AMMONIA GAS SENSOR BASED ON THE FREQUENCY-DEPENDENT IMPEDANCE CHARACTERISTICS OF ULTRATHIN POLYANILINE FILMS

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ABSTRACT

This paper describes a variety of experiments that reveal the potential application of impedance spectroscopy (IS) measurements to enhance performance of ultrathin polyaniline (PANI)-based films on flexible substrate to control ammonia gas exposure in the 0-20 ppm range. Further, the device is mechanically robust for making electrical contact without lithography. We have employed the IS technique to properly adjust the optimal operation frequency of an easy-to-process, inexpensive and user-friendly PANI-based resistometric detectors in which drift current and delay problems related to electrode effects and dielectric absorption of PANI are insignificant. These requirements place emphasis upon the material and device configuration, and the range of frequencies from 10 to 100 Hz corresponds to the ideal working region to operate the device to unify sensibility inside 5%, reproducibility, linearity, stability and low response time (< 1 min). These results are as efficient as those obtained using a more expensive commercial apparatus and can rival the affordability of traditional sensors. Linear Discriminant Analysis (LDA) and K-Means clustering confirmed that the device has the capacity to recognize ammonia concentration around 20 ppm with total accuracy of 95%. Our study provides evidence of a new way to improve the performance of PANI-based sensors that can potentially be employed to monitor the environment of livestock buildings, for example.

Keywords: layer-by-layer; screen printable device; alternating conductivity; polymeric sensor; PCA.

1. INTRODUCTION

Ammonia is a harmful gas found in livestock buildings that interferes in immunological response, growth and productivity of different animals [1,2,3,4,5], which motivates development of techniques to control its levels. Many countries have adopted standards requirements that ammonia level in livestock buildings may not exceed 20 ppm with lower detection limit of 1 ppm [6,7,8,9,10,11], but available methods and equipments for ammonia level control require much maintenance and are often expensive for small farmers. Indeed, a key requirement to successfully design ammonia sensors for animal confinement buildings is the ability to manufacture an affordable and user-friendly device (e.g., robust, easy-to-read display and with a complex range of built-in programs). These requirements place emphasis upon the material and device configuration to unify sensibility, accuracy, reproducibility, linearity, stability and low response time (< 1 min) of ammonia sensors.

In fact, several laboratories show that polyaniline (PANI)-based sensors [12,13,14,15] may provide many of these characteristics, due to their suitability for low-cost and fast solution processing techniques and to their ability to present high or low electrical conductivity (doped-dedoped process) in a reversible manner by alternating exposure to acids or base solutions, respectively. Herein, the ammonia gas sensing mechanism arises from the deprotonation process of acid doped PANI, and many scientific papers [16,17,18] report on the ease of PANI detector production for environmental ammonia gas analysis. Despite the feasibility demonstration of several ammonia gas sensors using PANI, many problems related to their low electrical stability and high response time (> 5 min) have not yet been resolved to avoid drift current and delay problems encountered in PANI-resistometric sensors [19,20]. These facts can presumably be explained by exploiting the electrode effects [21,22] and the dielectric absorption of PANI [23] that effectively creates hysteresis curves, delay response times and memory effects. These characteristics mainly result in low-reliability and slow response time to PANI-based sensors. Currently, impedance spectroscopy (IS) measurements appear as a new alternative to enhance the reliability of PANI-based sensors. IS analysis is able to distinguish between the conductive (bulk resistance) and capacitive contributions [24,25] of solid materials and related devices, and so it can be useful to establish an operating frequency for PANI-based sensors in which capacitive effects related to electrode-PANI contacts and dielectric absorption of PANI-based films are insignificant. Despite these observations, few IS studies have been reported on changes in the resistance behavior performance of organic sensors for different operation frequencies. In fact, research has been biased toward capacitance measurement at a single frequency (usually 1 KHz) rather than the investigation of both real and imaginary components of the complex impedance on the entire spectral range [26,27]. In order to accomplish such investigation, it is necessary to perform statistical analyses of the entire spectrum of complex impedance measurements to select the optimal

operation frequency range to improve the accuracy of PANI-based sensor for real life environments. This paper describes an experimental configuration and methods to support this task.

The initial motivation for this work on polyaniline and complex impedance measurements is to develop a novel ammonia resistometric sensor using well characterized material (PANI) – if successful, a sensor can be developed to monitor ammonia gas in the 0 to 20 ppm. In order to accomplish this goal, one of the most important aspects that must be controlled is the processing of PANI as a thin film on a low-cost processing technique and easy to find substrate. Here, polystyrene (PS) was used as substrate and the self-assembly (or simply layer-by-layer - LbL) technique was chosen to produce the polymer film because of its simplicity and versatile experimental setup [28,29]. Also, LbL films are attractive because of its high conformability and well-controlled thickness and architecture, which allow the synergistic combination of materials properties. Finally, LbL films of PANI have been produced from a long time, and their successful application as gas sensors and biosensors is well described [30,31].

2. EXPERIMENTAL PROCEDURES

2.1 Layer-by-Layer (LbL) processing of thin PANI/PVS films

Ultrathin LbL films formed by alternated layers of positively charged polyaniline (PANI) and negatively charged poly(vinyl sulfonic acid) (PVS) were prepared according to the procedures described by Santos *et. al.* [21]. PANI was dissolved in 2.5 pH in the concentration of 70 µg/ml, and PVS was diluted in ultrapure water, with 100 µL of a 25 wt % aqueous solution of PVS being mixed with 24 mL of aqueous solution with pH 2.5, giving a final concentration of 1 µg/ml. The rinsing solution for both materials was water with pH 2.5 (adjusted using HCl 1 M). The multilayers were assembled by the alternated immersion of flexible polystyrene (PS) substrate about (50 x 80) mm² and 100 µm thick in PANI and PVS solutions for 5 min each at room temperature. After each deposition, the substrates were rinsed for 20 s with subsequent drying under airflow. PS was used as substrate because of its economic viability and commercial availability. This substrate also presents limited flexibility, which is good to prevent PANI/PVS film crashing. Hydrophilic substrates were obtained using UV-Ozone cleaning, which consists of exposing the sample to ultraviolet radiation from a germicidal lamp (20 W) in atmosphere for 15 min. PANI/PVS adsorption was monitored by measuring the UV-VIS spectra with a Spectrophotometer UV-1650PC Shimadzu. A linear increase at the maximum absorption at 900 nm with the number of PANI/PVS layers was observed (*not shown*), indicating that the same amount of material was adsorbed in each deposition step. Similar results were reported

for a PANI/PVS LbL films on glass substrate [21]. Finally, a rough estimation about (4 ± 1) nm of the thickness of a single PANI/PVS layer was obtained by measuring the thickness of a 40-bilayer film using a DekTak 6 M Stylus Profiler from Veeco Instruments Inc.

2.2 PANI/PVS resistometric device structure

Figure 1 shows an illustration of the simple solution-based fabrication processes of ammonia sensors with a top silver electrode structure which incorporates LbL and silk screening techniques. The design problem is to choose a low-cost ($< \text{US\$ } 1$) device structure and an operate frequency to minimize the dielectric and electrode effects of PANI-based sensors.

A 25-bilayer film from PANI/PVS layers was fabricated by LbL technique onto PS substrate followed by heat treatment at 100°C for 1 hour in ambient air to remove traces of water (Fig. 1a). We chose the 25-bilayer film because it is visually more homogeneous than other films. After preparing the PANI/PVS layers on PS, a parallel pair of solution-processed silver electrodes ($3 \mu\text{m}$ thickness) was defined on the PANI/PVS surface by screen-printing technique, which uses CI-1001 ECM silver ink and a screen-mask (stencil screen) with well-defined windows (Fig. 1b). The length (L) and distance (W) between the Ag electrodes on PANI/PVS surface were 10 mm and $600 \mu\text{m}$, respectively (Fig. 1c). Finally, the sensor was heated at 50°C to remove traces of solvent.

2.3 Electrical Characterization and ammonia calibration method of the devices.

Complex impedance measurements, $Z^*(f) = Z'(f) - iZ''(f)$, of the PANI-based sensors were carried out using a 1260 Solartron frequency response analyzer in the 1 Hz to 1 MHz frequency range, with voltage amplitude equal to 1.5 V. DC impedance measurements were carried out with a 6517A Electrometer High Resistance Meter from Keithley with applied voltage also equal to 1.5 V. This applied voltage enables developing smaller and more cost-effective handheld device with the performance to run, for example, with a single battery. All electrical measurements were carried out in a homemade gas chamber with temperature varying between $22\text{--}25^{\circ}\text{C}$ and relative humidity around 70% to maintain the standard condition desirable for animal confinement buildings. Ammonia-air mixture was injected into the chamber at a rate of 1 ppm per minute. An air purge procedure was applied to reduce ammonia gas concentration on the chamber. Temperature and relative humidity inside the chamber were continuously recorded during the electrical measurements using a MT230A sensor from Minipa. Finally, a high-performance electrochemical diffusion ammonia sensor (Instrutherm DG-200) was used as a reference device for monitoring ammonia gas levels in

the chamber and to compare the PANI-based sensor accuracy against a more exacting standard device. The MT230A sensor has the ammonia detection range of 0 to 100 ppm, detection limit equal to 1 ppm and characteristic response time of 30 s.

2.4 Statistical Analysis: PCA, LDA and K-means

In order to evaluate the real and imaginary components of the complex impedance response for the sensors (Section 2.2), we considered Principal Component Analysis (PCA), Linear Discriminant Analysis (LDA) and K-Means. The set of five sensors were simultaneously exposed to the same ammonia gas level (0, 9, 20 and 28 ppm) during the electrical characterization.

PCA and LDA methods support the transformation of the multivariate dataset into another coordinate system that enhance particular properties associated to data scattering. Similar to PCA, LDA is also a linear combination of the original variables to construct a Discriminant function. An increasing number of studies have reported that both methods are capable to extract pattern information from gas sensing field, as described in [32], [33], [34] and [35], to analyze the accuracy of sensing devices. In our approach, the discrimination between ammonia concentrations was obtained using K-Means clustering after PCA and LDA data transformation. K-Means clustering groups samples with the nearest mean, minimizing the within-cluster sum of squares [36,37]. Euclidean distance is used as a metric for K-Means modeling, its mean value defines the centroid, and variance is used as a measure of cluster scatter. These methods have efficient algorithms under R Statistical environment [38], which were employed in our approach. Particularly, the K-Means converged fast to optimum quickly, so that we could obtain the accuracy of PANI-resistometric sensor using these two methods.

The statistical methods described above support investigation of the piecewise frequency range in IS experimental results. It differs from the classical procedure in the choice of the range of Principal Components (PCs) and Linear Discriminants (LDs) to be used before clustering. We adopted a piecewise frequency statistical analysis considering the following intervals of 1-10 Hz, $10-10^2$ Hz, 10^2-10^3 Hz, 10^3-10^4 Hz, 10^4-10^5 Hz, and 10^5-10^6 Hz. Such procedure enables selection of frequency range with the highest discrimination in terms of the real and imaginary components of complex impedance as function of ammonia gas level – here; it translates into the highest classification success rates. The level of ammonia gas must not exceed 20 ppm in a properly controlled livestock building. Consequently, a simple and inexpensive indicator sensor that is able to accurately inform if the ammonia concentration is above or below 20 ppm is extremely desirable in the monitoring of such environments.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The following results indicate the effect of ammonia gas level on the complex impedance, $Z^*(f) = Z'(f) - iZ''(f)$, which describes the behavior of PANI-based sensor as a function of the electric field frequency (f). Special care was taken to verify whether ammonia played a role in the variation of $Z'(f)$ and $Z''(f)$ components. For clarity of presentation not all the $Z'(f)$ and $Z''(f)$ vs. f curves have been included. The performance measurements will give the requirements for monitoring ammonia gas for livestock buildings.

3.1 Complex impedance of the PANI-based as function of NH_3 concentration

Figure 2 shows how $Z'(f)$ and $Z''(f)$ components of PANI-based sensor vary with NH_3 from 0 (Fig. 2a) to 9 ppm (Fig. 2b), and to 28 ppm (Fig. 2c). We observed the *quasi*-Debye dispersion patterns to all $Z'(f)$ and $Z''(f)$ curves that are similar to those observed for parallel resistor-capacitor (RC) circuit; i.e., a resistor modeling dissipative effects at low-frequencies, and a capacitor representing stored charge at high frequencies. For this circuit configuration, $Z'(f)$ is nearly flat for lower frequencies followed by a cut-off frequency - f_c around 10^4 Hz when $Z''(f)$ shows a peak almost coincident with f_c . The resistor R affects $Z^*(f)$ for $f < 100$ Hz, while the capacitor C affects $Z^*(f)$ for $f > 10^4$ Hz, whereas both R and C contributions are observed to occur in between 10^2 Hz and 10^4 Hz. In fact, the effect of ammonia increases the radius of the approximate semicircular plot observed in the Argand Diagram (the inset of Fig. 2). This diagram has the disadvantage of not indicating frequency response directly [39], but may nevertheless it may be very helpful in identifying the contributions of both bulk (R) and dielectric (C) properties of PANI-based films around f_c .

Figure 3 shows the change in the relative percentage of $Z'(f)$ of PANI-based sensor as function of time (in the absence of ammonia gas) to evaluate the behavior of the PANI-based device from dc regime ($f \rightarrow 0$) to single frequencies between 1 Hz and 100 KHz. In this figure, $Z_0(f)$ is the value of $Z'(f)$ at $t = 0$ s. Within the limits of experimental error, time has little effect on $Z'(f)$ for $f \geq 10$ Hz, but a larger effect if $f < 10$ Hz. Since electrode effects usually occur near the low-end frequencies, while dielectric effects at high [25,30], it is concluded from the results showed in Figs. 2 and 3 and foregoing discussed that a reasonably complete and self consistent picture has emerged regarding the optimized operation frequency of the device is found in the 10-100 Hz range. In fact, the conduction process of the PANI-based sensor is represented by R which dominates $Z^*(f)$ in this frequency range. Moreover, in the 10-100 Hz range, we may also infer that $Z^*(f)$ approaches $Z'(f)$ and also becomes independent of time

when two or more consecutive measurements are observed. Consequently, a smaller variation of $Z'(f)$ as function of time indicates a more precise parameter to reach a high stability sensor.

Regarding possible electrode effects, let us consider that a parallel RC circuit is solely responsible for the experimentally complex impedance behavior in the 10^2 - 10^6 Hz frequency range (Fig. 2). Consequently, the net result for higher frequencies is a progressive loss of the device sensibility due to the capacitive effects. This is explained in terms of the output signal of the sensor that is attenuated due to the time take to charge the PANI/PVS films as the frequency changes. In addition, ammonia has the anticipated effect of increasing the electrical resistivity of PANI/PVS films at low frequencies,. However, for frequencies lower than 10 Hz, we observed a high contribution of contact resistance between Ag-electrode and PANI-based film. As proposed by G. Neshet et al. [40], the evidence we found points to an interfacial interaction between Ag and PANI in which the contact resistance (electrode effects) is much higher than the bulk resistance (resistive effects). Indeed, the effect of ammonia on $Z'(f)$ and $Z''(f)$ depends on the analyzed frequency to be much higher than f_c (capacitive effects), around f_c (resistive and capacitive effects), in between 10 Hz and 100 Hz (resistive effects), or much lower than f_c (electrode effects). This finding demonstrates that important the operation frequency plays a major role in the process of optimizing the performance of PANI-based sensor considering only resistive effects.

3.2 PCA, LDA and K-Means analysis

The K-Means clustering under the results of PCA and LDA on complex impedance of PANI-based devices (Fig. 2) are shown in Figures 4 and 5, respectively. The results are shown in terms of the piecewise frequency range described in Section 2.4. Table I illustrates the total accuracies of K-Means with PCA and LDA methods using piecewise frequencies and four ammonia concentration groups (0-9, 9-14, 14-20 and 20-28 ppm).

From Figs. 4 and 5, and the results shown in Table I, we observed that PCA and LDA plots follow different patterns regarding the data dispersion, with clearer data separation in LDA results than those obtained with PCA, for all frequencies range. However, notice the overlap between the maximum total accuracies obtained from both methods, which is in the 10-100 Hz frequency range – this is in agreement with the experimental results of Fig. 3. It is also observed that for PCA plots, independently of considering piecewise frequency range, the sample data of ammonia concentration levels were overlapped for all set of 4 ammonia concentration groups, resulting in inaccurate classification. LDA plots, on the other hand, present clearer separation into 4 groups according to their ammonia concentration. In addition,

LDA gives the highest classification success rate, i.e. accuracy of 100% for frequencies and ammonia concentration lower than f_c ($\approx 10^4$ Hz) and 20 ppm, respectively. It is also noticeable that LDA plots were overlapped for frequencies higher than f_c , and the total accuracy of the device is 95% for frequencies below f_c . This study presents evidences that resistive, and not capacitive, effects are a more precise parameter to reach high performance of PANI-based ammonia gas sensors from 0 to 30 ppm. In addition, our statistical analysis indicates that ammonia levels were correctly identifiable as shown when using K-means clustering with LDA methods, and the device has the capacity to recognize, for example, ammonia concentration levels around 20 ppm with accuracy of 95%, according to the K-Means. One limitation of this methodology is that it fails to provide the impact of electrode effects on the complex impedance of the sensor in the 1-10 Hz range (see section 3.1). Despite this limitation, our findings confirm that resistive effects dominate the capacitive behaviors for frequencies below than 10^4 Hz, and how important the operation frequency is to optimize the performance of the sensor.

3.3 Sensor evaluation results

Our goal is to identify the reproducibility and linearity responses of the sensor. We considered a restricted operate frequency for the sensor to be as 100 Hz and a set of five PANI-based sensors which are simultaneously exposed to the same ammonia gas level from 0 to 30 ppm. We chose 100 Hz to eliminate 60 Hz power line interference from any AC power line signals, but we could choose any frequency in between 10 Hz and 100 Hz as the operation frequency of the sensor, as illustrated in Figs. 2, 3 and 5. The reproducibility and linearity responses of the sensor are shown in Figure 6.

From Fig. 6 a standard deviation lower than 5% (standard deviation bars) is observed which indicates adequate performance of the sensors. The reproducibility, well-defined operating range (0-30 ppm) and the standard deviation in ammonia gas level of 5% is satisfactory for many applications in animal confinement buildings. Consequently, a linear response is desirable because it leads to a simple calibration of the sensors, and more importantly, a constant sensitivity and precision in ammonia gas level over the entire linear range. The scatter diagram shown in Fig. 6 reveals a linear relationship between $Z'(f)$ and the ammonia gas level indicating that a linear regression model (dot line) might be appropriate for this important ammonia gas level range.

Finally, the PANI-based sensor can be dedoped and doped in a reversible manner by alternating exposure to ammonia and clean air, as shown in Figure 7. Such dedoping-doping

dynamic cycle can be performed for a number of times, and the relative percentage of $Z'(f)$ of PANI-based sensor is thus converted to ammonia level values using the linear regression showed in Fig. 6. Figure 7 also shows that the response time (the time period for the change in $Z'(f)$) of the PANI-based sensor and of the high-performance electrochemical diffusion ammonia sensor (the reference sensor) are quite similar. Moreover, when the levels of ammonia increases, the response time of the PANI-based sensor is identical to the one obtained from the reference sensor (about 1 min), but its recovery time is greater than 30 min. A possible explanation for this phenomenon is that the ammonia diffusion and removal rates in PANI/PVS film are different. It means that the impedance of the sensors gradually decreased (doping process) or increased (dedoping process) and finally reached stable equilibrium at different rates. These observations are similar to those in Hong et al. [35] findings for electronic nose instruments. Despite the high recovery time of the PANI-based sensor, our findings suggest that this device is robust, easy to process, inexpensive and presents high-sensitivity characteristics. Consequently, the device presents the minimal requirements for a successful application as ammonia gas sensors for animal confinement buildings.

4. CONCLUSIONS

This paper has highlighted the importance of exploring the AC electrical behavior of easy-to-process, inexpensive (< US\$ 1) and user-friendly PANI-based ammonia gas sensors with potential application to health control in animal confinement buildings. We employed the complex impedance technique for proper adjustment of the operation frequency of the device. This approach has the potential features to provide an effective method to distinguish the electrode, resistive and capacitive contributions of PANI-based sensor in a wide frequency range. Consequently, it establishes an operating frequency in the range from 10 to 100 Hz with which drift and delay problems are insignificant, and therefore enhances the reproducibility, stability, sensibility (< 1 ppm), reversibility and response time (< 1 min) of solution-processed sensor. These results were as efficient as those obtained using a more expensive commercial apparatus. In addition, Linear Discriminant Analysis (LDA) combined to K-Means clustering illustrated our ability to detect ammonia concentration around 20 ppm with accuracy of 95%, with a few complex impedance data points misclassified. Contrary to expectations, our results showed different recovery and response times for the proposed device. However, our results are in agreement with the performance of the electronic nose described in ref. [35]. The reasons for our results could be attributed to the difference between the ammonia diffusion and removal rates in PANI/PVS film. Finally, our study provides a stimulus for a new way to improve the performance of PANI-based devices from Impedance Spectroscopy measurements, and we believe that our method could be useful if employed in different organic devices.

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TABLE CAPTION

TABLE I: Piecewise and total accuracy of K-Means clustering under PCA and LDA.

FIGURE CAPTIONS

GRAPHICAL ABSTRACT: Solution-processed ultrathin PANI films as inexpensive ammonia sensor for livestock buildings.

FIGURE 1: Schematic of the fabrication processes of solution-based ammonia gas sensors with thin PANI/PVS layer on PS and Ag electrodes using LbL and screen-printing techniques, respectively.

FIGURE 2: Real (■) and imaginary (○) components of the complex impedance of PANI-based sensor exposure to (a) 0 ppm, (b) 9 ppm and (c) 28 ppm of ammonia gas levels. The line is only to guide the eyes.

FIGURE 3: Relative percentage of $Z'(f)$ of PANI-based sensor as function of time obtained from dc ($f \rightarrow 0$) to frequencies equal to 1, 10, 10 kHz and 100 kHz.

FIGURE 4: K-means clustering under PCA for ammonia discrimination in PANI-based sensor. Plots (a), (b), (c), (d), (e) and (f) represent piecewise frequency analyses.

FIGURE 5: K-means clustering under LDA for ammonia discrimination in PANI-based sensor. Plots (a), (b), (c), (d), (e) and (f) represent piecewise frequencies analyses.

FIGURE 6: Relative percentage of $Z'(f)$ at 100 Hz of PANI-based sensor as function of time obtained from a set of five identical PANI-based sensors (S_1 , S_2 , S_3 , S_4 , and S_5). The line is only to guide the eyes.

FIGURE 7: Dynamic response of the PANI-based sensor (○) and the reference sensor (-). The ammonia concentration was varied from 0 to 40 ppm.

Figure 1

Figure 01
MC Santos

Figure 2

Figure 02
MC Santos

Figure 3

Figure 03
MC Santos

Figure 4

Figure 04
MC Santos

Figure 5

Figure 05
MC Santos

Figure 6

Figure 06
MC Santos

Figure 7

Figure 07
MC Santos

Figure 04
MC Santos

Figure 05
MC Santos

MC Santos
Figure 06

Accuracy (%)							
Frequency range (Hz)		1-10	10-10 ²	10 ² -10 ³	10 ³ -10 ⁴	10 ⁴ -10 ⁵	10 ⁵ -10 ⁶
Method	[NH ₃] (ppm)						
	0-9	100	100	100	100	100	40
	9-14	97.8	100	100	100	56	37.8
	14-20	82.2	70	72	58	46	35.6
	20-28	66.7	68	60	58	50	31.1
	Total (0-28)	86.6	84.5	83.0	79.0	63.0	36.1
Method	[NH ₃] (ppm)						
	0-9	100	100	100	100	100	66.7
	9-14	97.8	100	100	100	74	53.3
	14-20	80	80	80	80	70	64.4
	20-28	100	100	100	100	76	66.7
	Total (0-28)	94.5	95.0	95.0	94.0	80.0	62.7