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An ammonia sensor based on in situ-synthesized polyaniline nanostructures

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Nowadays, a good deal of research is focusing on the development of new analytical procedures for detection of hazardous agents, such as bacteria, harmful pollutants, toxic vapors, and many others. The majority of the research is aimed at developing new sensors and analytical equipment. This paper demonstrates a simple construction of an ammonia sensor based on commercially available electronic connectors with active elements from polyaniline. The main goal of this research is to present the simplicity of sensor manufacturing, without the need for advanced apparatus such as electropolymerization or electrospinning set-up. The active element of the proposed sensor is composed of polyaniline synthesized in situ on the surface of conductive glue. The layer of the conductive glue is a key element in this sensor as it protects the metallic pin against destruction during *in situ* synthesis of polyaniline (acidic and oxidizing conditions).

Keywords: *ammonia sensor; polyaniline; nanostructures*

1. Introduction

In recent years, the interest in polymers has been increasing, especially since 1977, when Alan J. Heger, Alan G. MacDiarmid and Hideki Shirakawa showed that subjecting a conductive polyacetylene to bromine or iodine vapor increases its electrical conductivity to the values characteristic of the conductivity of metals. This was the beginning of the search for new conducting polymers. Attention of researchers has been directed towards the use of polymers as materials for chemical microchips and sensors [1].

According to the definition of the International Union of Pure and Applied Chemistry (IUPAC), a sensor is a device that transforms chemical information into an analytically useful signal. It consists of two elements: a chemically selective receptor layer and a transducer element. An example of a selective element can be polyaniline layer [1, 2].

Polyaniline (PANI) is the oldest known and one of the most thoroughly studied conducting polymers. Due to the variety of characters and transformations, it is one of the most interesting electroconductive polymers [3]. Polyaniline is schematically repre-
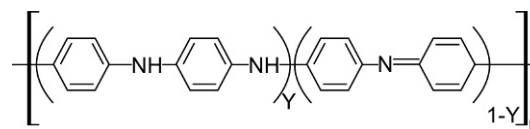

Fig. 1. The structural formula of polyaniline.

sented as a set of oxidized and reduced structures (Fig. 1).

Polyaniline can be obtained by both aniline electropolymerization and by chemical synthesis (for example, by using $FeCl_3$ as an oxidant or by oxidizing aniline using $(NH_4)_2S_2O_8$). A conductive polymer is created as a result of protonation and deprotonation due to the action of corresponding acids, and for oxidation purposes, different admixtures can be used, *e.g.* HCl. Undoped PANI and PANI doped by classic inorganic additives has poor mechanical properties, however it is one of the most stable conducting polymers in time. The conductivity of pure polyaniline reaches up to 10^4 S/cm. As a result of protonation of appropriate acids, it is possible to obtain soluble and melt-processable form of polyaniline which allows us to obtain conductive composites with different polymers [4].

The constant need to protect the human life and health involves continuous monitoring of air, soil

Table 1. Summary of threats to humans depending on the concentration of ammonia vapor in the air [5].

Effects on human	The concentration of ammonia [ppm]	Allowable residence time
Distinctive odor detectable by most people	25	Unlimited
The maximum allowable fixed concentration	35	8 working hours, 7 days a week
Clearly perceptible smell	50	According to essential needs
Sharp odor – without harmful effects on the body during short-term inhalation by a healthy human	100	Leave the room immediately
Mucosal irritation of eyes, nose, respiratory tract	400 – 700 Threshold of risk	1 hour usually does not cause serious consequences
Coughing attack, feeling of "obstructed" breathing, strong irritation of the mucous membranes of eyes, nose and respiratory tract	1,000 – 1,700	Half hour can lead to serious consequences
Strong cough, throat spasms, strong feeling of "obstructed" breathing together with caustic irritation of mucous membranes of eyes, nose and respiratory tract	2,000 – 5,000	Half an hour can cause death by suffocation
A strong feeling of general paralysis and nervous suffocation	5,000 – 6,000	Death occurs within a few minutes

and water. As a result of human activity, the amount of industrial pollutants, such as volatile organic and inorganic compounds, heavy metals, and radioactive isotopes, increases [1, 2]. One of such hazardous gases is ammonia.

Ammonia is a hardly flammable chemical compound, which presents small risk of fire as it burns only in the presence of a strong source of fire. Evaporation of ammonia in the open air does not pose the risk of explosion, but there is a danger in the case of indoor evaporation, when a rare combination of proportions of air and, for example, mercury occur as a source of ignition [5]. Ammonia also has the ability to attach to other compounds. This causes the formation of new compounds, which often leads to changes in the chemical properties and color of the compounds.

Ammonia is used mainly in refrigeration, for example in the food industry. Food products are characterized by different sensitivity to ammonia. Ammonia has the most significant impact on fresh products such as eggs, dairy products, fruits and vegetables. To a lesser extent, it affects frozen products and products wrapped in plastic. In case of leakage of ammonia, they are in a more favorable situation as their contact with ammonia is reduced. That is the

main reason why it is necessary to monitor both the food as well as the use of sensors to detect ammonia. It contributes to enhancing the safety of stored goods and the possibility of protection against its spoiling [5, 6].

The human nose can detect a concentration of ammonia in the air of about 15 – 20 ppm. Such concentration is completely safe and does not cause any harm to the health. If ammonia concentration is between 50 and 100 ppm, staying in a closed room is very difficult, despite the absence of its negative impact on human health. The threshold level considered to be harmful to the health is any value exceeding 1000 ppm [6]. The threats to humans depending on the concentration of ammonia vapor in the air is presented in Table 1.

This paper demonstrates a simple construction of an ammonia sensor based on commercially available electronic connectors with active elements from polyaniline. Comparing with the previously described methods of signal analysis [7, 8] a different technique for signal detection (conductivity) was used and the relation between the signal response of the sensor and the concentration of ammonia was obtained.

2. Experiment

2.1. Preparation of conductive glue

The sensors were constructed on an electronic base of SIL-2, which was modified twice. The first modification was made to create a contact on the electrode surface by means of conductive glue. To prepare the conductive glue, a compound of 1 g polystyrene and 0.5 g of carbon powder (mesh 5 μm) was used. After mixing, the components were dissolved in tetrahydrofurane solution.

2.2. Preparation of connectors

The second modification was made to create conductive polymer fibers in the electrode spaces. All sensors were prepared by using commercially available electronic connectors called SIL-2. A thin layer of conductive layer was applied on the surface of the connector before synthesis of polyaniline nanostructures. After drying, a thin (100 μm) gap was formed for preparing a place for the synthesis of a polyaniline nanostructure. Fig. 2 shows the scheme of the sensor.

2.3. Synthesis of polyaniline nanostructures on the sensor surface

1 ml of 0.44 M solution of aniline hydrochloride in 1 M water solution of hydrochloric acid was mixed with 1 ml of 0.88 M solution of ammonium persulfate in 1 M water solution of hydrochloric acid [9]. Afterwards, 20 μl of the prepared solution were dropped on the SIL-2 connector and incubated for 40 minutes. After incubation, the mixture was removed and the obtained sensor was cleaned with distilled water (Fig. 2).

2.4. Preparation of air samples of ammonia

In order to develop a model of pollution sources, solutions of ammonia in water were prepared. To determine the concentrations of ammonia in the immediate vicinity of the emitter, the aspiration method was used. For preparing air samples with different concentrations of ammonia vapors in air, a series of water solutions of ammonia, containing from 0.25 to 2.5 % of ammonia (Table 2), was prepared.
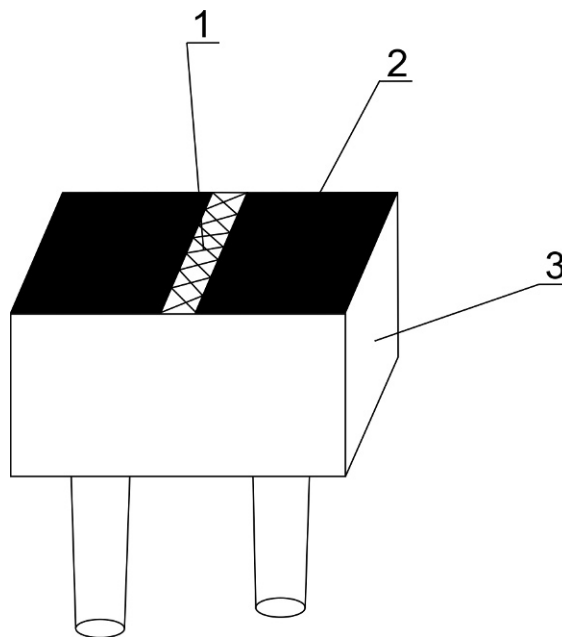

Fig. 2. Sensor scheme: 1. Gap filled by conductive polymer 2. Conductive glue layer 3. SIL-2 connector.

Table 2. The model of ammonia pollution sources.

Concentration of ammonia water [%]	Concentration of ammonia in the air [ppm]
0.25	44
0.75	217
1.25	382
1.75	543
2.50	990

1 dm^3 of air gathered under the ammonia solution was taken into a scrubber along with 100 ml of distilled water at a flow rate of 1 dm^3/min. To the obtained mixture, 2 drops of methyl orange solution were added and the solution was titrated by hydrochloride solution. The amount of ammonia in the analyzed sample was calculated from the stoichiometric reaction of ammonia and hydrochloric acid [10, 11].

2.5. Analysis of a sample with the sensor

To analyze conductivity, a measurement system consisting of the following components: a PC, the Elmetron conductometer, and adapter for sensors, was set up. The obtained sensors with polyaniline nanostructures were connected to the conductome-
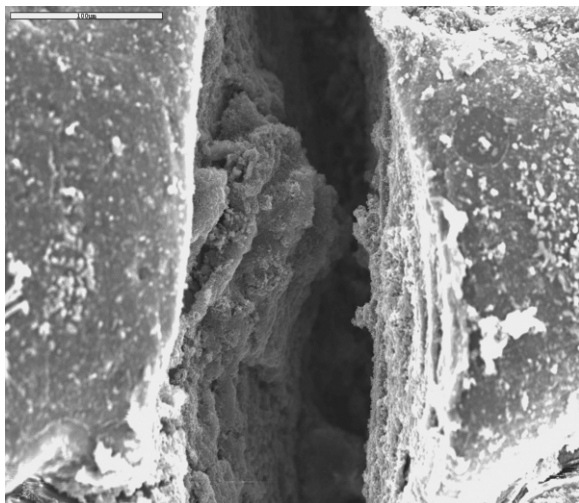
Fig. 3. Magnification 350 times (shiny surfaces of graphite adhesive layer, space in the middle of the polymer fibers).
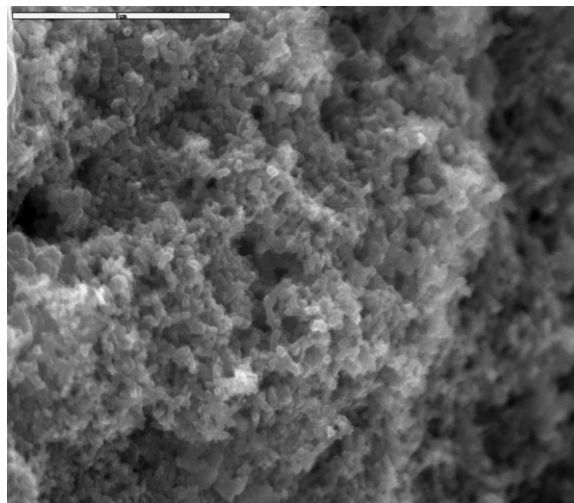

Fig. 4. Magnification 10,000 times (morphology of the polymer structure).

ter and placed in a closed pipe with a gas inlet and outlet. 5 ml of air samples contaminated with different concentrations of ammonia were applied to the analytical adapter.

3. Results and conclusion

In order to investigate the morphology of the sensor's surface area, the sensors were analyzed using scanning electron microscopy (SEM) at different magnifications, presented in Fig. 3 and Fig. 4.

The morphology of the polymer layer shows that the sensor's nanostructure is thin with a regular distribution.

The sensors were tested at room temperature (23 °C).

Due to the fact that each of the tested sensors was characterized by a different value of initial conductivity (conductivity ranged from 4 to 15 μS), to analyze the results, a concept of relative sensitivity (g) was used. In the concept, relative conductivity is a instantaneous value of conductivity indicated by the sensor relative to baseline.

The concentrations of ammonia vapor floating in the vicinity of the point emitters of ammonia ranged from 44 to 990 ppm. It should be noted that lower concentrations are barely perceptible by the human

nose. The concentrations of ammonia vapor on the point emitters are summarized in Table 2.

The study showed changes in the conductivity as a result of exposure to ammonia vapors; the changes in the conductivity of individual sensors were strongly dependent on the concentration of ammonia vapor (Fig. 5, where: g – relative sensitivity, c – concentration of the pollutant, t_o – time). The contaminations caused that the conductivity of the sensor decreased, and the higher the concentration, the lower the conductivity. The higher the concentration of the pollutant, the longer the recovery time of the sensor.

A linear response was obtained depending on the concentration of pollutant – this dependence is shown in Fig. 6.

The studies have shown that the concentration has a significant impact on the sensor's response time – the higher concentration, the shorter the response time, but the longer the recovery time (the response time is a time between the stimulation of a sensor by pollution and approaching the minimum value of conductivity whereas the recovery time is the time of the conductivity raise up to the initial value) (Fig. 7).

Preliminary research conducted in the presence of other gases showed that the analyzed sensors responded selectively to the stimulation with am-
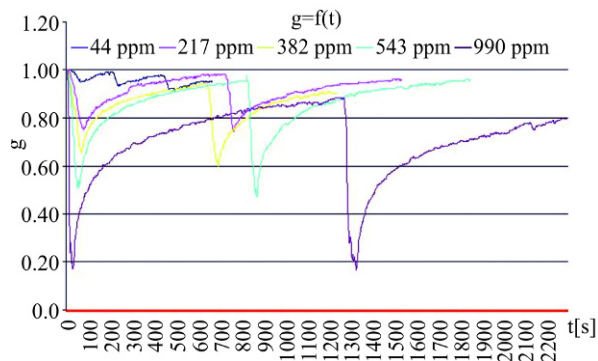
Fig. 5. Changes in relative sensitivity of the sensor subjected to different concentrations of ammonia in the air.
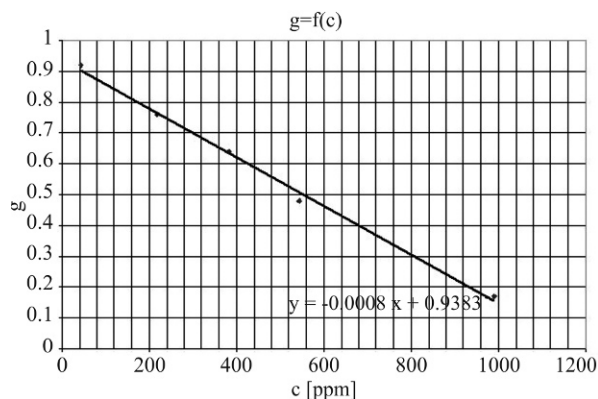

Fig. 7. Time dependence of sensor response on the concentration of impurities.

Fig. 6. Dependence of sensor response on the concentration of impurities.

Fig. 8. Response of the sensor to different pollutants vs. time.

monia vapor. The distinguishing feature of the sensor's response is the nature of the sensors subjected to the influence of the analyte. Sensor excitation time is important (the time at which the sensor approaches the lowest conductivity) – it was constant for a given analyte concentration, however, a slight variation among the studied population of sensors occurred.

Preliminary studies showed that the analyzed sensors responded selectively to the stimulation with ammonia vapor. The sensor was tested with ammonia, glutaraldehyde and hydrochloric acid vapors. Selectivity was determined by the shape of the response curve vs. time: there were differences in the shapes of the sensor response curves between ammonia, glutaraldehyde and hydrochloric acid vapor – results presented in Fig. 8.
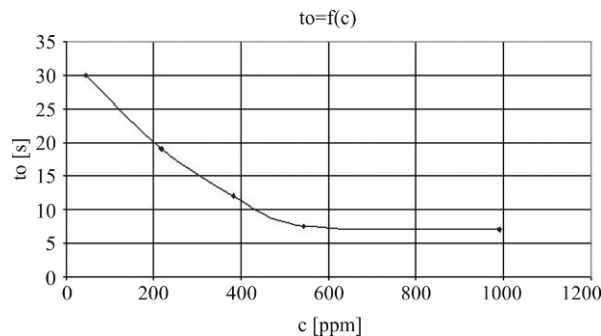
The studies showed that the temperature change does not affect the analytical parameters of the sensor and the changes in humidity only slightly affect the sensor operation (insignificant increase in conductivity). A dry environment leads to a decrease in the conductivity, whereas the conductivity increases as the humidity is rising. The changes in the conductivity have a high degree of reversibility, which indicates that no degrading chemical reactions occur [12]. The sensor operates properly in the temperature range of 18 – 25 °C, but it has not been tested at lower temperature.

The research on the design of the sensors for detecting ammonia vapor in the air showed that the developed sensors are suitable for the detection of such contaminants in the air. It should be noted that after appropriate calibration, the suggested solution

is suitable for both qualitative and quantitative analyzes. The study showed the changing nature of the sensor's response, depending on the concentration of the analyte in the air, ranging from 50 to 1 000 ppm.

4. Summary

The results obtained demonstrate the possibility of manufacturing ammonia sensors based on polyaniline. A good deal of research performed previously described different preparation methods of ammonia sensors, such as electropolymerization, formation of LB layers, and ink printed deposition of polyaniline nanoparticles [7, 8, 13]. The conductivity of polyaniline layers in ammonia sensor presented in this paper decreased in similar way, but the authors didn't show the relation between the signal response of the sensor and the concentration of ammonia. The sensors described by Crowley and others showed a possibility of ammonia detection by means of amperometric analysis of printed polyaniline electrode. The obtained results showed lower detection limit, which might be caused by the method of electrode preparation and the method of measurement. Previously described methods of signal analysis used different techniques for signal detection, such as amperometry or resistance analysis. Physicochemical properties of the sensor were strongly dependent on the conditions in which the active polymer layer was made. The conditions of the polymerization process strongly determine the morphology of the active layer. Previously performed research showed that the sulfonation degree, UV-Vis absorption, thermal stability, electrochemical behavior, crystalline density, and conductivity of self-assembled polyaniline affected the morphology [14–16]. The morphology of self-doped PANI changed from nanoclusters and nanotubes to a coral reef like nanostructure with increasing the AN to SAN molar ratio in the copolymerization reaction. The coral reef like nanostructure has never been observed in the SPANIs before. The thermal stability, electrochemical behavior, crystalline density, and conductivity were strongly dependent on the degree of doping level and the nanostructure of the SAN doped polyanilines. The conductivity of polyaniline

with a coral reef like structure was lower than the conductivity of polyaniline with a nanotube structure. The technique presented in this paper used a polyaniline nanostructure synthesized *in situ* on a metallic surface protected with a conductive layer as an ammonia sensor. A simple conductometer with an adapted connector was used for signal analysis, which, in the future, can be replaced by a system based on microprocessors for data analysis or for identification of contamination.

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