Polypyrrole based gas sensor for ammonia detection

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Abstract. The nature of polypyrrole response to toxic gases does not allow using the sensor in a conventional way. The main aim of this study is to acquire the information about the concentration using different approaches: a linear approximation, a non-linear approximation and a tangent method. In this paper a two-steps procedure for sensor response measurements has been utilized. Polypyrrole films were electrochemically synthesized on the interdigitated electrodes. Gas sensing measurements of polypyrrole based sensor were carried out at room temperature. The influence of the flow rate on the sensing performance to NH₃ were investigated. The preliminary studies of aging of the sensor were also explored.

1. Introduction
Today, protection of the environment and persons is more important than before. For that reason there is a need for improved or new sensors for measuring both physical and chemical changes, such as humidity, temperature, pressure and chemical species [1,2]. For this purpose there were many attempts in order to manufacture the suitable sensing materials. Nowadays there is a great interest in making conducting polymer sensors [3]. Conducting polymers, especially polypyrrole (PPy), are emerging as intelligent materials and they have a wide range of applications in the field of optical, electronic, electrochromic devices and sensors. The reasons for such widespread interest of polypyrrole (PPy) are its easy deposition from aqueous and non-aqueous media, adherence to many types of substrates, stability in air and aqueous media and high electrical conductivity [4]. Controlling the materials properties of conducting polymers such as morphology, electroactivity and conductivity, which are strongly dependent on how conducting polymer are synthesized, is required for the successful implementation of conducting polymers in devices [5]. Polymer gas sensing films can generally be prepared by several techniques including a solution casted method [6], a thermal evaporation [7], a drop-coating [8] and a Langmuir-Blodgett technique [9]. The simplicity of preparation and the possibility to control experimental conditions by electrochemical techniques make it the most employed way. In this case, the electrochemical synthesis of conducting polymer is the most convenient [4]. Moreover, it is now well-known that many chemical or physical properties of electrodeposited polypyrrole can be strongly varied by modifying the electropolymerization parameters including: current density [10], temperature [11], solvent [12,13], pH [14], counter-ion [15], counter-ion concentration [16], pyrrole concentration [17] and electrodeposition potential [18]. The most important advantages of polypyrrole based gas sensors is their easy and cheap fabrication [19], temperature operation and high sensitivity [19]. Therefore, polypyrrole has been widely used as an effective material for the detection of toxic, hazardous and flammable gases [20].
The nature of PPy response to toxic gases does not allow using the sensor in a conventional way. Therefore, an alternative approach is sought [4,21]. The main aim of this study is to acquire the information about the concentration using different approaches: a linear approximation, a non-linear approximation and a tangent method. In this paper a two-steps procedure for sensor response measurements has been utilized. In the first step, the gas is turned on for 5 minutes (gas-on) and in the second step is turned off for 30 minutes (air-on) forming a 35 minutes cycle. Such times were chosen to compare the results with the literature. Gas sensing measurements of PPy/LiClO$_4$ were carried out at room temperatures. The influence of the flow rate has also been investigated. The preliminary studies of aging of the sensor were also explored.

2. Experimental

2.1. Electrochemical polymerization
Polypyrrole films were electrochemically synthesized on the interdigitated gold electrodes (BVT Technologies) in a one step process from aqueous solution of 0.1 M pyrrole monomer (97 %) and 0.1 M lithium perchlorate (≥ 98 %) (all from Sigma Aldrich).

![Figure 1. Schematic picture of the interdigitated gold electrode.](image)

Gap between fingers: 50 μm  
Finger width: 50 μm  
Finger length: 7 mm

Electropolymerization processes were performed potentiostatically at potential of 1 V vs. reference electrode (80 Ω·cm$^{-2}$) in a one-compartment cell with a three electrode system. An Ag/AgCl (R-10 Hydromet) electrode was used as the reference electrode and a platinum gauze electrode (80 mesh 25 x 35 mm) as the counter electrode. The working electrode was the interdigitated gold electrodes with a finger width of 50 μm and a gap size of 50 μm (see figure 1). Before and after each experiment working electrode was rinsed with deionized water and isopropanol.

2.2. Gas sensing measurements
The sensor was placed inside a glass chamber of 123 mL volume, which was always kept under continuous flowing of testing gas mixture or air at a constant flow rate of 50 mL min$^{-1}$ (sccm – Standard Cubic Centimeters per Minute) or 100 mL min$^{-1}$. NH$_3$ with a concentration of 10-100 ppm was utilized to evaluate the sensing performance. To alleviate the baseline drift, the sensing films were exposed to synthetic air overnight before data collection. Then, the sensors were cyclically exposed for 5 min to ammonia (gas-on step). Between each exposition to ammonia, the sensors were exposed to the synthetic air during 30 minutes to allow desorption of ammonia molecules from the sensors (air-on step). The resistance was monitored continuously over time (a measurement was made every 5 s). The testing gas was generated by mixing premixed gas (200 ppm of NH$_3$) with synthetic air controlled by the mass flow controllers (Tylan GmbH). The resistance changes of based sensors were monitored with a computer controlled multimeter (RIGOL DM3068). All the gas sensing measurements were performed at room temperatures in dry gases.
3. Results

3.1. Sensing characteristic

To take advantage of the polypyrrole polymer as a sensing layer, a two-step procedure has been conducted. The first step begun when the gas was turned on for the 5 minutes (gas-on step), while the second when the gas was turned off for 30 minutes (air-on step). These two steps formed a 35 minutes cycle (see Figure 2a). The literature does not show a repetition of the cycles for this type of sensor. Patois et al. [4] and Carquigny et al. [21] show only the first cycle of PPy sensor response, allowing them to establish that this polymeric material can be used as a gas sensor. The repeatability of the PPy sensor response to 80 ppm of NH$_3$ was presented for the first time in Figure 2a. It can be noted that this sensor does not work as a typical sensor, where the level of resistance determines the concentration. As the NH$_3$ gas is introduced into the chamber, the resistance of the sensors always increases. Ammonia reacts with the PPy and induces a modification in electrical properties of the sensor’s sensitive layer. The decrease of the sensor’s resistance observed under exposition to the synthetic air, corresponds to desorption of ammonia molecules from the polypyrrole film. The mechanism of interaction between a polymer film and an ammonia has been already studied by Carquigny et al. [21]. Since polypyrrole can be considered as a p-type semi-conducting material composed of both neutral and oxidized monomer units, the ammonia adsorption onto the PPy films was shown to begin with the loss of an electron by the nitrogen’s doublet of some nitrogen atoms of the polymer backbone, leading to the formation of NH$^+$ radical groups. This electron transfer between ammonia molecule and the polymer’s positive hole induces a diminution of the positive charge density which leads to an increase in the resistance. Consequently, after adsorption of NH$_3$, the polymer becomes less conducting, and the measured resistance increases. On the contrary, during desorption of the ammonia molecules, the sensor’s resistance decreases [4,21]. Figure 2b displays the comparison of the gas sensor responses to 10-100 ppm of NH$_3$ depending on the flow rate of NH$_3$/air cycles with each cycle lasting for 35 minutes. The behavior of the gas sensors was estimated using the normalized resistance changes ($R/R_0$), where $R_0$ is an initial resistance of the first cycle. Figure 2b shows that the curves have different nature depending on the concentration of the pollutant gas and the flow rate in the gas chamber. It is expected that one can find a specific parameter in the cycle so specific gas concentrations can be determined.

![Figure 2. PPy sensor response to 80 ppm of NH$_3$ (a), and to different concentrations of NH$_3$ (b).](image-url)

Therefore, the different parameters of the cycles were calculated and plotted as a function of the concentration. Namely, the data was approximated to the exponential function (parameters $t_{AN1}$, $t_{AN2}$, $NR_1$ and $NR_2$), the linear function (parameters $a_1$, $a_2$, $t_{AL1}$, $t_{AL2}$) and the tangent function (parameters $t_{SL1}$, $t_{SL2}$). The calculations were carried out for both the gas-on step ($t_{AN1}$, $NR_1$, $a_1$, $t_{AL1}$ and $t_{SL1}$) as well
as air-on step (\(t_{AN2}, NR_2, a_2, t_{AL2} \text{ and } t_{AS2}\)) which is presented in Figure 3, 4, 5, 6 and 7 respectively. The \(t_{AN1}, t_{AN2}, NR_1 \text{ and } NR_2\) parameters were calculated based on equation:

\[
R = R_c + A \cdot (1-\exp(-t / t_{ANx})), \quad (1)
\]

where \(R_c\) and \(A\) are the parameters of exponential function (where \(x = 1 \text{ or } 2\) for gas-on and air-on step respectively). The values of \(t_{AN1}\) were approximately linear with concentration for the gas-on step (Figure 3a). As can be seen \(t_{AN1}\) depends on the concentration. The resistance variations marked as normalized response (\(NR_1\) and \(NR_2\)) were calculated according to the following equation:

\[
NR \% = A / R_c \cdot 100\%, \quad .. \quad (2)
\]

The parameter NR (originally called sensitivity in [22]) was also calculated. The values of NR were approximately linear with concentration for the gas-on step, as well as for air-on step (Figure 4a and 4b). However, \(NR_1\) values depend on the flow rate. In the case of air-on step, \(NR_2\) values are very similar, regardless of the flow rate. To determine \(t_{AL1}\) and \(t_{AL2}\) parameters and the values corresponding to the slope (\(a_1\) and \(a_2\)) the first 12 measurement points (obtained during the first minute of gas-on step) for each acquisition were used for the approximation. This values were presented in Figure 5 a,b and 6 a,b. The \(a_1, a_2, t_{AL1} \text{ and } t_{AL2}\) parameters were calculated based on equation:

\[
R = a_x \cdot t + b_x, \quad (3)
\]

where \(a_x, b_x\) are the parameters of linear function (where \(x = 1 \text{ or } 2\) for gas-on and air-on step respectively).

![Figure 3. The \(t_{AN1}\) (a) and \(t_{AN2}\) (b) parameters calculated using exponential function.](image1)

![Figure 4. The \(NR_1\) (a) and \(NR_2\) (b) parameters calculated using exponential function.](image2)
The value of $t_{AL2}$ for the concentration of 10 ppm and a flow rate of 50 sccm could not be calculated. It can be noticed, that both a $t_{AL1}$ parameter and the slope $a_1$ are linear with concentration for the gas-on step for both the flow rate of 50 sccm and 100 sccm. According to Figure 3b, 5b and 6b it can be seen that the air-on step brings less information about the concentration, because of the non-linearity of mentioned characteristics.

![Figure 5. The $a_1$ (a) and $a_2$ (b) parameters (slope) calculated using linear function.](image)

![Figure 6. The $t_{AL1}$ (a) and $t_{AL2}$ (b) parameters calculated using linear function.](image)

The procedure of obtaining $t_{S1}$ and $t_{S2}$ parameters was based on the calculation of the tangent function to the sensor response curve after one minute from the beginning of the gas-on or air-on stages. In order to do this, the derivative of the sensor response in point corresponding to one minute exposure to the target gas or synthetic air in the cleaning phase was estimated. Then, the formula of the linear tangent function was obtained and the value corresponding to the maximum resistance (during gas-on step) or minimum resistance (during air-on step) was selected for the calculations of $t_{S1}$ and $t_{S2}$ parameters, respectively. The formula for calculation the tangent function is presented below:

$$f_{tangent} = R_s'(t_{60}) \cdot (t - t_{60}) + R_{60},$$  \hspace{1cm} (4)

where $t_{60}$ represents the time of one minute to the target gas or air in the cleaning stage, $R_{60}$ is the value of sensor resistance corresponding to that time and $R_s'(t_{60})$ is derivative of the sensor response curve after one minute exposure. The obtained results are shown in Figure 7a and b. The results
shown, that despite the fact that values of the $t_{S1}$ and $t_{S2}$ parameters are decreasing for the increasing values of gas concentration, it is impossible to estimate useful trend for gas concentration estimation. This was possibly caused by the fact, that consecutive measured points in raw sensor response didn’t create smooth curve. Calculated tangent functions were very sensitive to the disturbances in sensor responses and due to this fact, parameters $t_{S1}$ and $t_{S2}$ cannot be utilized for further analysis.

Figure 7. The $t_{S1}$ (a) and $t_{S2}$ (b) parameters calculated using tangents method.

Among investigated parameters in this preliminary study, the best indicator of the gas concentration was based on linear approximation of the measured points during the first minute of exposure to target gas. The method based on the exponential approximation was unpractical due to its complexity. However, method based on the $t_{S1}$ and $t_{S2}$ parameters calculated from the tangent function was too sensitive for the small disturbances in sensor response. Further investigations are conducted to find more robust and discriminative parameters, e.g. by utilizing multivariate methods.

Figure 8. The aging process of PPy sensor (80 ppm of NH$_3$, flow rate of 100 cm$^3$/min).

3.2. Stability of PPy sensor
The stability of the sensor is very important parameter to be considered. Stability performance of PPy sensor to 80 ppm of NH$_3$ gas after 1, 20, 21 and 35 days is shown in Figure 8. It can be noted, that the drift in sensor response is noticeable (Figure 8a) but for this data it seems to have linear trend. The values of $t_{AL1}$ parameter is approximately linear with the number of days for the gas-on step (Figure.
8b). Polymer based sensor usually possess a common drawback of decrease in normalized response due to ageing-induced effects [22]. In the report [22], the PPy sensor exhibited maximum normalized response for 100 ppm of 36%; however, it dropped from 36% to 20% after 35 days. However, in this study the normalized response increase from 11% to 19% after 35 days (see Figure 8b). This result indicate that the PPy sensor prepared using presented procedure can be used as a reusable sensing material for the detection of NH$_3$ gas operating at room temperature, although, the indicated parameters are sensitive for aging.

4. Conclusions
In this work, polypyrrole based gas sensor for ammonia detection has been studied. Polypyrrole was electrochemically synthesized from an aqueous solution of 0.1 M pyrrole and 0.1 M lithium perchlorate. That prepared sensor was cyclically studied (5 minutes gas-on step and 30 minutes air-on step) in response to different concentrations of ammonia gas. Such times were chosen to compare the results with the literature. It can be expected that measurement cycle may be reduced to about 5 minutes. However, for some applications requiring fast measurement time it might be too long. When the NH$_3$ gas was introduced into the chamber, it was noticed that the resistance of PPy sensor was increasing. Based on the sensor response curves, various parameters have been determined in order to find the best indicator of the gas concentration. The data was approximated to the exponential function (parameters $t_{AN1}, t_{AN2}, NR_1$ and NR$_2$), the linear function (parameters $a_1, a_2, t_{AL1}, t_{AL2}$) and the tangent function (parameters $t_{S1}, t_{S2}$). The calculations were carried out for both the gas-on step ($t_{AN1}, NR_1, a_1, t_{AL1}$ and $t_{AL2}$) as well as air-on step ($t_{AN2}, NR_2, a_2, t_{AL2}$ and $t_{AL2}$). The results show, that the $t_{AN1}, NR_1$ and NR$_2$ values were approximately linear with concentration for the gas-on step. However, the non-linear parameters had a high computational complexity. It was noticed that the linear method parameters ($t_{AL1}$ and $a_1$) were linear with concentration for the gas-on step for both the flow rate of 50 sccm and 100 sccm. Based on calculations, it can be seen, that the air-on step brought less information about the gas concentration because of its non-linearity. The method based on $t_{S1}$ and $t_{S2}$ parameters calculated from the tangent function has proven to be too sensitive for the small disturbances in sensor response. The further investigations will include the influence of the condition of PPy synthesis on its gas sensing properties, sensor responses to the other volatile compounds, data processing and analysis to enable efficient recognition and identification of measured gas.

5. References
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Acknowledgments

Financial support of the Polish Ministry of Science and Higher Education by the „Diamond Grant” programme for the project “Conducting polymers in environmental gas sensors” (0251/DIA/2013/42) and by the Statutory Funds for Research of Faculty of Electronics, Telecommunications and Informatics, Gdansk University of Technology is greatly appreciated.