

Polyaniline and polythiophene-based gas sensors

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Three samples of semiconducting polymer, polyaniline, emeraldine base form (PAn-EB), polyaniline, emeraldine salt form (PAn-ES) and polythiophene (PT), were prepared and their sensing properties to reducing gases were investigated. The gas sensing characteristics were obtained by measuring the sensitivity as a function of various controlling factors, like operating temperature, composition and concentration of the gas, and finally the response time. The sensitivity of three semiconducting polymers to acetone, ethyl alcohol and liquefied petroleum gas (LPG) was compared. It was revealed that PAn-EB is the most sensitive to ethyl alcohol and liquefied petroleum gas, and can be used as gas sensor. The strong interaction between ethyl alcohol and porous PAn-EB can explain the selective sensitivity to ethyl alcohol and LPG and negligible sensitivity to the other reducing gases.

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1. Introduction

The permanent environmental monitoring is a necessity today and much research has focused on development of sensors and biosensors able to provide real-time information about the presence and quantity of toxic gases and vapors in air, contaminants in natural waters, toxic substances in foods, etc. and this requirement led to apparition of new sensor devices. The old sensors are mainly based on inorganic semiconductors, insulators or metals and catalytic materials.

Electrically conductive polymers have been known for many years and are very studied due to their interesting properties and applications. The increased interest in development of such polymers is based on their high electrical conductivity, good environmental stability, possibility to be doped with a variety of *p*- or *n*- dopants and their application as active materials in electronics and optoelectronics. The electronic conductivity of polymers can be changed over several orders of magnitude in the presence of gases, vapors or liquids that are in the microenvironment and this property can be applied in the fabrication of chemical sensors. Among conducting polymers, polyaniline (PAn) and polythiophene (PT) are the most studied electronic materials due to a sum of factors, such as; low cost and easy to prepare monomers and polymers, high thermal and oxidative stability, good electronic conductivity [1]. In the present work we investigate the possibility to use these two polymers for monitoring three reducing gases.

There are some excellent reviews about the use of conducting polymers as active elements in realization of chemical and biochemical sensors [2-7] but PAn and PT, to our knowledge, have not been used in detection of the vapors of acetone, ethyl alcohol and liquefied petroleum gas.

2. Experimental

The three polymer samples used as active materials in detection of gases are based on polyaniline and polythiophene and their chemical structures are presented in Fig. 1.

Polyaniline emeraldine salt (PAn-ES) was synthesized by using a reported procedure [8]. Freshly distilled aniline monomer (3 ml, 0,033 mol) was dissolved in 1M HCl (1 l), and the resulting solution was cooled at 5 °C. Then, a solution of 1M (NH₄)₂S₂O₈ (100 ml) was added dropwise, under vigorous stirring, into the aniline solution. The reaction mixture was stirred for additionally 3 h. The resulting precipitate was washed with distilled water and dried. Yield: 80%. The solid product having the structure of emeraldine salt was insoluble in organic solvents.

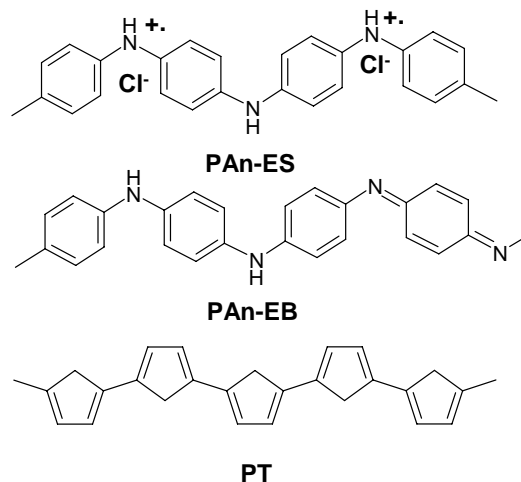


Fig. 1. Chemical structure of the semiconducting polymers used as active materials.

Polyaniline emeraldine base (PAn-EB) was prepared by immersion and stirring of PAn-ES powder in 0.1 M NH_4OH solution for 3 h. Finally, the fine powder was filtrated and washed with water and dried.

Polythiophene (PT) was synthesized by chemical polymerization of thiophene using FeCl_3 as oxidant (monomer/oxidant = 1:3 molar ratio) in chloroform solution. The resulted polymer was insoluble in organic solvents and was a black fine powder.

The polymer powders compacting in a disc shape (17 mm in diameter) was carried out in a stainless die by uniaxial cold pressing at approximately $5 \times 10^6 \text{ N/m}^2$.

The specific surface area was determined using equation [9,10]

$$A = \frac{s}{v \times d} = \frac{6}{d \times D_m} \quad (1)$$

where s and v are the particle surface and volume respectively, d is the bulk density and D_m is the average grain size. The number 6 is the shape factor. It is assumed that the particles of a specimen have the same size and the same shape. The bulk density, d , was evaluated from the weight and the dimensions of the samples. The porosity was also calculated ($p = 1 - d / d_x$).

For electric measurement, two silver electrodes were applied on a face of the ferrite disc, as in Fig. 2.

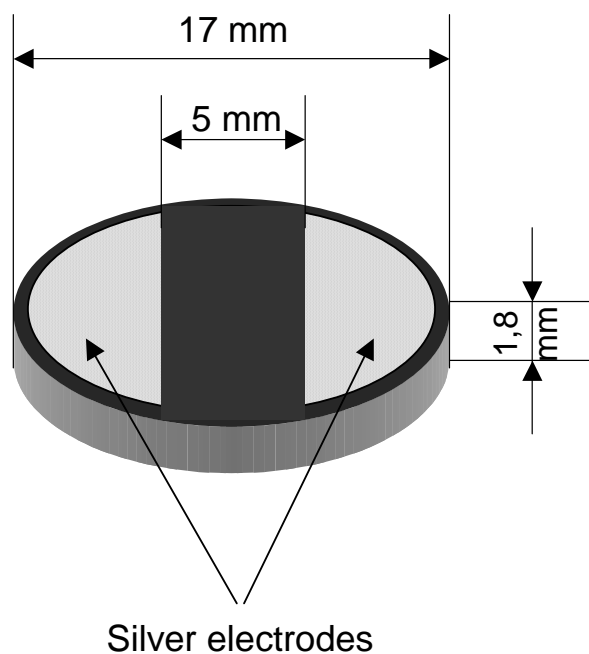


Fig. 2. The design of semiconductor polymer sensor with silver electrodes.

The electrical resistance was measured by a two-point method with a digital LCR meter at 100 Hz. For gas sensing measurements, the sensor element (semiconductor polymer disc) was provided with a heater and the assemble heater-sensor element was introduced in a glass chamber (2 dm^3) as Fig. 3. The test gases were injected with a syringe into the glass chamber. The measurements were done in the temperature range from 100°C to 240°C . A cromel-alumel thermocouple located in close proximity of the sensor element was used to measure the working temperature.

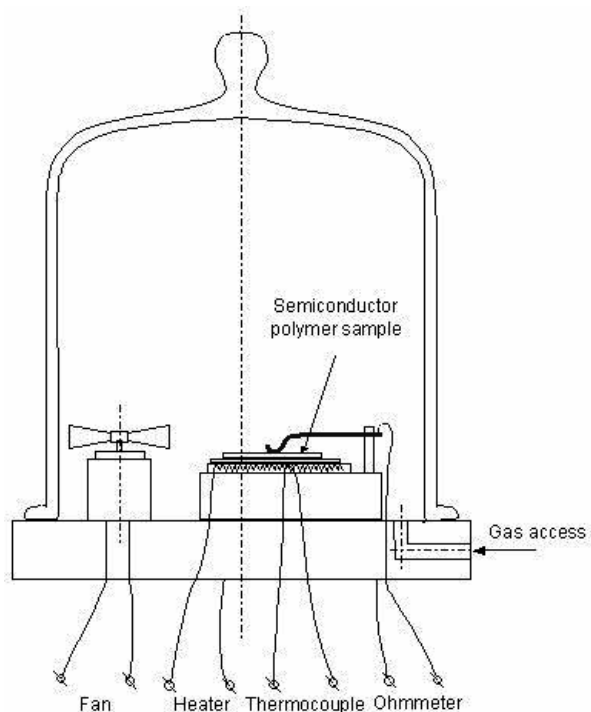


Fig. 3. Experimental arrangement for gas sensing measurements.

The resistance of the semiconductor polymer sensor placed into the measuring chamber was measured at fixed temperatures, both in air and in the presence of the test gas. The sensitivity (S) was calculated using the relation,

$$S = \frac{\Delta R}{R_a} = \frac{R_a - R_g}{R_a}, \quad (2)$$

where R_a is the polymer resistance in air and R_g is the polymer resistance after the exposure to the test gas, at a given temperature. Taking into account the thermal inertia of polymers, all measurements were carried out under the thermal stabilization conditions. All data were collected at least 20 minutes after gas exposure.

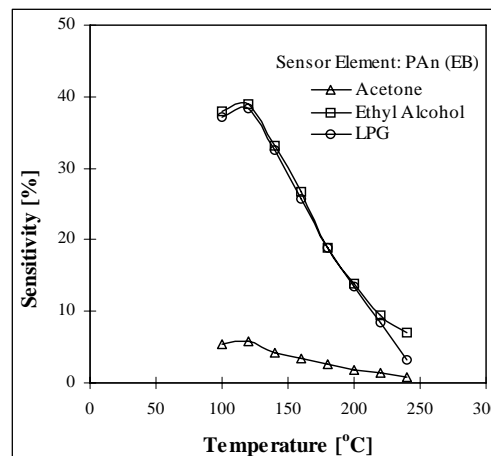
3. Results and discussion

All polymer samples were prepared as powders, and it is evident that their morphology is dependent on the semiconductor polymer nature. The structural characteristics are summarized in Table 1.

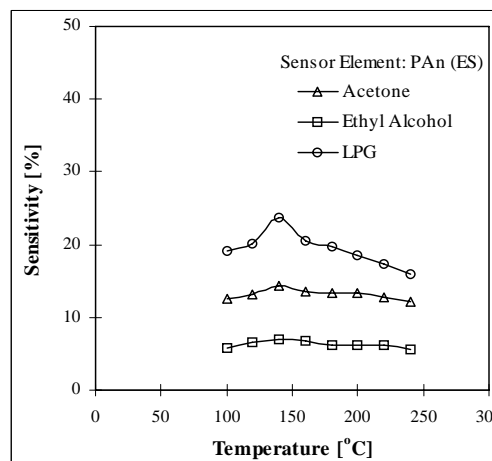
Table 1. Structural characteristics for the studied samples.

Sample	Density d (g/cm ³)	Porosity P (%)	Surface specific area A (m ² /g)
PAn-EB	2.84	44.96	6.72
PAn-ES	3.36	36.15	5.24
PT	4.17	25.07	4.36

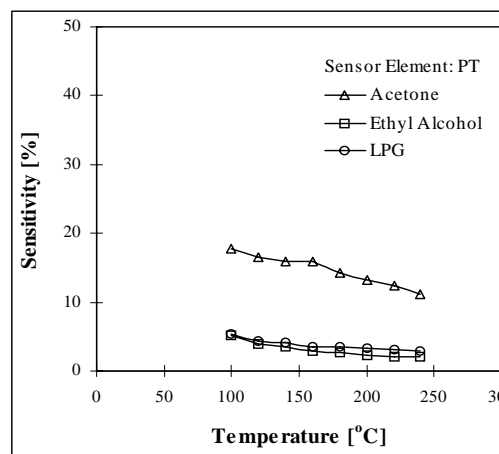
The main conclusion from Table 1 is that a decrease in bulk density results in an increase in specific surface area and porosity. Among the investigated semiconductor polymers, PAn-EB is characterized by the highest porosity, 44.96 %, that imply a much more active surface towards test gases. But PT semiconductor polymer is characterized by the smallest surface area (4.36 m²/g). We have tested the sensitivity of the three sensors to the presence of small quantities (150 ppm) of volatile organic compounds (ethyl alcohol, acetone and LPG). All sensitivity measurements were performed at temperatures between 100°C and 240°C. At lower temperatures the electrical response to the test gases was reduced. A first observation is that all sensors respond to the volatiles tested but they do it in varying extents. Figure 4 illustrates the gas sensitivities of the three semiconductor polymers as a function of operating temperature, towards acetone, ethyl alcohol and LPG vapours. Each of the curves shows a maximum of the sensitivity corresponding to an optimum operating temperature of the sensor element. For PAn (EB) the sensitivity maximum appears at 120°C and for PAn (ES) it appears at 140°C. Therefore, the semiconductor polymer sensors have need of thermal excitation to response to the investigated gases and the best response can be obtained if each sensor operates at its optimum working temperature.



(a)



(b)



(c)

Fig. 4. Diagram for sensitivity of three semiconductor polymers to reducing gases.

The sensitivities of the three semiconductor polymers towards the three reducing gases are compared in Figure 5. Here, the sensitivity values correspond to the optimized working temperatures for each polymer sensor. Although the all sensors respond to all volatiles tested they do so in varying proportions. One can remark from Fig. 5 that PAn (EB) sample has good sensitivity to ethyl alcohol and LPG. The sensitivity to LPG of PAn (EB) semiconductor polymer is approximately one and half times larger than the PAn-(ES).

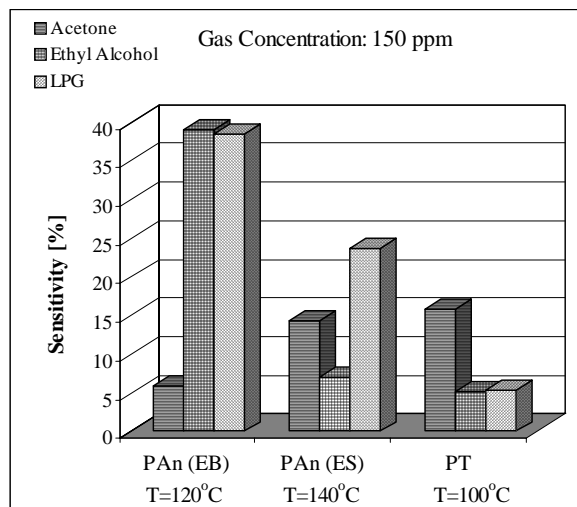


Fig. 5. Diagram for sensitivity of three semiconductor polymers to reducing gases

There are some attempts proposed to explain the change of electrical properties of (semi)conducting polymers in presence of gases. The first one is based by modification of electrical conductivity of conjugated polymers in presence of oxidizing or reducing agents that acts as dopants for the polymer chain. Another explanation is based on modification of physical properties of the polymers, i.e., morphology, crystallinity, etc in presence of gases and volatiles that could also explain the change of electrical conductivity through an increase in the interchain electron transfer.

In the present case, the action of vapors of ethanol, acetone and LPG on sensor active elements based on semiconducting polymer is based on their absorption on polymer surface followed by diffusion through the inner-domain spaces having as final effect a reducing of interchain distances. A doping process of the conjugated polymer by the volatiles tested to explain the lowering of electrical resistance is less probable.

4. Conclusions

The possibility of the modification of resistance of the polymers such as polyaniline and polythiophene in the presence of volatile compounds was used for the building of chemical sensors. From present work one can conclude that semiconductor polymer PAn (EB) can be used for ethyl alcohol or LPG sensing.

These results are preliminary and further studies for the improving of sensor's performance characteristics with respect to: sensitivity, response time and durability are necessary.

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