

ХІМІЧНІ СЕНСОРИ
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CHEMICAL SENSORS

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**UTILIZATION OF THIN ELECTROPOLYMERIZED POLYPYRROLE
AND POLYANILINE FILMS AS SENSITIVE LAYERS IN
CHEMORESISTOR SENSOR ARRAYS**

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Summary

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In this work chemosensitivity of the thin electropolymerized polypyrrole and polyaniline films is studied by analysis of the experimental data obtained from the arrays of electroconductive polymer sensors. Sensor response towards vapors of various organic solvents is analyzed and several possible mechanisms of interaction of the organic solvent with the doped polymer film is considered. By comparative study of the polypyrrole and polyaniline-based sensors responses an explanation of dependence of sensor response on analyte acidity and polarity factors is proposed.

Keywords: electroconductive polymer, polyaniline, polypyrrole, chemosensor.

Анотація

**ЗАСТОСУВАННЯ ТОНКИХ ЕЛЕКТРОПОЛІМЕРІЗОВАНИХ ПЛІВОК ПОЛІПІРОЛА
ТА ПОЛІАНІЛІНА В ЯКОСТІ ЧУТЛИВИХ ШАРІВ В МАСИВАХ
ХЕМОРЕЗИСТИВНИХ СЕНСОРІВ**

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В роботі вивчені хемочутливі властивості тонких електрополімерізованих плівок поліпірола та поліаніліна за допомогою аналізу експериментальних даних отриманих з масивів електропровідних полімерних сенсорів. Проаналізовані відгуки сенсорів на пари різних органічних розчинників й розглянуті деякі можливі механізми взаємодії органічного розчинника з допованим полімером. Проведено порівняння відгуків сенсорів на основі

поліпірола та поліаніліна і запропоновано пояснення залежності відгуків від показників кислотності й полярності аналіту.

Ключові слова: електропровідний полімер, поліанілін, поліпірол, хімічний сенсор.

Аннотация

ПРИМЕНЕНИЕ ТОНКИХ ЭЛЕКТРОПОЛИМЕРИЗОВАННЫХ ПЛЕНОК ПОЛИПИРРОЛА И ПОИАНИЛИНА В КАЧЕСТВЕ ЧУВСТВИТЕЛЬНЫХ СЛОЕВ В МАССИВАХ ХЕМОРЕЗИСТИВНЫХ СЕНСОРОВ

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В работе изучены хемочувствительные свойства тонких электрополимеризованных пленок полипиррола и полианилина посредством анализа экспериментальных данных полученных с массивов электропроводящих полимерных сенсоров. Проанализированы отклики сенсоров на пары различных органических растворителей и рассмотрены некоторые возможные механизмы взаимодействия органического растворителя с допированным полимером. Проведено сравнение откликов сенсоров на основе полипиррола и полианилина и предложено объяснение зависимости откликов от показателей кислотности и полярности аналитов.

Ключевые слова: электропроводящий полимер, полианилин, полипиррол, химический сенсор.

1. Introduction

It is known that electroconducting polymers (ECP) due to a number of their specific properties (e. g. electrochromism or change of conductivity during oxidation-reduction) can be utilized as sensitive elements of the various chemical sensors [1]. ECP possess several advantages as compared to other materials: they work at a room temperature, have low relative density and do not corrode; besides, ECP can be easily synthesized in form of the thin films — sensitive layers, which change their physical and chemical characteristics (conductivity in particular) when treated with different chemicals.

The latter feature makes it possible to use polymers of this class in gas sensors [2]. From this point of view the most interesting ECP specimens are polyaniline (PAn) and polypyrrole (PP), since they show relatively high stability towards the influence of environmental factors (temperature, humidity), may be easily obtained in both powder and thin film forms and also can be doped by various dopants [1, 3].

Earlier we have investigated the effect of nature of the dopant on the response of a sensor array based on polyaniline [2]. Despite some common features, PAn and PP have series of differences. PAn, contrary to PP, is stable in both doped and non-doped

forms and can be shifted from one state to another not only by oxidative doping but by reductive doping as well. At the same time we supposed that sensitivity and selectivity of the ECP-based sensors can be significantly improved by utilization of the films of both classes in the sensitive elements.

It is well known that during the contact of PAn films with the vapors of majority of organic solvents conductivity of the polymer increases. For PAn films this phenomenon is observed independently of the nature of used dopant [4]. At the same time, not very numerous published results of the works dedicated to investigation of possibility of ECP utilization in the chemical sensors are quite contradictory: some of them denote increase of conductivity of a given polymer under the effect of organic solvents vapors [5, 6] and the other ones denote conductivity decrease [3, 6, 7]. Apparently, this difference is conditioned by the nature of used dopants or by the method of ECP films synthesis.

The purpose of this work was to study sensitivity of the thin electropolymerized polypyrrole films towards the influence of vapors of the different organic solvents, investigate effect of the dopants nature on the response of such sensors and to develop chemoresistive sensor array with the PAn and PP sensitive layers.

2. Experimental

The sensors array was fabricated by photolithography of 150 nm thick gold on standard glass-ceramic substrate and then wafer was diced in 6-element chips. The chips were mounted on small printed circuit board and were connected by wire bonding. Each element contained the 20 pair of raster electrodes of 15 μm thick separated by 25 μm distance with common area of 2 mm^2 .

The films were synthesized by electrochemical oxidative polymerization of monomer. PAN was obtained from a 1 M aqueous solution of the HX acid with 0.15 M of corresponding anilinium salt An-HX where HX is one of the following: HNO_3 , HCl , HClO_4 , H_2SO_4 or camphorsulfonic acid (CSA). PP was obtained from 0.1 M solution of background electrolyte in acetonitrile (AN) with 0.3 M of pyrrole; lithium salts (LiClO_4 , LiCF_3SO_3), tetrabutylammonium salt (Bu_4NPF_6) and CSA were used as a background electrolyte. Films synthesis was performed in a three-electrode nonpartitioned cell; the working electrode was an array (six elements) of gold grating electrodes deposited on a glass-ceramic substrate, the auxiliary electrode was a platinum gauze, and the reference electrode was a silver chloride electrode.

The polymerization was conducted in a cyclic potential mode in the range from 0.0 to +1.2 V for 2–5 cycles at a sweep rate of 50 mV/sec (PAN) or in the controlled potential mode at +1.2 V during 5–10 min. (PP). The obtained films were rinsed with a 1 M solution of the HClO_4 (PAN) or acetonitrile (PP) and dried in air at room temperature.

The polyaniline films doped with heteropolyacids (HPA — $\text{PMo}_{12}\text{O}_{40}^{3-}$, $\text{PMo}_{11}\text{VO}_{40}^{4-}$) were synthesized in two stages; first, films of $\text{PAN}\cdot\text{H}_2\text{SO}_4$ or $\text{PP}\cdot\text{PF}_6$ were deposited electrochemically and dedoped by treatment with aqueous ammonia solution; they were then redoped in a 0.01 M. solution of the HPA in acetonitrile (held for 24 h). The obtained films were washed with acetonitrile and dried in air at room temperature.

The resistance of the polymeric films obtained in this way was in the range of 10–30 kOhm, consistent with the parameters of the sensor electronics unit. The electrochemical synthesis was conducted with a PI-50-1 potentiostat and a PR-8 programmer.

Measurement of the films responses towards the vapors of organic solvents (analytes) was performed as described in detail in [2]. Alcohols (ethanol, *iso*-propanol, butanol, *n*-pentanol), acetone, aromatic hydrocarbons (benzene, toluene, *p*-xylene) and halogenalkane (chloroform) were used as analytes. Sen-

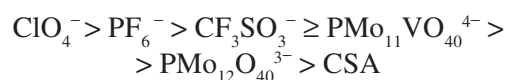
sor array responses for each gaseous analyte were measured at a fixed concentration corresponding to the saturated vapors pressure at room temperature.

3. Results and discussion

Results of measurement of polypyrrole (PP) films doped with various anion-dopants shows that, in contrast to polyaniline, for this polymer both positive (conductivity increase) and negative (conductivity decrease) responses are possible. Fig. 1 shows diagrams of responses for PAN and PP films doped with similar dopants. Obtained results indicate that the magnitude of relative response and its sign are at a great extent determined by the nature of used anion-dopant.

Only positive responses (for polar, low-polar and non-polar analytes) were observed for a PP film doped with perchlorate anions. When moving to other anion-dopants, namely hexafluorophosphate anion (PF_6^-), threefluormethanesulphoacid anion (CF_3SO_3^-) and phosphorvanatomolybdic acid ($\text{PMo}_{11}\text{VO}_{40}^{4-}$) responses become partially negative, and the positive responses in this case are observed under the influence of low-polar and non-polar analytes, while negative responses are observed for polar solvents. Finally, when using PP films doped with anions camphorsulfonic acid (CSA) and phosphormolybdic acid ($\text{PMo}_{12}\text{O}_{40}^{3-}$) anions responses become negative for all used analytes.

If we place the responses on a common scale and take the most positive response as a biggest one and the most negative as a smallest one then the response magnitude decreases according to the following series of the used anion-dopants:



The interesting regularity here is that the size of according anion-dopant increases in the same order, i. e. the smaller is anion-dopant, the bigger is a PP film response to the influence of organic solvent vapors. Thus decrease of the size (and charge) of anion-dopant will lead to a consequent increase of conductivity under the influence of analyte vapor and, on the contrary, increase of the size (and charge) of anion-dopant will lead to the conductivity decrease. It is possible that PP films doped with anions of greater size (CSA) and charge (heteropolyanions) adsorb lesser quantity of analyte when exposed to its vapor, since the analyte mainly interacts with the anion-dopants and not with the polymeric chain, and it finally leads to the polymer dedoping.

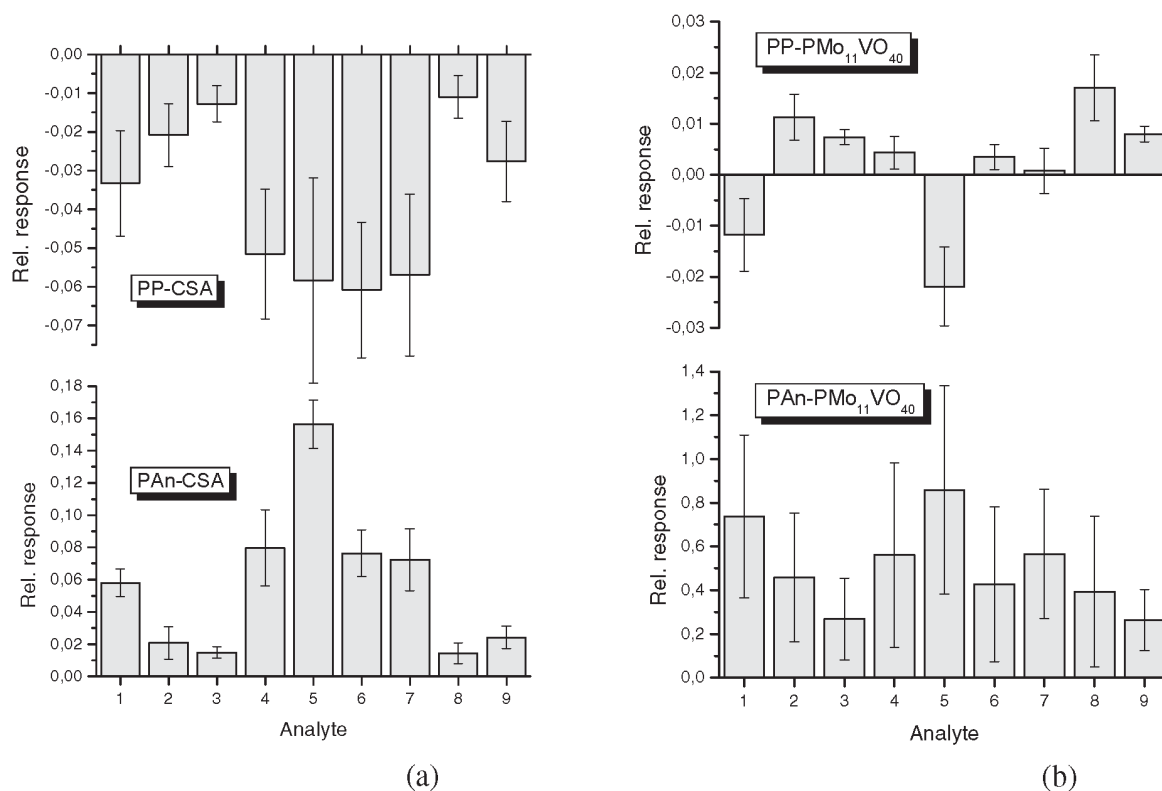


Fig. 1. Diagrams of responses for PAn and PP films each doped with the similar anion-dopants CSA (a) and $\text{PMo}_{11}\text{VO}_{40}$ (b) to vapors of the 9 different analytes (mean relative responses). The error bars shown correspond to $\pm\sigma$, where σ is a standard deviation. Analytes are the following: 1 – acetone, 2 – amyl alcohol, 3 – benzene, 4 – chloroform, 5 – ethyl alcohol, 6 – isobutyl alcohol, 7 – isopropyl alcohol, 8 – toluene, 9 – xylene.

Earlier when studying possibility of PAn films utilization as a sensitive elements of the sensors for organic solvents recognition [2] we stated the assumption that one of the factors determining magnitude of the PAn film relative response to the influence of organic solvents vapors is a specific interaction of the analyte molecules with a polymer molecules (the secondary doping phenomenon). We have shown the correlation of the relative response magnitude and normalized Dimroth-Reichardt parameter value (E_T^N) characterizing relative Lewis acidity of the analyte. Possibility of the PAn films interaction with molecules of organic solvents is provided by electron-donor (base) properties of the polymer due to the presence of unshared electron pair at the nitrogen atom.

The secondary doping phenomenon exists for PP films as well [8], however its nature is somewhat different. In case of PP unshared electron pair of the heterocycle nitrogen atom participates in forming of the system of π -coupled connections of polymeric chain, in consequence of which this polymer does not show base properties. The cymbate dependence between the response magnitude and E_T^N parameter

value is not observed, i. e. polymer does not definitely perform as an electron donor towards the organic solvent molecules.

At the same time it is known that it is more typical for pyrrole (and apparently for pyrrole elements in the polymeric chain) to show acidic (i. e. proton-donor) properties. In this case magnitude of the PP film response to the influence of analyte vapors may be determined by a tendency of organic solvents to form hydrogen bonds (Fig. 2, a). Besides, response of the PP films may depend on degree of solvation of polycation-radical fragments of polymer and anion-dopants, that is on the strength of ion-dipole interaction between the analyte molecules and PP chain (Fig. 2, b).

Considering the obtained data, all used analytes may be divided into two following groups:

- 1) non-polar and low-polar organic solvents (aromatic hydrocarbons, chloroform);
- 2) polar organic solvents (alcohols, acetone).

Treatment of the PP films with the organic solvents from the first group, as a rule, leads to the increase of conductivity. Apparently it is conditioned by the “secondary doping” phenomenon (i. e. confor-

mational changes of the polymeric chain under the influence of organic solvent molecules consequently leading to forming of the regular structure of polymer), main point of which for polyheterocycles consists in π - π -interaction between the analyte molecules and π -coupled system of the polymeric chain [8].

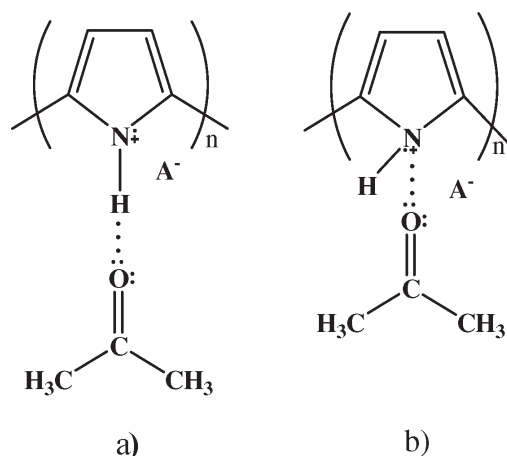


Fig. 2. Possible variants of interaction of the organic solvents molecules with polypyrrole polymeric chain: a) forming of the hydrogen bond; b) ion-dipole interaction.

In the case of polar organic solvents, on the contrary, decrease of the films conductivity is observed, which probably is related to dedoping of the polymer. This effect may be a result of superposition of several interactions, namely: 1) acid-base — between analyte molecules and NH group of the pyrrole ring, in this case analyte molecules perform as a base; 2) ion-dipole — between analyte molecules and polycation-radical fragments of the polymer; 3) forming of the hydrogen bonds between analyte molecules and pyrrole rings.

Thus, as a result of the performed research we have shown that the nature of polymer affects the response of the ECP-based sensor array to the influence of the organic solvents vapors. In contrast to PAN, for which response magnitude depends on acceptor ability of the organic solvent molecules, in case of PP films magnitude of the relative response is determined by ion-dipole interaction between the cation-radical fragments of the polymer and mole-

cules of the organic solvent, tendency of the latter to form hydrogen bonds with proton of the NH group of pyrrole ring (polar and low-polar analytes) and also by possibility of π - π -interaction between aromatic systems of the polymer pyrrole rings and benzene rings of the analyte (non-polar organic solvents).

4. Conclusion

Results of investigation of the responses of thin electropolymerized polypyrrole films doped by different anion-dopants show the following.

1. The nature of polymer significantly influenced the responses of ECP-chemoresistor sensor array for organic solvents vapors.

2. It was shown that the main factors that define the response values of PAN-films doped with different acids on organic solvents vapors are the film morphology, acceptor ability of analyte molecules and possibility of additional donor-acceptor interaction of dopant with analyte molecules (in the case heteropolyacid-dopants).

3. Results of investigation of the responses of thin polypyrrole films doped by different anion-dopants show that for this polymer both positive (conductivity increase) and negative (conductivity decrease) response values are possible.

4. It was found that the magnitude and its sign of sensor response on organic solvents vapors are to the great extent determined by the nature of anion-dopant (mainly its size and charge) and analyte polarity. It was shown that positive responses mainly correspond to little/nonpolar organic solvents, while the negative responses as a rule take a place for polar analytes.

5. During this research a multichannel array of miniature chemoresistive polymer sensors based on raster gold electrodes system on a glass-ceramic substrate with sensitive layers of polypyrrole and polyaniline was developed. Utilization of both types of sensitive films doped with a set of different dopants has led to significant extension of the sensitivity range of the polymeric sensors, which is very important for achievement of better discriminative performance of the sensor array.

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