Study of functional properties of gas-sensitive cobalt-containing polyacrylonitrile films

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Abstract. The design of the sensor materials with challenging gas-sensitivity can be solved by materials selection and their compatibility with the manufacturing technologies that allows to operate the process of formation of nanocomposite structure and to receive the required material. The polyacrylonitrile (PAN) as the conducting polymer with a highly π-conjugated polymeric chain due to flexibility for tailoring the structure of the final products by the pyrolysis method under the influence of incoherent IR-radiation is chosen. The aim of the work was to study the peculiarities of formation procedure of cobalt-containing PAN films. The gas-sensing Co-containing PAN films have been fabricated. The different temperature and time have been used to form the films. Depending on intensity and exposure time of IR-radiation the thermostructured PAN films with resistance values of $10^8$ Ω to $10^{10}$ Ω have been fabricated. It is shown that the heat-treated PAN is the p-type semiconductor. Irrespective of the level of the modifying additive in film-forming solution and the time-temperature modes little change of film resistance has been found. It has been found that the Co-containing PAN films are gas-sensing films and have high selectivity to Cl$_2$ and NO$_2$. A stationary state gas distribution method was used for testing gas-sensing properties. Obtained the Co-containing PAN films are perspective for low-temperature applications as Cl$_2$ and NO$_2$ sensors.

1. Introduction
In recent years, research in the field of nanoscience and nanotechnology has emerged due to the applications of nanocomposite and nanoscale materials.

Conducting polymers with conjugated π-bonds chains and polymer-nanocomposites are developing field of modern nanotechnology. They have become worldwide research interest for the structure-property relationships. The latter is particularly interesting classes of nanostructures for their advantages of obtaining the desired properties by incorporation of the nanoscale materials into polymer matrix [1,2]. For the discovery of conducting polymers, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa were awarded the Nobel Prize in Chemistry in 2000 [3]. Typical conducting polymers include polyacetylene (PA), polyaniline (PANI), polypyrrole (PPy), polythiophene (PTh), poly(phenylene) (PPP), poly(phenylenevinylene) (PPV), polyfuran (PF), and their derivatives. These conjugated polymers can be electrical insulators, semiconductors or conductors, depending on the level of doping and nature of the dopants. Insulators can be converted into semi-conductive or conductive states upon treating with dopants and/or subjecting to chemical or electrochemical redox reactions. The electrical conductivity of these conjugated polymers can increase by several orders of magnitude. To extend the
functions or to improve the performances of these polymers, they are frequently doped with other functional materials to form composites [3,4].

Polyacrylonitrile (PAN) and copolymers of PAN have been widely studied for almost a century for commercial and technological exploitations. PAN is still a promising object of research to create nanofibers and porous nanotubes and for a variety of applications: medicine, energy, agriculture, filtration, technical textile, protective materials, etc. [5]. Technologically PAN interesting for its ability to form stable structures of different conductivity during heat treatment forming a ladder structure through processes of cyclization of nitrile groups –C≡N and dehydrogenation. The crosslinking of the chain molecules in the form of –C=N–C=N– is a process that prevents melting during subsequent carbonization when using temperatures higher than 200 °C [5-7]. Heat-treated PAN unlike other conductive polymers, is a material with semiconductor properties without need to embed dopants.

The problem of obtaining functional materials with the best characteristics using the specified process parameters for their formation is relevant for modern micro- and nanoelectronics. Ability to change the electrical conductivity from the dielectric to metallic while chemical structure is turning from the linear form to polyconjugated upon heat treatment has driven impressive research efforts in development of optimal technologies for the organic conjugated polymer materials.

Gas-sensing properties of the PAN-based films strongly depend on microstructure, components and structure of film material. There are certain correlations between surface morphology of the PAN-based films and the PAN-polymer molecule structure that caused by processes occurring during the formation of the sensing material. The problem is to study the correlation using methods of empirical research and that is the reason for its insufficient study.

The goal of this paper is to examine the features of cobalt-containing PAN film surface and to study gas-sensing properties that are based on the selective absorption of gas molecules inheriting the adsorption-resistive effect [1-17].

Embedding transition metal of low concentration in organic matrix [18-20] or controlling molecular structure of organic polymer through using different methods of polymer material fabrication are effective techniques to improve functional characteristics of composite materials including adsorption-resistive properties of PAN-based films [21-23]. Varying the time-temperature parameters has been used to fabricate PAN-based film with various molecular structure of polymer that caused change in conductivity of thermostructured PAN polymer [24,25].

2. Experiment

To fabricate films the following components were used: polyacrylonitrile (PAN) (Aldrich 181315) as polymer organic matrix, cobalt chloride (II) CoCl₂ as modifying additive for increasing the selectivity and adsorption activity of PAN, dimethylformamide (DMFA) as a solvent. Film-forming solutions were deposited (centrifuged) on polycr substrates and dried in oven at T = 160 °C, t = 30 minutes. The Co-containing PAN films were formed under the influence of incoherent IR-radiation under low vacuum conditions [19,20,23,26]. IR-annealing was conducted in infrared camera, halogen lamps KG-220 with high radiation in the area of 0.8-1.2 μm were used as the source of radiation. Time-temperature modes of IR-annealing were selected experimentally, since the intensity and duration of infrared radiation provide an opportunity to control the properties of the films by changing the molecular structure of the polymer. The radiation intensity at the first stage of IR-annealing corresponds to temperatures varying from 250 to 350 °C during a 5-20-minute time period, and the intensity of radiation at the second stage corresponds to temperatures of 300 – 500 °C during a 2-10-minute period.

The film surface morphology was observed by atomic force microscopy (AFM) using scanning probe microscope Solver P47 Pro (NT-MDT). The 5 × 5 μm² area AFM-images of the films are processed with Image Analysis program.

Resistance measurements were carried out using E6-13A Terrmometr. The gas sensitivity (S) is defined as the ratio S = (Ro – Rg)/Ro, when Ro > Rg, where Ro is the resistance in air, Rg is the resistance in the atmosphere of analyte.
3. Results and discussion

It is known that there are control parameters to create PAN-based material with desired properties: formation conditions of the organic polymer structure and distribution of the modifying additive in the "organic matrix" composite material [2-4, 17]. Creation of gas sensing material is connected with a search for the optimal microstructures, operating temperature, response time and quantitative content of modifying agent that suit the analyte molecules.

It is known that when pyrolyzed over the temperature of 300 °C, the linear chains of dielectric PAN undergo chemical conversion of polymer with a cyclic structure which contains conjugated double bonds. As a result of the heat treatment of the films PAN acquires properties of a semiconductor structure due to chemical changes at a molecular level. The main processes that determine the unique electrical properties of PAN are intermolecular and intramolecular cyclization, intermolecular cross-linking that enable to form polymer with semiconducting properties [27].

The resistance values of fabricated films are in the range $10^8 \div 10^{10}$ Ohm. Such resistance values are explained by different structure of heat-treated PAN. It is found that the increase of the IR-radiation intensity and concentration of a modifying additive decreases the resistance values of fabricated films (Figure 1).

![Figure 1. The dependence of the Co-containing PAN film resistance on the weight concentration of modifying additive: 1 – T_{IR2} = 400 °C; 2 – T_{IR2} = 450 °C; 3 – T_{IR2} = 500 °C.](image)

As observed from figure 2 the resistivity of the Co-containing PAN films decreases with increase in temperatures with in the experimental range that is characteristic of semiconductor materials.

Figure 3 shows the Arrhenius plots of temperature dependence of resistivity of Co-containing PAN films. It has been observed that the dependence represented by equation $R = R_0 \exp(-\Delta E/(2kT))$, where $\Delta E$ is the activation energy, $k$ is Boltzmann’s constant and the factor 2 accounts for the thermal excitation of both positive and negative charges [28]. As shown from Figure 3 the resistance of the films decreases linearly with increasing temperature in coordinates ln $R$ – 1/T. Such dependence indicates the semiconducting behavior of the obtained films.

Regardless of the weight concentration of modifying additive in the initial solution, and temperature-time conditions of film formation the slight increase in temperature decreases resistance due to the relatively weak temperature dependence of the carrier mobility, which is typical for organic semiconductors [2].

According to Hall effect measurements revealed that the PAN films have p-type conductivity [2,19]. It is known that for the semiconductor gas sensor with inorganic material of p-type as a sensitive layer, reducing gas atmosphere causes to a decrease in its conductivity, owing to a decrease in electron concentration in the surface layer and an increase of the height of intergranular barriers [29].
Figure 2. Temperature dependence of the Co-containing PAN film resistance on the weight concentration of modifying additive: 1 – ω (Co) = 0.25 wt.%; 2 – ω (Co) = 0.5 wt.%; 3 – ω (Co) = 0.75 wt.%; 4 – ω (Co) = 1 wt.%; 5 – ω (Co) = 0 wt.%

Figure 3. Arrhenius plots of temperature dependence of the resistance of the Co-containing PAN films on the weight concentration of modifying additive: 1 – ω (Co) = 0.25 wt.%; 2 – ω (Co) = 0.5 wt.%; 3 – ω (Co) = 1 wt.%

Figure 4 depicts the dependences of the Co-containing PAN film gas sensitivity on different temperature in atmosphere of chlorine c(Cl₂) = 36 ppm and nitrogen dioxide c(NO₂) = 21 ppm. Temperature-dependent adsorption studies revealed that operating temperature of the sensing film is close to room temperature, it gives the possibility to create energy-efficient sensors.

Gas sensitivity of the Co-containing PAN films was found to decrease with increasing weight concentration of a modifying additive that was shown in Figure 5. The results of the sensing tests of the films revealed the best sensitivity was observed for the sample with weight concentration of modifying additive ω (Co) = 0.5 wt.% toward nitrogen dioxide NO₂; and ω (Co) = 0.25 wt. % toward chlorine Cl₂.

Figure 4. Sensitivity dependence on temperature of the Co-containing PAN films, the weight concentration of modifying additive and detected gas: 1 – ω (Co) = 0,5 wt.%, NO₂; 2 – ω (Co) = 0,25 wt. %, Cl₂

Figure 5. Sensitivity dependence on the weight concentration of modifying additive of the Co-containing PAN films: 1 – to Cl₂; 2 – to NO₂

Thus, potential applications of the Co-containing PAN films include environmental monitoring of gas emissions as non-heated semiconductor sensor. Samples which showed the best indicators of the submitted parameters are the films with 0.25 wt. % and 0.5 wt. % weight concentration of modifying additive.

4. Conclusion
The design of environmentally-sensitive products involves selecting appropriate materials, technology and manufacturing equipment. From the experimental data, it was established that the obtained Co-containing PAN films are sensitive to gas oxidizers such as NO\textsubscript{2} and Cl\textsubscript{2} at room temperature, and the sensitivity depends on their resistance values. Advantage of PAN-based material is the possibility of obtaining films with functional properties, and there is no need to use complex technological equipment [13-16, 18-26].

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