Nitrogen dioxide sensing properties of PEDOT polymer films

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Abstract

This work presents a simple and fully electrochemical route for the polymerization of poly(3,4-ethylenedioxythiophene) (PEDOT) films for fabricating a NO$_2$ gas sensor prepared by electropolymerization of 3,4-Ethylenedioxythiophene (EDOT) monomer in lithium perchlorate/acetonitrile solution. The main aim of this study is to determine the sensing properties of conductive polymer at elevated temperatures. The effects of the humidity, working temperature and sensing response of the PEDOT to environmental gases are investigated. The use of the PEDOT film as NO$_2$ gas meter of total flow of NO$_2$ is evaluated.

Keywords: Gas sensor, Sensor, PEDOT, Gas dosimeter

The gas sensors have been extensively used for qualitative and quantitative detection of chemical substances especially for environmental monitoring [1,2], personal protection, safety and process control [3]. Conducting polymers are widely used in order to enhance the speed, sensitivity and versatility of various sensors and biosensors [4]. These polymers, especially PEDOT, are emerging as intelligent materials and they have a wide range of applications in the field of optical, electronic, electrochromic sensors and devices [5]. The reasons for such widespread interest of PEDOT are its high conductivity, electrical and spectrochemical properties associated with its low band gap, electrochromic and antistatic properties and good stability. All of these paved this polymer way into numerous important applications [6,7]. Furthermore, a major appealing quality of PEDOT is its inherent stability compared to the other polymers. Namely, PEDOT can be exposed at 100°C for up to 1000 h without an appreciable change in conductivity [8].

Controlling the conducting polymers properties, such as morphology, electroactivity and conductivity, which are strongly dependent on how conducting polymer are synthesized, are required for their successful implementation [9]. Functional groups determine the polymer properties [10,11] and play the key role in the sensing mechanism [12,13]. Polymer gas sensing films can generally be prepared by several techniques including a solution casting method [14], a thermal evaporation [15], a drop-coating [16], electrospinning [17] and a Langmuir-Blodgett technique [18]. Preparation of conductive polymer films for sensing applications by electropolymerization is a less popular approach. However, electropolymerization is often the preferred method because reaction conditions, such as the polymerization potential, solvent, supporting electrolyte, temperature and substrate materials, can be adjusted to tailor the resulting films properties [19]. The most popular polymer sensors are chemiresistors, in which the resistivity of a conducting polymer is sensitive to an analyte gas. The composites of PEDOT are favored material by choice, for example MWCNT-PEDOT [14], Pd/PEDOT:PSS [20] and PEDOT:PSS/graphene [21] based sensors for ammonia, PEDOT:PSS/graphene for CO$_2$ monitoring [22], PEDOT-PSS/TiO$_2$ based sensor for NO$_2$ and NH$_3$ [23], WO$_3$-PEDOT:PSS [24] and PEDOT-RGO for NO$_2$ detection [25]. In turn, PEDOT:PSS alone fabricated by drop coating or imprinting method has been used as the sensing material for the detection of NO [26] and NH$_3$ [3,27]. However, to our knowledge, the gas sensing characteristics of the pristine PEDOT film prepared by electropolymerization is reported for the first time. The main aim of this study is to determine the properties of the environmental gas sensors using PEDOT at elevated temperatures. In this study, the PEDOT film is electrochemically synthesized using 3,4-Ethylenedioxythiophene (EDOT), lithium perchlorate (LiClO$_4$) and acetonitrile (CH$_3$CN). The effects of the humidity, the working temperature and sensing response of the PEDOT to different gases are investigated. PEDOT response to NO$_2$ is much higher than to the other investigated gases, but irreversible. The use of the polymer film based gas sensor as the accumulating-type NO$_2$ sensor (gas dosimeter, total amount integrator) is presented. Moreover, the
NO2 concentration can be determined by calculation of the rate of the resistance change.

1. Experimental

Like other conducting polymers, such as polypyrrole, PEDOT can be readily deposited onto metal surfaces using electropolymerization method. The electrochemical polymerization was performed in conventional three electrode cell using a VersaStat 4 equipped with VersaSTUDIO software on commercially available interdigitated gold electrodes (BVT Technologies) with a finger width of 50μm and a gap size of 50μm (see Fig. 1) A platinum wire was used as the counter electrode. The working electrodes (inter-digitated gold electrodes) were rinsed with deionized water and isopropanol. All potentials are given vs. the Ag/AgCl/3 M KCl reference electrode. The PEDOT films were electrodeposited in 0.01 M EDOT/0.1 M LiClO4/CH3CN mixed solution by applying 1.2 V in potentiostatic mode with an electropolymerization charge limited to 40 mC (until the pair of fingers connection). The resistance of the sensor decreases with the time of electropolymerization. After the electrochemical treatment, an adherent dark blue film was observed on the electrode, which demonstrated that PEDOT layer was formed on the surface of gold electrodes. No changes in the film adhesion was observed during electropolymerization. After polymerization, the modified electrode was washed thoroughly with water and isopropanol.
For the surface characterization scanning electron microscope FEI Quanta FEG 250 with an Everhart-Thornley secondary electron detector was used. For elemental analysis the Energy Dispersive X-ray Spectroscopy was performed by EDAX Genesis APEX 2i with ApolloX SDD spectrometer.

The existing functional groups of electrochemically prepared PEDOT were measured by an Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectrometer (PerkinElmer Spectrum 100) in the 4000–650 range with a resolution of 4 cm⁻¹. Spectral data were collected by the TimeBase software (PerkinElmer). All the spectra were normalized with respect to the peak of 1050 cm⁻¹.

Gas sensing properties were measured in a glass chamber of 123 mL volume, which was always kept under continuous flow of testing gas mixture or air at a constant flow rate of 100 mL min⁻¹. NO₂ with the concentration of 10 ppm–100 ppm and NH₃, H₂S and SO₂ with the concentration of 100 ppm were utilized to evaluate the sensing performance. To alleviate the baseline drift, the sensing films were exposed to the synthetic air (Linde Gas, purity 5.5) overnight before data collection. The resistance change of PEDOT based sensors were monitored with a computer controlled multimeter (RIGOL DM3068). The gas sensing measurements performed at elevated temperatures were obtained by heating the glass chamber by a tube furnace. A different RH of 0%, 30% and 60% for selectivity tests were obtained by mixing a given ratio of water-saturated air with dry synthetic air.

![Fig. 3. EDS map of sulfur, conduction pathway between gold electrodes.](image)

2. Results

2.1. Film characterization

Morphology of electropolymerized PEDOT films are shown in Fig. 2. The obtained structure is having a globular morphology (Fig. 2b) with expanded surface area in comparison to the bare electrode (Fig. 2a). The morphology of PEDOT sensor deposited on gold formed cauliflower like structures (Fig. 2c) with size of about 2 μm. These structures are constructed with nanoparticles matrix appeared to be densely packed and characterized by a high porosity. It can suggest a high degree of polymerization. A cross section image (Fig. 2d) shows that PEDOT formed a layer of cauliflower like microstructures and the layer thickness is comparable to the size of the granules (2 μm).

EDS mapping of the sulfur, which is a marker for the presence of a PEDOT layer, showed that properly performed synthesis leads to the formation of interconnecting paths between electrodes. As exhibited in Fig. 3, PEDOT provides continuous pathway across interdigitated electrodes. However, the PEDOT layer is not evenly distributed. It forms bridges only in certain areas between gold electrodes, which is responsible for the electric resistance.

The FTIR spectra of obtained PEDOT layer before and after exposure on NO₂ are presented on Fig. 4. Presented spectrum is typical for the structure of the PEDOT obtained by the electropolymerization method, with high degree of polymerization. Comparing the spectrum measured for the as prepared sample and samples exposed to nitrogen dioxide no significant changes can be observed in the arrangement of absorption peaks. This demonstrates the stability of the obtained system. However it can be seen a decrease in peak intensities for higher wave numbers (>1400 cm⁻¹), in the range characteristic for vibration of double bonds. Simultaneously

![Fig. 4. FTIR spectra of pristine PEDOT (a), PEDOT after NO₂ exposure (b).](image)

![Fig. 5. Response of the PEDOT sensor (initial resistance of 0.5 kΩ) for different gases at 80 °C (a) and selectivity to humidity (b). RH is given for 25 °C.](image)
one can observe the increase in intensity of the peaks in the lower range of wavenumbers, dominated by stretching vibration carbon single bonds. Such a changes in the FTIR spectra can be explained by the partial oxidation of the surfaced PEDOT. After overoxidation, PEDOT exhibits two new bands at 1097 and 1221 cm⁻¹ attributed to the symmetric and antisymmetric vibrations of the sulfone groups -SO₂ in the thiophene units [28]. Upon overoxidation, a peak at 1853 cm⁻¹ is visible and likely originates from carbonyl groups, C=O [28]. This is in agreement with previous studies on polythiophenes, demonstrating the formation of carbonyl groups on the thiophene ring, interrupting the conjugation of the chain, upon overoxidation [28]

2.2. Sensing properties

The response of the PEDOT sensor towards NO₂, SO₂, H₂S and NH₃ gases of the same concentrations of 100 ppm has been investigated. As shown in Fig. 5a, PEDOT shows an obviously higher response to 100 ppm of NO₂ at 80 °C compared with NH₃, H₂S and SO₂. The inset picture in Fig. 5a presents the irreversible sensor response to 100 ppm of NO₂ at 80 °C. As the NO₂ is released into the chamber, the resistance of the structure increased continuously with exposure time. This is because NO₂ is a well-known oxidizing gas, which in contact with the \( \pi \)-electron network of polymer is likely to result in the transition of an electron from polymer to the gas. PEDOT is oxidized by NO₂ when PEDOT film is in contact with NO₂ gas. With the used concentrations (10 ppm–100 ppm), the conductivity decreases. It suggests that with the increase of oxidation time, the oxidation proceeds, resulting in the decrease of conductivity [18]. Furthermore, NO₂ as a strong oxidant causes overoxidation of the polymer, which was proved by FTIR analysis.

The selectivity to humidity tests were also performed, which are shown in Fig. 5b. The relative humidity values are given for room temperature (25 °C). The exposure of the PEDOT film for 60 min to 100 ppm of NO₂ at 80 °C (0% RH) results in a 22% change of resistance. The exposure for 60 min to 100 ppm of NO₂ at 30 °C (0% RH) results in a 8.6% change of resistance, which is more than two and a half times lower at 80 °C (see Fig. 5b). Higher operating temperature improves the sensor response. Moreover, an influence of humidity at 30 °C is much higher than at 80 °C. At 80 °C and RH of 60% change is insignificant (below 0.5%), while at the temperature of 30 °C and RH of 60%, the change of 8.1% may be observed, which is more than sixteen times greater. It should be noted that the response of the PEDOT at 30 °C (0% RH) results in 8.6% change of the resistance, which is practically the same as in the case of the influence of humidity at 30 °C. So, higher operating temperature helps to overcome the influence of humidity.

![Fig. 6. The resistance dependence on gas concentration.](image)

![Fig. 7. A conversion of concentration to the number of moles of NO₂ or grams for 0.5 kΩ.](image)

2.3. Accumulating-type NO₂ sensor

The accumulating sensing principle is a novel and promising concept to measure directly and accurately different amounts of a gaseous analyte species. As it has been previously reported, the observation of the change of resistance of a thin layer of a storage material exposed to an analyte gas, gives an information about the total amount of the passed analyte molecules [29]. By accumulating analyte molecules in the sensitive layer, even small levels contribute to the sensor signal [30]. In contrast to typical chemiresistor, which measure the actual concentration of analyte, \( c_{\text{gas}} \), the accumulating sensing principle is based on the idea of detecting the total amount of the gaseous species, \( A_{\text{gas}} \).

\[
A_{\text{gas}} = \int c_{\text{gas}}(t) V(t) \, dt, \quad (1)
\]

where \( V \) is the time-dependent gas flow rate.

As mentioned before, PEDOT exposed to NO₂ irreversibly change the resistance. The irreversible increase of the resistance is not a desirable effect in the case of gas sensors. However, it can be desirable in the case of integrating gas sensor, known also as a total amount gas flow, totalizer, gas counter or accumulating gas sensor. In Fig. 6 the resistance is plotted as a function of time for different concentrations at a flow rate of 100 cm³/min. It can be seen that during the exposition, the integrating NO₂ sensor works similar to a dosimeter [31]. As a result of PEDOT interaction with NO₂ molecules, a continuous increase of resistance proceeds. In times without NO₂ the sensor response remains constant, and thus satisfies the assumptions of accumulating sensing material. Moreover, the resistance change for a given time (rate of resistance change) depends on gas concentration. Namely, the slope increase with increasing concentration of NO₂, implying that the plot may contain more information. The possibility of application of PEDOT film as accumulating-type NO₂ sensor is presented in Fig. 7. The amount of an accumulated gas is recalculated knowing NO₂ concentration and time, while the resistance (or resistance change) is plotted as a function of total amount of NO₂ (in moles or in grams). It can be seen that nearly linear dependence was obtained and the sensor signal depends linearly on the flow rate. One can deduce that the sensor response is directly proportional to the total offered amount. Similar dependence was obtained for potassium carbonate based sensors [29,31], which was proposed to be used as an accumulating type of sensor.

It was shown that two types of accumulation sensors exist [29]. Namely, partial and total adsorption. In the case of the first one, only
a fraction of the analyte molecules, proportional to the concentration, is stored in the layer. In the case of the second one, all analyte molecules passing the sensor are stored in the sensitive layer. In this preliminary studies it has been noticed that in a measuring range PEDOT film exhibits a total adsorption, since is independent on the flow rate. Still more detailed studies need to be performed.

2.4. Gas concentration sensor

As mentioned before, at higher NO2 concentrations, the instantaneous adsorption of NO2 molecules is higher, causing the rate of change to be higher. The rate of change of resistance as a function of NO2 gas concentration is shown in Fig. 8.

The relationship between the rate of change of resistance and NO2 concentration is approximately linear, and this linearity can be used to obtain information about the instantaneous NO2 gas concentrations. According to the calculation, which is proposed by Wu et al. [30], the value of $K = \frac{dR}{dt}$ is directly proportional to the concentration. These equations are in good agreement with our experimentally obtained curves in the case of NO2 gas. Wu et al. developed the rapid determination of oxygen concentrations via the analysis of the rate of change of resistance as a result of step change of concentration for SnO2 gas sensor [30]. Patois et al. used the calculation of the slope values as an information about the sensitivity of the polyppyrole gas sensor [32]. However, the proposed in the literature sensors [30,32] do not allow building the total flow dosimeter without any additional summative circuits because of reversible response. Moreover, it is only possible to determine the instantaneous concentration when a step change of concentration occurs, what is uncommon in real systems. Presented in this work results show that it is possible to construct a total flow dosimeter of nitrogen dioxide.

3. Conclusions

The higher operating temperature accelerates the electrochemical reaction, thereby improves the response and helps to overcome the effects of the influence of humidity. A polymer gas sensor used as the gas dosimeter is a new approach. PEDOT exposed to NO2 reversibly change the resistance. However, it is found that the resistance change for a given time depends on gas concentration. PEDOT layer behaves like a total amount integrator. Once, the resistance is plotted as a function of total amount of NO2 one can obtain nearly linear dependence. In this work it has been noticed that in a measuring range PEDOT exhibits a total adsorption. Hence, PEDOT can be used as an accumulating sensing material but more detailed studies need to be performed. In order to translate studies into practice and for use as gas sensors, the structure should be optimized, e.g. the polymer thickness, the distance between electrodes, etc.

Acknowledgments

The project was financed by the Polish Ministry of Science and Higher Education based on decision 0251/DIA/2013/42 (“Diamond C” grant) programme for the project “Conductive polymers and nanofibers in environmental gas sensors”) and by the Faculty of Electronics, Telecommunications and Informatics, Gdańsk University of Technology (Statutory Funds).

References


Biographies

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