

# LEUCO-EMERALDINE BASED POLYANILINE – POLY-VINYL-PYRROLIDONE ELECTROSPUN COMPOSITES AND BIO-COMPOSITES: A PRELIMINARY STUDY OF SENSING BEHAVIOR

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**Abstract.** The responsive nature of polyaniline (PANI) to gaseous pollutants is highly dependant on the film composition and processing. In initial studies LEB-PANI was used to develop a room temperature sensor for NO<sub>2</sub> detection. It has been observed that the relative response to NO<sub>2</sub> in constant humidity is dependant on the concentration of polyaniline in electrospun films of PANI and poly-vinyl-pyrrolidone (PVP). In subsequent studies analysis of exposed bio-doped PANI/PVP matrices reveal PANI particles self assembling into hollow fibrous structures. In this paper the results from initial efforts for the development of a PANI based bio/chem sensor are discussed.

## 1. INTRODUCTION

The electroactivity of conducting polymers has been extensively studied for use in chemical and biological sensing applications [1-3]. The quality and stability of PANI has been evaluated by many researchers under various processing mechanisms and environmental conditions. There has been and continues to be much research focused on understanding the charge transfer nature of PANI and the requirements of the polymer for operation in various environments: humid air, dry air, under different gas atmospheres, and biological. Prigodin *et. al.* [4] details the charge transport mechanisms for a conducting polymer in its metallic state as a function of temperature. Other authors correlate the charge

transport mechanism to reactions between anions in the doped polymer and protons from water or humidity localized on the film's surface. [5-9].

Typically there are three polymorphs of PANI: leucoemeraldine (insulating), emeraldine (semi-conducting), and pernigraniline (organic metal) with conductivity ranging from 10<sup>-12</sup> Scm<sup>-1</sup> to 10<sup>2</sup> Scm<sup>-1</sup> [10]. The primary structure of PANI consists of benzenoid rings with an imine backbone and quinoid rings with an amine (double bonded NH) backbone. The benzenoid rings react to oxidative agents and the quinoid rings react to reducing agents. On exposure to oxidative gases, hydration, or acidic media, the benzenoid rings transform into quinoid [11], this process is reversible. The protonation of deprotonation of PANI is highly dependent on its localized environ-

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ment. Typically, if it is exposed to an oxidative gas atmosphere, such as  $\text{NO}_2$ , PANI will become doped and an increase in its conductivity will result. Contrary, for a reducing gas atmosphere ( $\text{NH}_3$ ), PANI becomes doped and more resistive.

Polymer blends of PANI with insulating polymers such as PVP have also been studied for their effectiveness in electron transport [12]. Inherently PVP is a steric stabilizer [13] and co-dopant [14] for PANI particles yielding a superior matrix for ion exchange in sensing experimentation. PVP has been acclaimed for its effectiveness in dispersion of PANI particles [14,15] and dictation of particle structures.

The electrospun PVP-PANI matrix also provides a hospitable environment for biological materials. Enzymes are unstable by nature, it is pertinent to immobilize the enzyme in an environment which will aid in the retention of its structure (stable phase). Due to the hydrophilic nature of PVP researchers in our lab have successfully, for the first time, immobilized enzymes (urease) using the electrospinning technique. Results show that the enzyme retains its activity in these films [16]. Electrospun bio-composites of PANI-PVP and Urease have been also studied for their effectiveness in enzyme activity retention. Langer *et al.* [17] showed that Choline Oxidase immobilized in electrochemically prepared PANI films will also retain activity. It is hoped that the electrospun PANI bio-composites show enhanced selectivity and sensitivity to ammonia gas produced from urease-urea reactions. Initial efforts are described in this paper.

## 2. EXPERIMENTAL METHODS

### 2.1. PANI/PVP Composites for $\text{NO}_2$ Sensing

In order to form the composite fibers, Lecuoemeraldine Based Polyaniline (FLUKA-Selectophore®) was mixed with  $5.0 \cdot 10^{-5}$  M PVP (Sigma-Aldrich) with an average molecular weight of 1,300,000 in ethanol solution. While the molar concentration of PVP stayed constant, the total contribution of PANI and PVP was 100% in 2 ml of ethanol. The PANI concentration varied between 20 – 80% wt./volume. The composite was then electrospun onto alumina substrates with gold interdigitated contacts, alumina substrates with platinum interdigitated contacts, and aluminum foil for formation of self-supporting films.

### 2.2. Bio-doped PANI

Solutions consisting of 50% wt./vol. PANI and 80% wt./vol. PANI were mixed with  $5.0 \cdot 10^{-5}$  M PVP in ethanol. Three solutions of the active enzyme Urease E.C.3.5.1.5 (Sigma-Aldrich 16,000 U/gm) were made and consisted of 0.022 gm urease in buffer solution of pH 4, 0.026 gm urease in buffer solution of pH 10, and 0.13 gm of urease in PBS (Phosphate Buffered Saline) buffer solution (pH 7.3). 1 ml of PVP-PANI solution was mixed with 1ml of the urease solution for electrospinning onto aluminum foil.

For proof of principle, two concentrations of Urea (ACS Reagent, Sigma, EC 200-315-5) were used for analysis: 0.25 M and 0.001 M. Reactivity measurements to Urea were made using a Thermo Orion ammonia electrode.

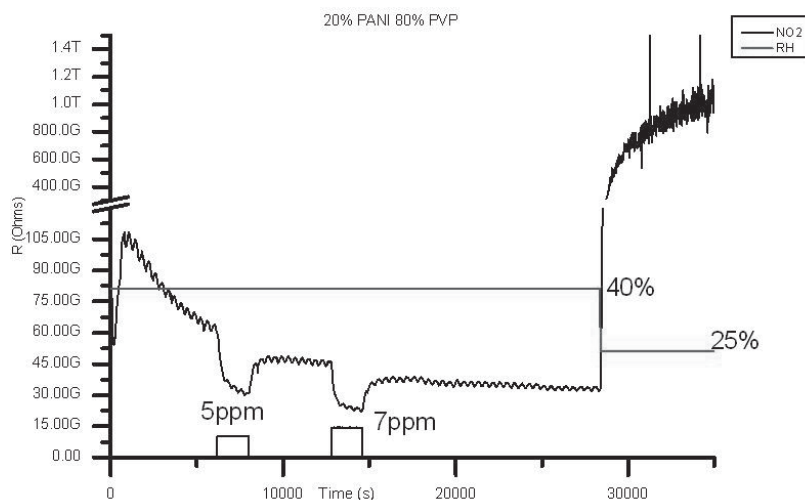
### 2.3. Electrospinning

It is believed that electrospinning PANI/PVP solutions will further enhance the dispersion of PANI particles and improve the sensory nature of PANI. The setup is typically operated in air and consists of a DC voltage power supply (Gamma High Voltage Research, Model ES 30P-6W), a programmable syringe pump (KD Scientific, model 200), and an aluminum collector plate. The voltage applied by the power supply is high enough to break to surface tension of droplets of the solution formed at the end of the syringe inducing the formation of a jet. Electrostatic forces between the collector plate and the tip of the needle aid the flow of the fibers from the needle to the collector.

Fibers of PVP-PANI and PVP-PANI-Urease are formed using 20 and 22 gauge needles at 15 kV and 20 kV and with flow rates ranging from  $5 \mu\text{l}/\text{min}$  -  $50 \mu\text{l}/\text{min}$ . The distance between the needle and the collector varied between 5-6 cm.

### 2.4. Sensing Setup and Characterization

Sensing tests to various gas atmospheres of the PVP-PANI fibers processed in 2.1 were performed in the sensor testing facility at University of Brescia, Italy, where under applied voltage change in sample current was measured in wet synthetic air and a constant temperature of  $20^\circ\text{C}$ . A flow-through technique was used for sensing experiments in which the synthetic air was the carrier gas for  $\text{NO}_2$ . Results from sensor exposure to  $\text{NO}_2$  concentrations ranging from 1 to 7 ppm are reported.



**Fig. 1.** 20% wt./volume LEB-PANI composite response to  $\text{NO}_2$  with relative humidity at 40% and 25% and temperature constant at 20 °C. Resistance decreases with exposure to  $\text{NO}_2$ .

Scanning Electron Microscopy (SEM) characterization was conducted using a LEO-1550 FEG SEM. A high tension of 15 kV was used and the samples were sputter coated with gold prior to analysis.

### 3. RESULTS AND DISCUSSION

#### 3.1. $\text{NO}_2$ Sensing Experiments

The PVP/PANI composites were initially exposed to several vapors, of which only responses to  $\text{NO}_2$  are discussed here. These studies suggest that even with the base form of polyaniline, LEB-PANI, we can measure an increase in the matrix conductivity in the presence of low concentrations of  $\text{NO}_2$  (1-7 ppm). However the response to  $\text{NO}_2$  in the presence of relative humidity (25% and 40%) for 20% wt./vol. and 80% wt./vol. PANI concentrations are shown most substantial and thus results for these sensing experiments will be further discussed (Figs. 1 and 2). The amplitude of the response however is an order of magnitude higher in the 20% wt./vol. PANI sample than in the 80% wt./vol. PANI sample.

The equation for relative sensitivity is given by (1):

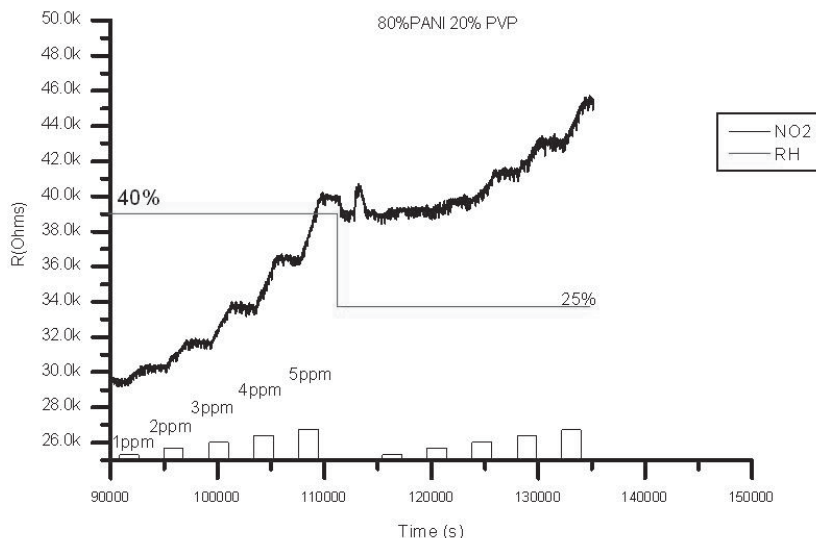
$$S = |\Delta R|/R_0 \cdot 100 \quad (1)$$

Where  $\Delta R$  is the change in resistance on exposure to gas analyte and  $R_0$  is the initial measured resistance value (before exposure). For exposures of 5 ppm of  $\text{NO}_2$  the relative sensitivity for the 20% wt./

vol. PANI sample is 45% and for the 80% wt./vol. PANI sample  $S=9.5\%$ .

During exposure  $\text{NO}_2$  oxidizes PANI, which typically results in an increase in the conductivity of PANI. PANI concentrations tested in these experiments ranged from 50%- 80% and 20% wt./vol. Ghosh *et al.* [18] showed an increase in doped PANI conductivity with increasing wt.% concentration in PVP, however our analysis show that at high concentrations and in the presence of  $\text{NO}_2$  the conductivity of PANI actually reduces and an opposite reaction is observed. The reverse reaction seems to take place at concentrations above 50% wt./vol. PANI in the PVP-PANI solution. Figs. 1 and 2 illustrate the effects of  $\text{NO}_2$  and relative humidity on 20% wt./vol. PANI and 80% wt./vol. PANI. More work is being done to study the cause of this reverse reaction.

It has been observed that there may be internal redox reactions occurring within the high concentration PANI composites due to the processing of these films in air. At high concentrations the PANI film is more susceptible to environmental doping or oxidation from air, this is evident in Fig. 2 where the conductivity of the 80% wt./vol. PANI film is on the order of  $10^3$  Ohms compared to the conductivity of the 20% wt./vol. PANI film ( $10^9$  Ohms).



**Fig. 2.** 80% wt./volume LEB-PANI composite response to  $\text{NO}_2$  with relative humidity at 40% and 25% and temperature constant at  $20^\circ\text{C}$ . Resistance increases with exposure to  $\text{NO}_2$ .

### 3.1.1. Effect of Humidity

The charge transfer mechanism between the water vapor and PANI competes with doping or de-doping mechanisms from redox reactions. In the presence of increasing humidity the materials reaction to  $\text{NO}_2$  decreases (as confirmed in the literature [6,8]). However, it appears the material's sensing mechanism only initiates in the presence of the water vapor (Fig. 2). Typically on exposure to water vapor, PANI becomes protonated, and an increase in conductivity can be observed

Many authors have also detailed the effects of water vapor on the PANI conduction mechanism. Understanding the effects of humidity or hydration on the sensing mechanism is necessary for environmental monitoring applications. It has been shown that water assists protons in conduction by creating pathways for charge hopping between PANI grains. The reactions between water and PANI can be explained in several ways: (1) PANI particles increase in size with water adsorption on the surface [7], (2) grain boundary barriers break down with exposure to water vapor [6], (3) there is an exchange of protons between the water vapor and the PANI particles [19], or (4) water causes an base-metal transition in PANI-PVP composite.

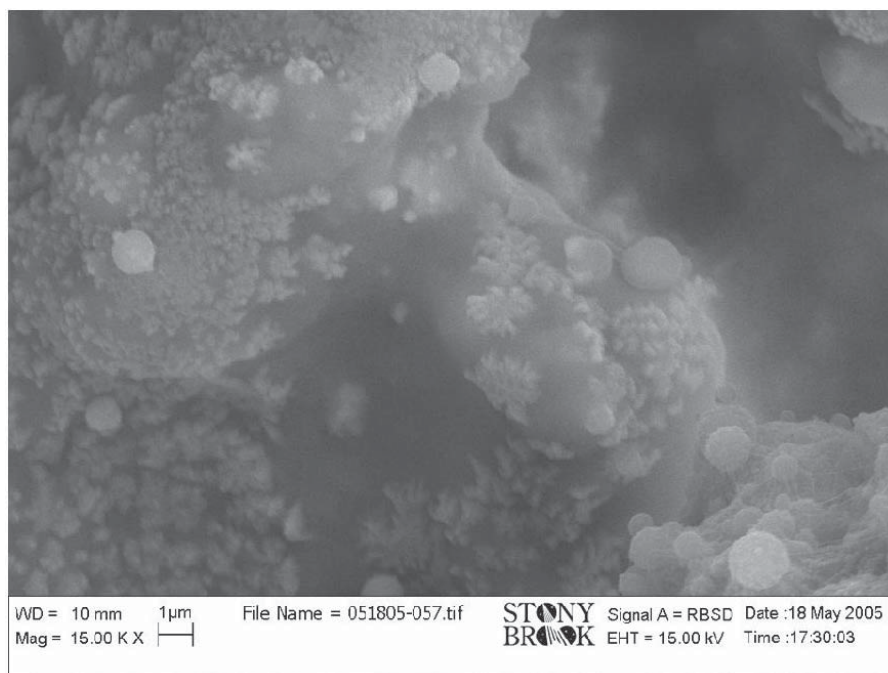
In the electrospun matrix, the PVP fibers allow for increased flow of water vapor to the PANI aggregates. PVP is a hydrophilic polymer and researchers have shown that the water molecules bond to 'carbonyl and C-N sites' of the polymer [20]. Due to

the nature of the interactions between PVP and the water molecules, it is predicted that a percentage of the water vapor will remain trapped in the PVP-PANI matrix, unless the system is subjected to elevated temperatures. While in the system, the water attaches itself to both the amine and imine centers of the quinoid and benzenoid structural units. The amine acts as proton acceptor while the imine center acts as proton donor [6]. The trapped water may cause swelling of the PANI particulates or direct protonation with the exchange of protons from water molecules [6].

### 3.2. Bio-doped PANI

Results from the reactivity measurements for the three samples confirm that the urease retains its activity in the electrospun composite matrix. For solutions of higher pH (pH 10), the change in potential measured by the ammonia electrode was 0.8mV. However for solutions of low pH (pH 4), the change in potential was an order of magnitude higher.

SEM characterization (Fig. 3) suggests that the urease attaches to the surface of the PANI aggregates formed during the electrospinning process. As Fig. 3 will show the urease self assembles on the surface of PANI aggregates in a distinctive pattern. It is predicted that due to the immobilization of urease in the PANI-PVP matrix there will be an increase in the film's sensitivity to ammonia. Moreover, due to the nature the electron charge transfer



**Fig. 3.** SEM of 80% wt./vol PANI- PVP with 1 ml of 0.13 g Urease (in PBS buffer solution) film prepared by electrospinning.

properties of PANI, the reactivity of urease in urea solution should also increase. Further analysis is necessary to determine whether there are chemical bonds forming between PANI and the enzyme and what ion exchange processes occur between the two materials.

#### 4. CONCLUSIONS

The product of this study is an active matrix with a high surface to volume ratio providing sensitive robust membranes tunable for multi-functional sensor technologies or for systems that require protective coatings (i.e. protective textiles, armament systems, etc.), as well as a suitable environment for the immobilization of biological receptors.

Bio-doped PANI composites may also play a multi-faceted role in biological sensing: increasing reactivity of the bio-receptor and enhancing sensitivity of the PANI composite to the target analyte. Although there has been much focus on the use of PANI as a sensing membrane, the spotlight has been on the use of emeraldine based or pernigraniline (emeraldine salt). LEB-PANI has not been well studied for its effectiveness as a sensing mechanism for NO<sub>x</sub> and environmental monitoring.

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