.0946 V) and a Keithley 705 scanner which enabled the sequential sampling of the resistivity for each of the conductive polymer-coated fabrics held within the testing chamber. National Instruments' LabView for Windows controlled the data acquisition across an AT-GPIB interface board.

Analytical characterization of the fabric weaves was undertaken to improve our understanding of the film's interfacial properties. X-ray photoelectron spectroscopy (XPS) measurements were conducted using a Surface Science spectrometer. The XPS spectra were collected using Al Kα nonmonochromatized radiation and a hemispherical analyzer in the analyzer's constant-energy mode with a pass energy of 20 eV. A Hitachi field-emission scanning electron microscope (SEM) operating at an electron voltage of 20–25 kV was used to obtain images of the conductive polymer-coated fabrics. Because of the conductive properties associated with these fabric weaves, it was not necessary to generate an electrically conductive overcoat. Thermogravimetric analysis (TGA) was performed in air using a Perkin-Elmer TGA-7 analyzer under both isothermal (300 °C) and scanning conditions (10 °C/s).

2.3. Polymer bilayer deposition

Polymeric overcoats were deposited on the conductive polymer-coated fabrics by either spraying or dip-coating. Polyethylenimine (PEI) was obtained from Phase Separations, Inc. and polyisobutylene (PIB) from Aldrich, Inc. Fluoroalcoholpolysiloxane (SXFA, or 1-(4-hydroxy-4-trifluoromethyl-5,5,5-trifluoro)pentenemethylpolysiloxane) was prepared and donated by Dr Andrew McGill of Geo-Centers, Inc. [9]. Fluoropolyol (FPOL), an oligomer, was synthesized in-house by Dr Jim Griffith of the Naval Research Laboratory according to the following structure:

$$[CH_2CH(OH)CH_2OC(CF_3)_2(C_6H_4)C(CF_3)_2OCH_2$$

$$CH(OH)CH_2OC(CF_3)_2CH_2CHCHC(CF_3)_2O]_n$$
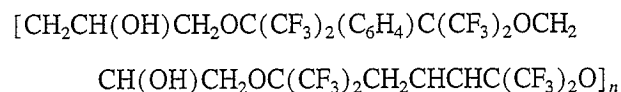
where $n = 5–10$ [10]. For those films prepared by spray-coating, a Badger model 200-3 air brush was used to exhaustively spray 15 ml of a 0.7% solution of the polymer dissolved in chloroform onto the fabric swatch. For those films prepared by dip-coating, 33% FPOL and 11% SXFA solutions were prepared in butyl acetate, with the polymer uptake by the fabric being monitored gravimetrically. In order to drive off any excess solvent, the dip-coated fabrics were pumped under dynamic vacuum (1 mm Torr) at 50 °C for 24 h.

3. Results and discussion

3.1. Conductive polymer-coated fabric characteristics

The conductive polymer-coated fabrics used in this study consisted of woven fiber filaments coated with conductive

polymer overlayers, grown by chemical polymerization or oxidative coupling of the monomer, pyrrole or aniline. The dopant anion, e.g. naphthalenedisulfonic acid (NDSA), anthraquinone-2-sulfonic acid (AQSA) or Cl⁻, was simultaneously incorporated into the polymer chain, giving the polymer network its conductivity. As will be alluded to later, the high levels of doping apparent in conductive polymers (10%–30%) make the dopant anion an important consideration in defining the sensor response of each polymer-coated fabric.

SEM images taken of the fabric weaves demonstrate the pristine nature of the chemically grown polymeric films. A SEM image taken of a NDSA-doped polypyrrole film on PET using an electron voltage of 20 kV and a magnification of 500 is shown in Fig. 2. The chemical deposition of the polypyrrole results in a smooth even overlayer on the PET thread, although regions do exist where the polymer aggregated during polymerization. The fabric weave consists of a series of overlapping conductive polymer-coated threads, which results in a much more complicated chemical sensor substrate than that found for films grown on chemiresistor devices, quartz crystal microbalances or field-effect transistors, for example. If we presume that the conduction process in polypyrrole and polyaniline operates according to a p-type hole-hopping mechanism, the conduction path for a single hole might be expected to traverse several threads. The swelling of conductive polymers due to gas analyte adsorption will generate considerable changes in the transport pathways of free charge carriers within these films.

TGA was performed on several fabric weaves in order to assess the relative thermal stability of the conductive polymer coatings on the PET thread. A scanning TGA of PET and polypyrrole-coated PET fibers in air is shown in Fig. 3. The

033011 20KV X500   60 μm

Fig. 2. SEM image of a NDSA-doped polypyrrole film on PET depicting the nature of the fabric weave and the character of the conductive polymer coating.
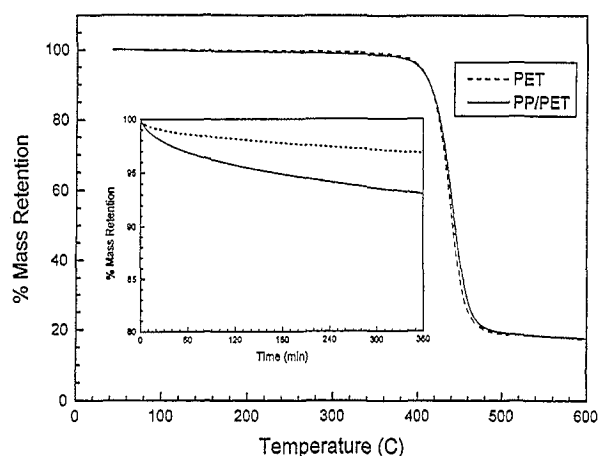
Fig. 3. Scanning TGA of PET fibers (broken line) and polypyrrole-coated PET fibers (solid line). Inset is an isothermal TGA (300 °C in air) of the same types of threads.

Fig. 4. Change in resistivity seen for a NDSA-doped polypyrrole film on PET on exposure to 29.4 ppm NH_3(g) and 50.1 ppm NO_2(g) in dry air.

degradation curves for these two materials are essentially identical, maintaining nearly 100% mass retention up to 380 °C, before dropping off over the course of 100 °C and leveling off at about 20% mass retention above 500 °C. An isothermal TGA (300 °C in air) for a similar set of PET and polypyrrole-coated PET fibers is shown in the inset of Fig. 3. In this plot, we can differentiate the loss mechanisms apparent in PET from those of the polypyrrole overcoat. The thermal stability of these films suggests the possibility of utilizing temperature as an additional parameter for improving selectivity and recovery time in fabric-based chemical sensors.

3.2. Fabric response to NH_3(g) and NO_2(g)

The conductive polymer-coated fabric weaves were initially exposed to ppm levels of NH_3(g) and NO_2(g) in order to assess the responsivity of these materials to toxic gases known to interact electronically with conductive polymer thin films. A plot of the change in resistivity for a NDSA-doped polypyrrole film on PET upon the introduction and cessation of 29.4 ppm NH_3(g) and 50.1 ppm NO_2(g) in a stream of dry air is shown in Fig. 4. For NDSA-doped polypyrrole films on fabric, ammonia resulted in an increase in the resistivity which was nearly linear with time and essentially irreversible, while nitrogen dioxide caused a monotonic decrease in the resistivity which was reversible in its response. The fabric shown in Fig. 4 was found to be nearly 14 times more sensitive to the detection of ammonia than nitrogen dioxide,
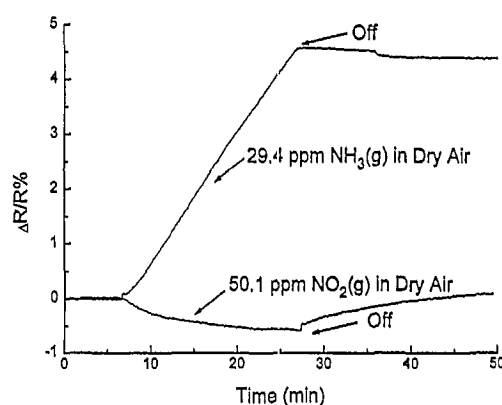
although both have demonstrated responses in the low ppm regime.

Because conductive polymers are generally acknowledged to exhibit behavior which is in accordance with p-type conductive materials, it is reasonable to expect that NH_3(g), a strong reductant, will result in a decrease in the conductivity due to the elimination of free hole charge carriers, while NO_2(g), a strong oxidant, will cause an increase in the conductivity due to the formation of additional free hole charge carriers within the film. It has been postulated that the parameters of interest in determining the direction and magnitude of a conductivity change within a conductive polymer film are the intrinsic work functions of the analyte vapor and the doped conducting polymer [11,12]. This simplistic model can be utilized as a starting point for understanding the conductivity behaviors evident in the conductive polymer-coated fabrics, but a more comprehensive model is necessary in order to explain the various responses observed for each of the different fabrics and gases examined.

Table 1 summarizes the $\Delta R/R$ percent changes measured for four different conductive polymer-coated fabrics upon exposure to the various gases examined in this study. The first two fabric weaves consisted of the same dopant and conductive polymer type (PP/NDSA), differing only in the thread substrate (PET or nylon). The third fabric also consisted of polypyrrole on PET, but in this case the dopant was AQSA. The final material was woven from PET fibers coated with Cl^--doped polyaniline. Focussing on the results obtained for NH_3(g) and NO_2(g), we note that the direction of the resistivity changes matched the expected responses,

Table 1
Effect of conductive polymer type, dopant, and substrate thread on measured sensitivity to various gas vapors

Fabric type	$\Delta R/R$ (%)				
	Dry air	29 ppm NH_3	69 ppm NO_2	28 ppm DMMP	H_2O 60% rel. humidity
PP/NDSA/nylon	0.23	1.76	−0.50	−0.40	−6.36
PP/NDSA/PET	0.55	3.82	−0.45	−0.31	−8.92
PP/AQSA/PET	0.42	1.13	−0.27	−0.35	−4.26
PAN/Cl^-	0.17	7.41	13.7	−0.09	−107.6

with the exception of the Cl^--doped polyaniline on PET fabric's response to $NO_2(g)$. This discrepancy may arise from a direct interaction of $NO_2(g)$ with the dopant anion (Cl^-), wherein the localized binding of electrons to the adsorbed nitrogen dioxide molecule hinders the generation of free hole charge carriers within the film. A final point to be made is that, of the two dopants utilized for the polypyrrole films, NDSA and AQSA, NDSA yielded the largest signal with respect to the detection of $NH_3(g)$ and $NO_2(g)$.

In order to achieve a better understanding of the electronic interactions taking place in the near-surface region of these conductive polymer-coated fabrics, we must also consider the role $O_2(g)$ plays in defining the conductivity of these materials. For each of the fabric weaves investigated, the introduction of pure $O_2(g)$ (1 l/min) to a film equilibrated in an inert atmosphere of nitrogen resulted in a small but steady increase in the resistivity that leveled off after several hours of exposure ($\sim 2\%$). Under normal atmospheric conditions (20% oxygen levels), we can expect that the surface of these fabric swatches will be electronically perturbed by the chemisorption of oxygen onto the surface of the conductive polymer. Because of this interaction, an additional factor to consider in assessing the resistivity changes observed in these materials is the displacement of weakly chemisorbed $O_2(g)$ molecules by competing analytes within the air stream – a displacement which naturally causes a resultant decrease in the resistivity of the film. In addition to the reversible response of oxygen within the surface of these fabric weaves, there is a slow irreversible decay in the conductivity which has been linked to the degradation of the conductive polymer via a reaction between oxygen and the polymer backbone that gives rise to the formation of nonconjugated moieties [13].

3.3. Influence of humidity on conductivity

As expected, humidity strongly influences the conductivity level apparent in the conductive polymer-coated fabric weaves, and, as is the case with the majority of chemical sensors, it is a parameter which must be dealt with in developing a reliable sensor device. With the exception of the Cl^--doped polyaniline on PET fabric, where only a decrease in the resistivity was reported, for each of the materials studied a dual response in the resistivity to increasing levels of humidity was reported. Fig. 5(a) illustrates the change in resistivity seen for a NDSA-doped polypyrrole film on PET upon the introduction and equilibration of two increasing levels of humidity, 14% and 29%. When the fabric's environment was changed from a stream of dry air to a stream of humid air, the resistivity underwent a rapid decrease, followed by a slow but steady decline for hours. Following equilibration, the resistivity increased slightly for all subsequent increases in the humidity. This dual response to humidity is mirrored in the resistivity changes seen for the conductive polymer-coated fabrics following a switch from a humid carrier stream to dry air (see Fig. 5(b)). As expected, the immediate
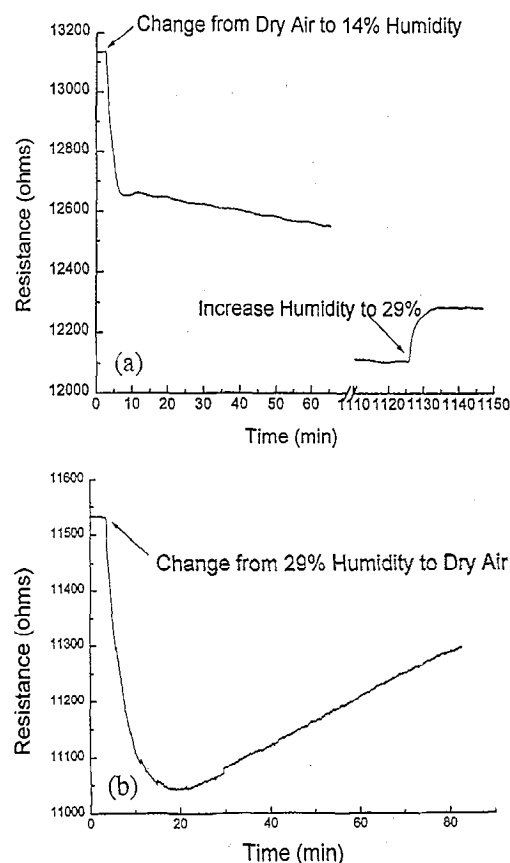

Fig. 5. Effect of humidity on a NDSA-doped polypyrrole film on PET following (a) step increases in the relative humidity from 0% to 14%, ending with an increase to 29%; (b) a return to dry air for a film equilibrated in 29% relative humidity.

response is a dramatic decrease in the resistivity, which is followed shortly by a gradual increase.

This dual response to humidity is likely attributed to two different interactions of water with the conductive polymer coating. The initial interaction may be attributed to the hydrogen bonding capability of water to interact with either the polymer backbone itself or with the donor molecules interspersed within the film. The polarization of electronic charge toward the adsorbed water molecule will result in the generation of additional free hole charge carriers which cause a net decrease in the resistivity. As the concentration of humidity increases above 15%, however, the conductive polymer likely begins to swell as more and more water is absorbed by the polymeric network. Swelling in conductive polymers causes an increase in the resistivity due to an overall increase in the mean free path followed by free hole charge carriers within the polymeric thin film. Swelling has been reported to cause similar effects for polypyrrole films exposed to different organic vapors [14]. Charlesworth et al. have presented a different explanation for the observed increase in resistivity, which is based upon the dielectric constant of the absorbed solute [15]. As the intrinsic dielectric constant of the adsorbed analyte increases, there is a concomitant decrease in the rate of hopping for charge carriers contained within the polymeric film, because of a decrease in their mobility.

The magnitudes of the negative resistivity changes recorded upon the introduction and equilibration of 60% humidity for several different fabric materials are shown in Table 1. As was mentioned previously, the Cl^--doped polyaniline on PET responded to increasing humidity levels with monotonic decreases in the resistivity. In addition to lacking the dual response reported for the polypyrrole-based fabrics, the polyaniline-coated fabric was more than 10 times as sensitive to humidity. We are currently pursuing this material for the detection of trace levels (ppm) of water vapor.

3.4. Response to chemical warfare agent simulant (DMMP)

In order to investigate the feasibility of using the electroactive polymer-coated fabric materials for the detection of chemical warfare agents, a series of experiments was designed to examine the responsivity of the fabrics to an organophosphonate chemical warfare agent simulant, dimethyl methylphosphonate (DMMP). A typical response curve obtained for the introduction of 28 ppm DMMP in dry air to a NDSA-doped polypyrrole on PET fabric is shown in Fig. 6. DMMP interacts electronically with the polymer, generating a resistivity drop that is responsive in the low ppm regime. Apparently, DMMP interacts with the conductive polymer to increase the quantity of free and mobile hole charge carriers. Kolesar reported a similar conductivity response for copper phthalocyanine exposed to diisopropyl methylphosphonate (DIMP) [16]. The response observed for the fabric materials is reversible and somewhat dependent upon the dopant and conductive polymer type, as well as the substrate material (see Table 1). The chloride-ion-doped polyaniline was not nearly as sensitive to DMMP, despite having responded so well to the other vapors studied here.

Because of the success achieved with the NDSA-doped polypyrrole fabric for the detection of DMMP, attention was focussed upon tuning the properties of the conductive polymer to improve our detection capabilities. More specifically, the effects of film thickness on response time and responsivity to DMMP were examined in a set of three different NDSA-doped polypyrrole on PET fabrics (Table 2). The three mate-
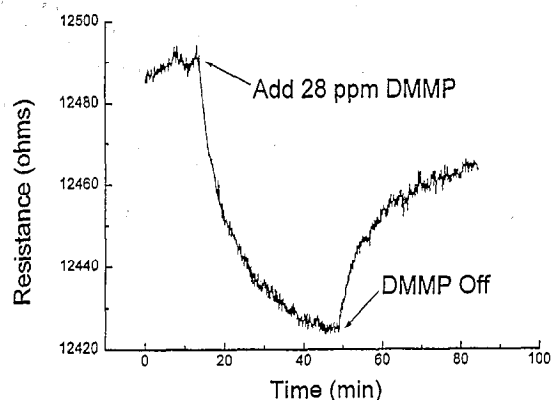
Table 2
Effect of conductive polymer thickness (or resistivity) on sensitivity and response time

Fabric resistivity for PP/NDSA on PET (Ω/cm^2)	Exposure to 28 ppm DMMP in dry air	
	Resistivity change (signal/noise)	Initial response slope $((-\Delta R/\Delta t)/\text{noise})$ (1/min)
211	8.7	0.65
775	59.4	3.53
3000	50	8.42

rials differed according to their inherent surface resistance, a factor which was not a feature of the extent of doping, but rather a measure of the film thickness. Qualitatively, the thickness of the conductive polymer films decreased in the order $3000 > 775 > 211$ Ω/cm^2. Examining first the magnitude of response to the introduction of 28 ppm DMMP in dry air, we found that the best signal-to-noise ratio was attained for the 775 Ω/cm^2 film, although the 3000 Ω/cm^2 was nearly as sensitive. The speed of response, however, was most rapid in the 3000 Ω/cm^2 film, as evidenced by the initial response slope recorded upon the introduction of DMMP. We attribute this result to the presence of a thinner film on the fiber surface which emphasizes the importance of electrical interactions in the near-surface region and, therefore, responds very rapidly to the adsorption of DMMP. In addition, the mobile charge carriers generated by the adsorption of a single molecule of DMMP are more easily detected in films possessing lower conductivities. The 775 Ω/cm^2 polypyrrole-coated material was selected for all further investigations as a compromise between response time and having a film thick enough to ensure a reasonable dynamic range.

The response of the conductive polymer-coated fabrics to DMMP within a carrier stream of dry air demonstrated the possibility of utilizing these materials for the detection of ppm levels of chemical warfare agents. Unfortunately, the same sensitivity was not observed for fabrics supported within a carrier stream of humid air. Following equilibration of the material's conductivity within any given humidity, the addition of DMMP failed to generate a measurable change in the resistivity. This was in contrast to the addition of $NH_3(g)$ in humid air, which caused an identical resistivity change in the film to that seen in dry air. Apparently, the chemisorption of DMMP onto the conductive polymer surface is relatively weak, and, as a result, the DMMP is unable to displace water molecules from surface sites which were previously accessible under dry conditions.

3.5. Polymer bilayers

Bilayer films, or polymer coatings deposited onto the surface of the conductive polymer-coated fabrics, were studied for two reasons: to investigate the feasibility of (i) improving sensitivity and selectivity to a given analyte by coating the

Fig. 6. Typical response observed for a NDSA-doped polypyrrole film on PET exposed to 28 ppm DMMP in dry air.

conductive polymer with a sorbent bearing particular functionality groups and properties which favor the adsorption of certain molecules over others, and (ii) depositing a hydrophobic coating on the conductive polymer film which would maintain its responsivity to the analyte of interest while avoiding problems associated with the chemisorption of water vapor onto the conductive polymer surface.

McGill et al. have investigated the sorbent properties of a number of different polymeric coatings, demonstrating their ability to preferentially adsorb particular classes of analytes based upon the functionality groups incorporated within the polymeric backbone [9]. In fact, predictions can be made a priori concerning the type and extent of analyte adsorption into a given polymeric film by elucidating the solvation parameters for the polymer and the analyte (e.g. polarizability, dipolarity, hydrogen bond acidity, hydrogen bond basicity, etc.). FPOL and SXFA, for example, are polymeric materials bearing hydrogen bond acidic groups that promote the sorption of solutes that are hydrogen bond basic. PEI behaves chemically in a complementary fashion, promoting the adsorption of hydrogen bond acidic analytes due to the hydrogen bond basic functionality which constitutes the repeating unit of the polymer chain. PIB, on the other hand, is a nonpolar inert film which is strongly hydrophobic in nature, and whose solubility properties are largely governed by London dispersion interactions. These four films were chosen as coatings for the fabric materials on the basis of the differences in their chemical properties.

As described in the experimental section, two methods were utilized for coating the fabric weaves with a thin film of polymer: spraying and dip-coating. In order to ensure their quality, the deposited films were characterized by XPS and SEM. A SEM image taken of a NDSA-doped polypyrrole film on a PET fabric weave which was dip-coated with 0.33 g/cm³ of FPOL is shown in Fig. 7. We can note, qualitatively, that the deposition results in a smooth film, which coagulates in certain areas, literally connecting two fibers together, as can be seen in this photomicrograph. This type of behavior was never seen in the conductive polymer-coated fabrics prior to deposition of the sorbent polymers. XPS analysis verified the presence of the FPOL coating on the surface of the conductive polymer-coated weave via the loss of the nitrogen 1s electron peak associated with the polypyrrole. The XPS data combined with the SEM analysis indicate the deposition of a smooth overlayer of FPOL which completely coats the polypyrrole underlayer.

Table 3 summarizes the relative resistivity changes recorded for the blank and each of the bilayer films in response to the different gases within a carrier stream of dry air. Although the coated films did not show dramatic changes in their responsivities following bilayer formation, there were some general trends noted which confirmed the theoretical expectations of coating these conductive polymers with sorbent polymers. For example, with regard to the introduction of water vapor (10% humidity), the film exhibiting the largest decrease in resistivity was the PEI-coated film, a polymer

Fig. 7. SEM image of a NDSA-doped polypyrrole film on PET coated with a thin layer of FPOL.

which has demonstrated in surface acoustic wave (SAW) coated devices its ability to absorb more than 3.5 times as much water as FPOL, and 16 times as much water as the hydrophobic PIB-coated devices [17]. The reason for this property is the hydrogen bond basic character of the PEI film which results in a set of linear solvation parameters that encourages the absorption of water, a molecule possessing strong hydrogen bond acidic properties. We expect the PEI-coated fabric to have the largest concentration of water molecules absorbed within its outer coating, and, hence, the greatest possibility for water to interact electronically at the interface between the conductive polymer film and the sorbent polymer coating. In a complementary fashion, if we examine the results obtained for the detection of $NH_3(g)$, we notice that it is the PEI film which exhibits the smallest change in its resistivity. This result can be attributed to the hydrogen bond basic character of PEI, which acts to reject the adsorption of the hydrogen bond basic $NH_3(g)$ molecule. In contrast, the SXFA-coated fabric, which has an outer layer possessing the strongest hydrogen bond acidic character of

Table 3
Impact of sorbent polymer overlayer on sensitivity of conductive polymer − coated fabrics to various gas vapors

Polymer overcoat	$\Delta R/R$ (%)			
	21 ppm NH₃	50 ppm NO₂	28 ppm DMMP	H₂O 10% rel. humidity
PP/NDSA blank	4.33	−0.57	−2.05	−13.3
FPOL coated	3.86	−0.76	−1.96	−12.1
PEI coated	0.12	−0.88	−2.01	−29.4
PIB coated	4.74	−1.90	−0.77	−9.4
SXFA coated	5.03		−0.12	−7.7

all the films, displayed the largest increase in resistivity due to the strong chemical sorption of $NH_3(g)$.

The results obtained for the detection of DMMP did not reflect our expectations based upon the chemical structure of the outer coatings. For the detection of DMMP, a molecule with strongly hydrogen bond basic character, we expected the SXFA- and FPOL-coated fabrics to generate the largest improvements in resistivity changes upon exposure to DMMP. FPOL, for example, has been demonstrated in surface acoustic wave devices to concentrate a factor of 31 times more DMMP than PIB [17]. SXFA coatings have been reported to absorb even more DMMP than FPOL [18]. In contrast to the results obtained using surface acoustic wave devices, however, the worst signal response was observed for the SXFA-coated fabric. There are at least two possible explanations for this result: (i) the functional groups of SXFA interact electronically with the polypyrrole in such a fashion that many of the active sites for communication with the film are eliminated; or, (ii) the SXFA binds so tightly to the DMMP molecules concentrated within the film that the DMMP cannot interact favorably at the polypyrrole/SXFA interface. Further examining the data obtained for the detection of DMMP, we note that the FPOL and PEI films had little to no effect on the response to DMMP, while, as expected, the PIB film caused a decrease in the resistivity change. Despite the presence of these sorbent polymer coatings, humidity still resulted in a complete swamping out of the signal generated by DMMP.

For the detection of $NO_2(g)$, a general trend was observed that appeared to follow theory. The PEI-coated film was more sensitive to $NO_2(g)$ than either the FPOL-coated fabric or the blank, perhaps because of the hydrogen bond basic character of this film and its sorption capabilities for the hydrogen bond acidic $NO_2(g)$ molecule. For reasons which are unclear, the PIB-coated polypyrrole film gave an abnormally large signal to $NO_2(g)$, as well as to $NH_3(g)$. PIB deposits in a porous and incomplete nature in these types of films, so the possibility exists that the $NO_2(g)$ is simply diffusing unperturbed directly through the film to the conductive polymer interface.

4. Conclusions

To the best of our knowledge, this paper demonstrates the first examination into the chemical sensing properties of conductive polymers coated onto woven fabric materials. Low ppm detection limits have been demonstrated for toxic gases such as ammonia and nitrogen dioxide, as well as the chemical warfare simulant, DMMP. The issues hindering the implementation of these fabric materials into a sensor format, however, are several: (i) prevention of a wandering background resistivity associated with the adsorption of water from normal humidity levels present within the atmosphere; (ii) improvements in selectivity to the target analyte; and (iii) enhancement of sensitivity into the ppb level regime.

The bilayer films prepared in this study helped address each of these issues, although they were unsuccessful at completely solving each of the problems.

Because surface modification of the conductive polymer films appears to be the most direct solution, we are currently investigating several different methodologies.

(i) Kepley et al. have established that the deposition of Cu^{2+} ions onto the surface of polymer films introduces a selective and reversible binding site for organophosphonates [19]. In a similar fashion, the deposition of copper salts onto the surface of conductive polymer-coated fabrics may bring about improved sensitivities to DMMP and chemical warfare agents.

(ii) The use of molecular imprints for chromatographic stationary phases has recently become more attractive, and the application of these techniques to conductive polymer-coated fabrics may be an effective route for introducing selectivity into these films [20].

(iii) Utilizing these fabric materials at slightly elevated temperatures may be an effective means of eliminating problems associated with the adsorption of water vapor.

(iv) Instead of preparing bilayer films, we are investigating the preparation of composite films of the conductive polymer and a sorbent polymer in order to improve sensitivity to particular classes of analytes. Freund and Lewis have investigated these types of composite films and had some success in engineering selectivity into them [21].

Ultimately, a selective sensor device will likely require the use of an array of fabric sensors, each tuned for a particular class of analytes. The pattern response obtained from this array can be fed to a microprocessor in order to determine the concentration and identity of the gas being detected. Electroactive polymer-coated fabrics provide a large surface area per unit volume and may be easily engineered into a variety of sensor configurations. The concept of active sensing material on woven polyester fabric may eventually be translated to a wearable light-weight clothing-integrated sensor system.

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