Materials Research. 2021; 24(suppl. 1): e20210031
DOI: https://doi.org/10.1590/1980-5373-MR-2021-0031

Electrospun PPY.DBSA/PVA Nanofibers for Ammonium Gas Sensor

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Received: January 12, 2021; Revised: July 19, 2021; Accepted: July 24, 2021

This work presents the results obtained in the production of poly (vinyl alcohol) (PVA) nanofibers with different concentrations of polypyrrole (PPy) doped with dodecylbenzene sulfonic acid (DBSA) - PPy.DBSA. The morphology of the nanofibers was studied by scanning electron microscopy (SEM) technique. The nanofibers were deposited on interdigitated electrodes (IDEs) for direct current electrical characterization (DC) and tested as ammonia gas sensors. The results showed a rapid detection of ammonia gas for higher concentrations of PPy.DBSA and for several alternating cycles in atmospheric N_2.

Keywords: *nanofibers, gas sensor, conjugated polymer, electrospinning.*

1. Introduction

Currently, there is a wide range of sensors used in security area for the detection of toxic chemicals and gases[1]. For effective detection and applicability, the sensor must have small dimensions, high sensitivity, stability, reliability and low cost. In a sensor, the detection material should have a large surface area and highly porous structure, as it is essential for high sensitivity and quick response[2].

Organic materials are an effective choice to obtain cost-effective and high-performance sensors. Conductive polymers and semiconductor materials are characterized by their ease of operation, fabrication, and low cost. Conductive polymers have an affinity for gases, especially those that result in a change in their electrical resistance caused by the adsorption and desorption of gases[3].

In addition to the materials used, the manufacturing method also influences the performance of the sensors, in this sense, the electrospinning technique can significantly contribute to improve the performance of such devices, as they have a high surface area up to 10^3 times, which is greater when compared to microfibers and thin films[4],and may present porous structure and electrical conductivity[5-9]. Kwon et al.[10] reported that sensors based on semiconductor polymer nanofibers have shown a high sensitivity and a shorter response time when compared to other manufacturing methods.

Although the electrospinning technique is apparently a simple technique, the difficulty lies in producing fibers for some types of materials, being necessary to choose materials that meet the minimum requirements for using the technique. Such parameters are: i) solution: viscosity, surface tension and conductivity; ii) process: applied electrical voltage, flow rate, type of collector and distance between collector and needle; iii) environment: humidity, atmosphere and pressure[10,11].

Research using the electrospinning technique for application in sensors has been growing since the last decade[12], but there is a lack in the development of sensors involving only organic compounds, in most cases the developed sensors have oxides, metallic or ceramic nanoparticles in their composition[13-19], or the material that interacts with the gas is impregnated on the surface of the fibers[20-22]. The present work aims to contribute to the study of the use of PPy as ammonia gas sensor and the effect of its processing through the electrospinning technique. In this study, it was found that both the presence of PPy and the quality of the fibers obtained influence the quality of the sensor.

2. Experimental

2.1. Materials

PVA, 99% hydrolyzed, was used with 130,000 Mw and pyrrole (Py) 67.09 $g.mol^{-1}$, both obtained from Sigma-Aldrich. Ferric chloride hexahydrate ($FeCl_3.6H_2O$) 270.30 $g.mol^{-1}$ was purchased from Synth and dodecylbenzene sulfonic acid (DBSA) 326.49 $g.mol^{-1}$ from Sigma-Aldrich.

A 6 wt% PVA solution in ultrapure water was pre-heated to 80 °C with vigorous magnetic stirring for 2 hours. In the oxidative polymerization of pyrrole, $FeCl_3$ was used as the oxidizing agent of the pyrrole monomer, in the molar ratio 2:3 $FeCl_3$/pyrrole to obtain polypyrrole doped with DBSA (PPy.DBSA) (Figure 1).

Initially, 1.88 g of the anionic surfactant (DBSA) and 0.05 L of distilled water were added to a 250 mL beaker under magnetic stirring. After dispersing DBSA, in another 100 mL beaker, 16.2 g of $FeCl_3.6H_2O$ were dissolved in 0.05

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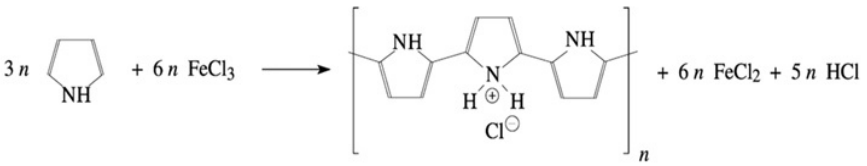

Figure 1. The oxidation of pyrrole with ferric chloride yields polypyrrole. Adapted from Omastová et al.[23].

L of distilled water. After 10 minutes, 16.2 g of $FeCl_3.6H_2O$, previously dissolved in 0.05 L of distilled water, were added dropwise to the aqueous dispersion containing pyrrole and DBSA. At the end of the polymerization, polypyrrole doped with DBSA (PPy.DBSA) was obtained, which was filtered and washed with distilled water in order to extract residues and by-products of the reaction. PPy.DBSA was dried in a vacuum desiccator at room temperature.

2.2. Electrospinning

The electrospinning system consisted of a syringe pump (New Era Pump System - N1000), a high voltage direct current power supply of up to 30kV, 3 mL syringe and needles (0.55 mm and 1.60 mm) diameter. A rotary collector with a diameter 2.54 cm (1 inch) at 300 rpm was used to collect the obtained nanofibers.

The membranes of PPy.DBSA nanofibers and PVA were prepared from the aqueous solution of PVA by adding different mass proportions of PPy.DBSA, 0%, 1%, 2.5%, 5% and 10%. The dispersions were agitated for 30 minutes on a magnetic stirrer and electrospun under the following conditions: i) 25ºC, ii) air humidity of 50%, iii) solution flow of 0.3 $mL.h^{-1}$, iv) distance of 15cm between the needle and the collector, v) 20kV voltage and the samples were spun for 20 minutes.

2.3. Substrate

Gold Interdigitated Electrodes (IDEs) were employed in this study. The IDEs had 25 pairs of electrodes, dimensions of 110 nm high (h), 8 mm length (L) and 100 µm in width and digits (w). The manufacturing process is described by Bittencourt et al.[1].

The substrates were produced at Laboratório de Microfabricação e Filmes Finos (LMF) and Laboratório Nacional de Nanotecnologia (LNNano) in Centro Nacional de Pesquisa em Energia e Materiais (CNPEM).

2.4. Gas system detection

In order to analyze the performance of PPy.DBSA/PVA nanofibers as sensors, current measurements as function of time (I vs. t) were carried out with a fixed applied voltage of 5 V. In order to detect changes in devices as a response to the analyte, a gas system coupled to a DC electrical measurement equipment (Keithley model 238) for the detection of ammonia gas was used in this work, as described in Figure 2.

The nanofibers deposited in the IDE´s, are inserted in the sample holder (4), a constant flow of N_2, (1) is applied to establish an inert atmosphere, serving as a baseline. The ammonia gas (NH_3) is released in (3) by bubbling N_2 (2) in NH_4OH (3) up to (4).

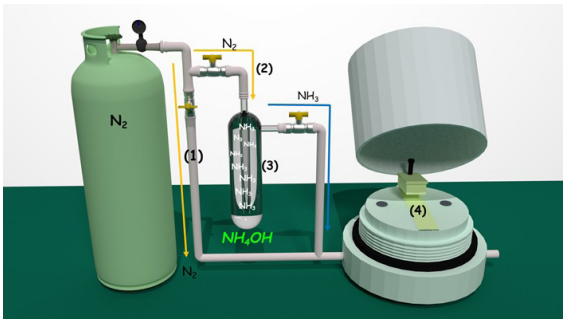

Figure 2. Gas detection system composed of an N_2 cylinder, line (1) that takes nitrogen gas to the sample holder (4) that contains the IDE's. In (4) the release of NH_3 occurs, by bubbling N_2 (2) in a solution of NH_4OH in (3).

2.5. Characterization

The membranes were morphologically characterized by scanning electron microscopy (SEM), at electrical voltage of 30 kV. Carl Zeiss model EVO LS15 in high vacuum and constant temperature. The scan is carried out with minimum exposure to the same region and the sample is covered with 3 layers of gold in the order of nanometers, become it very conductive on the surface. In addition, around the sample it is contoured with silver paint to ground the electrons that did not generate data. ImageJ® software was used to estimate the average diameter size. For the electrical measurements of DC and sensors, interdigitated gold electrodes (IEDs) and a Keithley 238 source (High Voltage Source Measure Unit) were employed, as described in Bittencourt et al.[1]. For the analysis of the sensors performance, variations in the electric current in relation to time during the flow of N_2 and NH_3 gases were monitored. 5V potential was applied to IDEs. The gas flow was 60 m^3h^{-1}, alternating at intervals of 2 minutes for N_2 and 1 minute for NH_3 for all samples.

3. Results

3.1. Scanning electron microscopy (SEM)

Figure 3 shows the SEM images of electrospun PPy. DBSA/PVA nanofibers in different mass fractions of PPy. DBSA. In order to obtain a uniform ejection of the charged jet and formation of uniform fibers, the electrospinning solution should have an appropriate concentration or viscosity. If the concentration of the solution is very low, it will not be possible to form continuous fibers from the charged liquid (the charged jet), as it suffers an instability of the flow and, consequently, leads to the formation of beads. It is also of great importance that the relative humidity of the environment

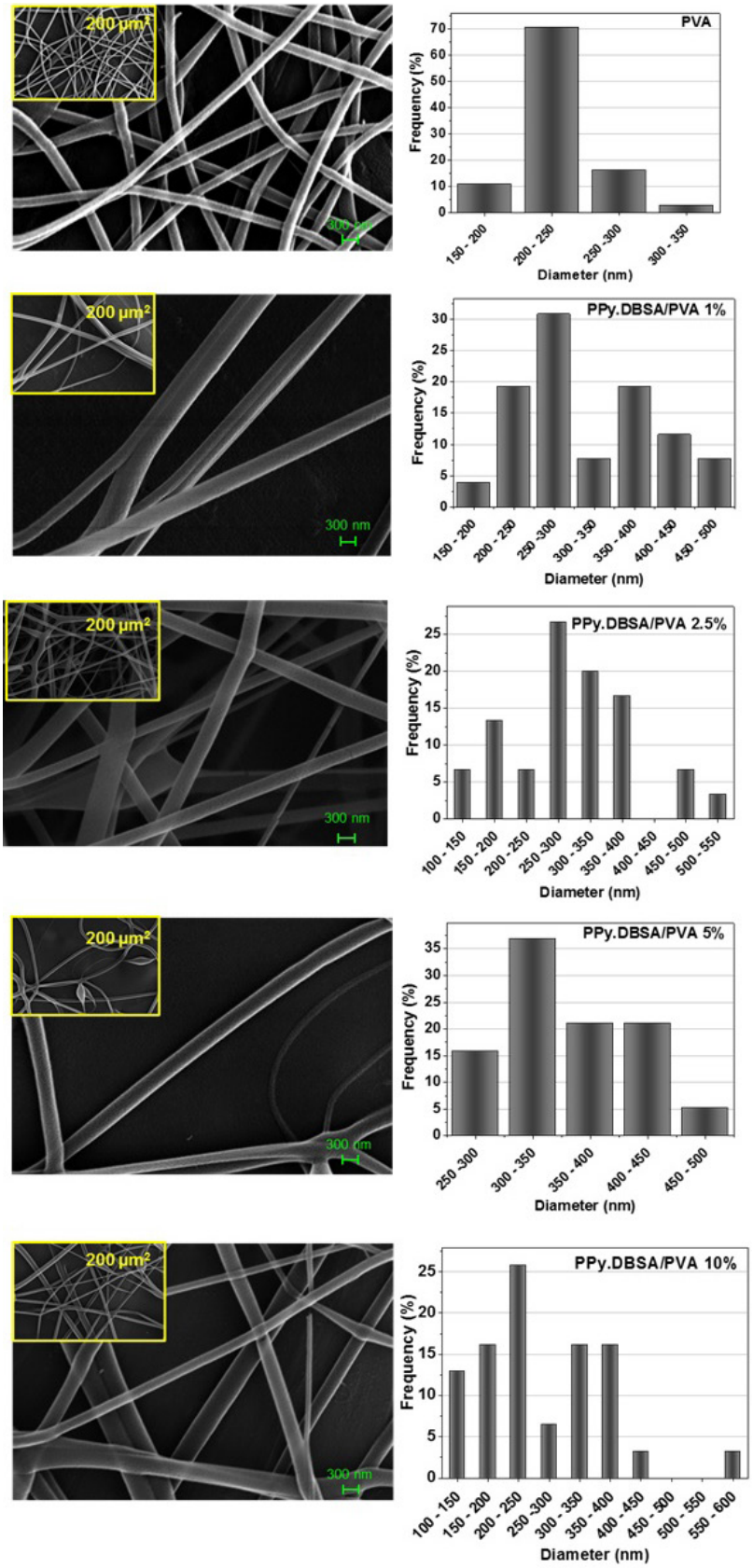

Figure 3. SEM and frequency of diameters of PPy.DBSA/PVA nanofibers in different mass proportions of 0%, 1%, 2.5%, 5% and 10%, with a magnification of 35,000x and 15,000x covering a surface of 200 µm^2.

is less than 60% for the production of PVA nanofibers. The results showed that the pure PVA nanofibers were randomly distributed, continuous, with good homogeneity and with a greater frequency of diameter between 200-250 nm, according to Lee et al.[24]. The diameters of the fibers varied from 150 to 350 nm. Observations revealed that this concentration led to the formation of bead-free nanofibers. This was due to the ideal viscosity for electrospinning, so the viscoelastic force was enough to prevent rupture of the charged jet and Coulombian force to lengthen the charged jet evenly.

The formation of PPy.DBSA/PVA nanofibers presented uniform morphology without the presence of beads, randomly distributed and good homogeneity for all concentrations of PPy.DBSA. This result is according with literature[25]. The average diameters of PPy.DBSA/PVA nanofibers in all concentrations were in the range of 250 ± 50 nm. Higher proportions of PPy.DBSA were tested in the PVA, but as it is a dispersion solution of particles in a liquid, the large amount of PPy.DBSA aggregates makes the electrospinning process impossible, interrupting the polymeric flow in the needle.

3.2. DC electrical measurements

For DC electrical measurements, the voltage applied to the interdigitated electrodes covered with the electrified fibers varied from -10 V to 10 V. Figure 4 presents the graph of current (I) versus voltage (V) obtained for electrospun PPy.DBSA/PVA nanofibers.

The electrical conductivity values of the manufactured nanofibers revealed a conductivity in order of 10^{-9} $S.m^{-1}$, a region between insulators and semiconductors. This effect was probably due to the conductor/insulator ratio, as at higher concentrations of PVA, the insulation characteristic predominates over the conductive characteristic of PPy. DBSA polymer.

It is possible to observe the linear behavior of the curve, this effect is due to the interfaces Au/active layer and active layer/Au, forming a neutral contact or ohmic contact. The ohmic contact between a metal and a semiconductor is defined as a negligible resistance compared to the resistance of the semiconductor volume. This type of contact is satisfactory when it does not influence the performance of the device and the current must flow easily into and out of the semiconductor. This implies that the density of free carriers at the interface is much higher than in the volume of the semiconductor, so the contact acts as a reservoir for charge carriers[26]. These factors explain the linear curves presented in the paper. On the other hand, the instrument used to carry out the measurements is quite sensitivity. The sensitivity of the measurement is the smallest change of the measured signal that can be detected. For Keithley 238 in the range max output ± 100 mA, the resolution is 1-10 pA. The current obtained for our devices is three orders of magnitude higher than this value, this is the reason that the error bars is not presented. Furthermore, the samples were made in triplicate and the results were reproductible.

3.3. Ammonia gas testing

The electrical characterization results of current (I) versus time (t) from the tests performed with ammonia gas in different proportions of PPy.DBSA are shown in Figure 5. The peaks represent the exposure time of the nanofibers to NH_3 gas and the levels of exposure to N_2 gas. There is a sensitivity in the immediate detection of ammonia gas for all nanofibers containing PPy.DBSA. This rapid detection is attributed to the larger surface area of the nanofibers and the easy diffusion of ammonia gas in the materials.

Nanofibers containing 2.5 and 10% PPy.DBSA showed better gas detections when compared to the other concentrations, as both materials remained stable in the cycle after the purging of ammonia.

Gas detection occurs because ammonia is an electron donating molecule, so when PPy is in the presence of ammonia, its electrical resistance decreases dramatically. However, after the removal of ammonia with nitrogen, the resistance of the sensor layer is totally or partially recovered.

Although all concentrations of PPy.DBSA presented rapid detection and sensitivity in several cycles of ammonia gas, the sensors containing 1 and 5% of PPy.DBSA showed low sensitivity. This fact can be related to the low formation of nanofibers with diameters below 200 nm, Figure 3, due to the dimensions of IDE; fibers with smaller diameters

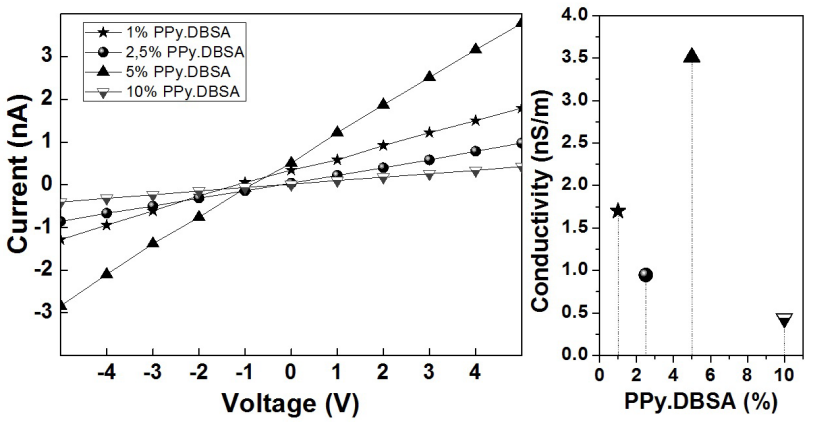

Figure 4. I *vs*. V characteristic (left) and conductivity curve (right) of the electrodes covered with electrospun PPy.DBSA/PVA nanofibers in different mass proportions of PPy.DBSA, 1%, 2.5%, 5% and 10%.

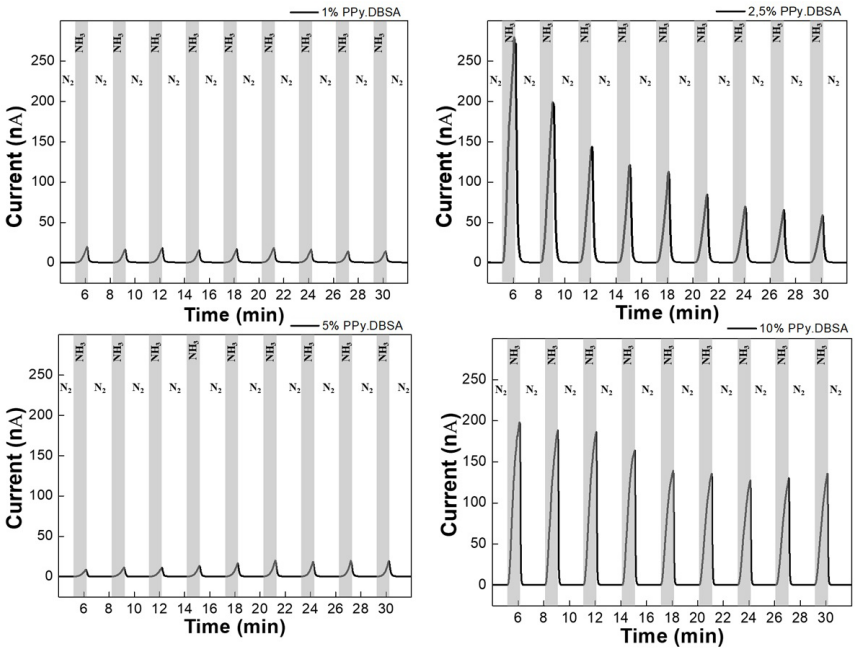

Figure 5. Gas sensor tests with PPy.DBSA / PVA in atmosphere of N_2 and ammonia (NH_3).

have better contact with the digits on IDE and consequently better sensitivity.

The results showed that the sensor response decreases due to repeated injections of ammonia gas, that is, that the detection process is not fully reversible, a fact also observed in the literature by Trojanowicz and vel Krawczyk[27]. The sensor response can be reversible when it is exposed to a very short time[28]. The total irreversibility in the detection of ammonia gas has already been observed in the literature, but for periods longer than 14 days[29]. The irreversible change in conductivity was explained as a nucleophilic attack from ammonia to the polymer, which leads to a loss of conjugation in the polymer's structure and, therefore, to an increase in resistivity.

4. Conclusion

PVA nanofibers was fabricated with heterogeneous mixture of PPy.DBSA. It is of great importance that the relative humidity of the environment is less than 60% for this procedure. The solution containing 2.5 and 10% PPy.DBSA showed the highest signal intensity in the tests for gas sensor, as most of nanofibers presented a diameter below 200 nm. Moreover, the detection of ammonia gas was more stable for the sample with 10% due to the higher concentration of the conductive polymer.

5. Acknowledgements

LabMEV–FCT/UNESP, CAPES-PRINT_UNESP, CNPq, INEO (Proc. 14/50869-6) and FAPESP (Proc. 2016/06288-4). This study was partially financed by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001.

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