

CONDUCTIVE POLYMERS AS ACTIVE MATERIALS FOR ENVIRONMENTAL SENSORS

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Abstract. Polyaniline (PAn) and polypyrrole (PPy), synthesized by electrochemical polymerization, were investigated as active materials for chemical sensors. The dependence of the electrical conductivity of PAn sensors on relative humidity was studied. The function of the resistivity change of PAn sensors was steepest in a range of relative humidity from 0 to 20%. We also prepared sensors on the basis of Quartz Crystal Microbalance (QCM). The dependence of the resonant frequency of QCM-based sensors with PAn and PPy coatings on relative humidity had a linear character over the whole range of humidity investigated (0–85%) and a response time less than 5 s. The high sensitivity of the obtained QCM sensors in dry SO₂ + N₂ atmosphere gives a possibility for preparing highly effective environmental and chemical gas sensors.

Key words: humidity sensor, gas sensor, QCM, QCM sensor.

INTRODUCTION

With the discovery of electrical conductive properties of *p*-conjugated polymers, such as polyacetylene (PA), polyaniline (PAn), polypyrrole (PPy), and polyparaphenylene (PPP), the interest of researchers in this class of materials has been constantly increasing. The ultimate goal in the study of conducting polymers is the preparation of materials that possess the mechanical and processing properties of a polymer and the electronic properties of a metal or semiconductor. A basic property of the conjugated polymers is the change in the electrical conductivity 10–15 orders of magnitude (up to the conductivity of metallic conductors) through reversible chemical or electrochemical doping processes [1, 2].

The doping process involves exposure of the polymer to electron donors or acceptors. Considerable theoretical and experimental efforts have been directed

towards understanding the way in which dopants add charges to (or remove them from) the polymer chains, and the nature of the transport processes that may then occur. The addition of charges to a conjugated chain causes the formation of localized defect states; these may be soliton states for *trans*-polyacetylene or more generally polaron or bipolaron states. A number of transport, magnetic, and optical properties of these materials are explained by these models [3], in spite of the solid state physics point of view that the macromolecular compounds are one of the most disordered systems. The polymers give unique opportunities for finding mechanisms of charges generation processes between localized states and for the determination of the role of chemical structure and geometry of molecules in these processes [4–6].

Conductive polymers have made a significant impact upon a number of different technologies and their applications range from optical and electrical devices (photovoltaics, transistors, batteries, etc.) to antistatic packaging and various coating applications (membranes, shielding, etc.). A variety of conductive polymers have been evaluated using microelectronic devices, such as chemiresistors, Quartz Crystal Microbalances (QCMs), and field-effect transistors (FETs). Examples of these studies include that of Kunugi et al., who utilized a specially modified QCM for making electrical and microgravimetric measurements of the uptake of alcohols onto PPy thin films [7], and Josowicz & Janata, who investigated the work function changes of the PPy-coated FET for the detection of lower aliphatic alcohols [8]. Several companies, including Neotronics and AromaScan, manufacture ‘electronic noses’ consisting of arrays of chemiresistor-based conductive polymer sensors.

Conductive polymers are an effective medium for chemical sensing, based upon electronic changes arising in the polymeric films with the gas-phase adsorption of electronically active vapours. The conductivity changes observed in these polymers are commonly attributed to the interaction of electronically active analytes with either the polymer backbone itself or the dopant molecules incorporated within the film, thereby modulating the mobility and/or the number of free charge carriers available [9].

A prototype portable gas monitor that relies on conductive polymers was built by J. J. Miasik, A. Hooper, and B. C. Tofield. The device, which uses doped PPy, is very sensitive to ammonia and appears to be useful for sensing hydrogen sulphide and nitrogen dioxide; moreover, it operates at room temperature. The sensor structure consists of the doped PPy, electrochemically synthesized on interdigitated gold electrodes screen printed on the alumina substrate. The prototype was designed for use in coal mines but it can be used in almost any chemical process industry [10].

The objects of our work – PPy and PAn (Fig. 1) – are unique among conductive polymers in that their electrical properties can be reversibly controlled both by charge-transfer doping and by protonation (PAn could be easily doped with mineral acids HCl, H₂SO₄, and HClO₄; and PPy with

$C_{12}H_{25}NaSO_3$). Moreover, they are rather easy to synthesize and their electrical conductivity is one of the most stable of the known conducting polymers [2, 11, 12]. PAN is the only conducting polymer known with nitrogen atoms occupying the bridging position in its backbone structure. Furthermore, because the nitrogen atoms are at the same time the protonation sites, there is the possibility of protonation induced modification of the electronic properties of PAN [13]. In addition, the wide range of associated electrical, electrochemical, and optical properties makes PAN and PPy potentially attractive for an application as active materials of sensors and other devices. The recent investigations of PAN conductivity at different relative humidity (RH) values showed the possibility of using this polymer for RH determination [14, 15]. Furthermore, doped PAN can be used for RH detection as films and tablets. The possibility of RH determination by means of measuring the resistivity of doped HCl PAN tablets in a variety of RH environments was shown by Taka [14]. It should be noted that when the RH of air changes from 0 to 100%, the electrical conductivity of PAN and PPy increases about 2 orders of magnitude [15]. Therefore, the dependence of the electrical conductivity of PAN and PPy on moisture content could be used in the preparation of humidity sensors on the basis of doped PAN and PPy.

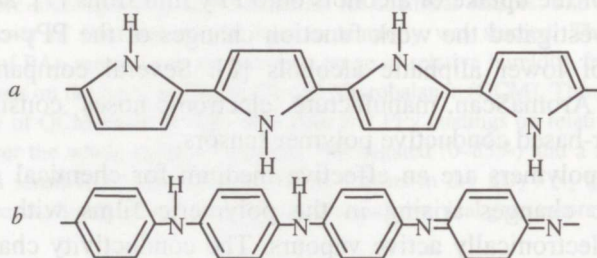


Fig. 1. Structures of neutral PPy (a) and PAN (b).

Since most chemical processes in industry are RH dependent, its accurate measurement is an essential and crucial task. Despite the importance of accurate monitoring of RH in laboratories, clinics, and industry, not many online techniques are available for controlling the humidity of the operational environments.

We investigated also the possibility of the preparation of sensors on the basis of QCM coated PAN and PPy films. The QCM is a piezoelectric device capable of extremely sensitive mass measurements. It oscillates in a mechanically resonant shear mode by application of an alternating, high frequency electric field using electrodes, which are usually deposited on both sides of the disk [16].

The mass sensitivity arises from a dependence of the oscillation frequency on the total mass of the crystal, its electrodes, and any materials present at the

electrode surface. The dependence of the oscillation frequency, f , on the mass change per unit area at the QCM electrode surface is described by the Sauerbrey equation [16, 17]:

$$\Delta f = - \left(\frac{f_0^2}{N \cdot \rho_q} \right) \Delta m = -C_f \Delta m,$$

where Δf the observed frequency change, Hz;

f_0 the resonant frequency of the fundamental mode of the crystal;

Δm the change in mass per unit area, g cm^{-2} ;

ρ_q the density of quartz, 2.648 g cm^{-3} ;

N the frequency constant for quartz, 1670 kHz mm ;

C_f the sensitivity factor for the crystal employed for the measurement, which depends on the thickness and, therefore, the fundamental frequency.

Electrochemical deposition of the conductive polymers (PAN or PPy) as active materials onto the QCM electrodes makes it possible to find the dependence of the oscillation frequency on the humidity of air, as PAN and PPy are hydrophilic and their weight change depends on the air humidity. In addition, possibilities of practical application of conducting polymers as active materials for gas sensors are being zealously investigated. Special attention is paid to the determination of the concentration of pollutants, caustic and combustible gases (SO_x , CO_x , NO_x , H_2S , NH_3 , H_2 , CH_4). That is this research is connected with problems of environmental protection (ozone layer depletion prevention) and also prevention of fires and failures in industry [10, 18, 19].

In the present work, the possibility of RH determination by means of PAN resistive sensors and QCM sensors based on PAN and PPy was investigated. Also, possibilities of practical application of PAN and PPy films, electrochemically deposited on QCM electrodes, as an active material for SO_2 detectors were investigated.

EXPERIMENTAL

For experimental determination of the humidity we used two types of sensors: resistive and QCM, i.e. based on conductive polymers (PAN, PPy), electrochemically deposited onto two types of substrates – glass substrates coated with an Au layer and piezoelectric quartz crystals. As wafers for PAN resistive sensors Au layers on various configuration glass substrates were chosen. The Au layers were made by the Physical Vapour Deposition method. An insulating slot was made into the deposited Au layers so that the electrodes were separated from one another by an approximately 0.1 mm line (Fig. 2).

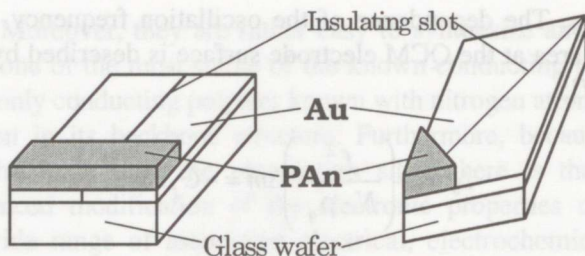


Fig. 2. Resistive sensors made on the basis of PAn film.

Thin PAn film was deposited by anodic oxidation on an Au electrode in 0.2 M aniline solution in 1 M H_2SO_4 . Before polymerization aniline was distilled in vacuum. The synthesis was potentiostatically controlled at 1.1 V versus saturated silver chloride reference electrode for obtaining the intermediately oxidized forms of PAn [13].

The deposition of PAn films was performed until both Au electrodes were short-circuited by a PAn film. For the resistivity measurements, a digital ohmmeter with high input impedance was used.

The PAn and PPy sensors based on the QCM coated with Au electrodes were prepared also by electrochemical oxidative polymerization of aniline and pyrrole (Fig. 3). PAn was synthesized by the method described above. PPy was deposited potentiostatically at 1.3 V versus saturated calomel electrode directly onto QCM Au electrode from phosphate buffer solution (pH 4) containing 0.1 M pyrrole and 0.2 M $\text{C}_{12}\text{H}_{25}\text{NaSO}_3$. The synthesis was performed at room temperature, in the atmosphere of N_2 . Under such synthesis conditions, a black PPy film with a smooth surface has been produced [20].

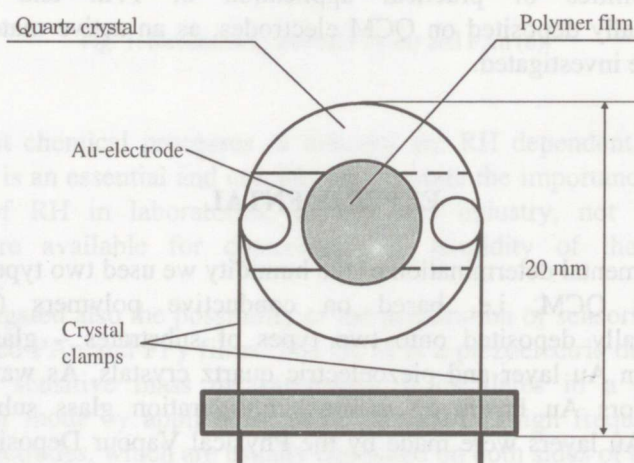


Fig. 3. A QCM sensor.

To investigate the dependence of the resistivity of resistive sensors and that of the resonant frequency of QCM sensors on RH, a series of saturated solutions of salts with known water vapour pressure over the given solutions were prepared (Table 1) and the sensors were put into environments over these solutions.

Table 1

The controlled humidity environments

Environment		Relative humidity, %
CaCl ₂	water free	0
LiCl	saturated solution	15
CaCl ₂	saturated solution	32.3
NaHSO ₄	saturated solution	52
KBr	saturated solution	84

Also, we explored the behaviour of the QCM sensors in SO₂ atmosphere, i.e. we investigated the frequency dependence of the QCM sensors on the SO₂ concentration at atmospheric pressure. To get different SO₂ concentrations, we used different SO₂ + N₂ mixtures in the SO₂ concentration range from 0 to 100% with 20% step. N₂ was chosen as an additional inert gas component to dilute SO₂ concentration. First we investigated the sensitivity of the QCM sensors to pure SO₂. The QCM sensors were cycled to improve the recurrence rate of the resonant frequency indications. They were inserted into a flask containing 100% of SO₂ and then quickly transferred into a flask containing room air. The total number of cycles for one sensor was five. After that the sensors were exposed to different SO₂ + N₂ mixtures (Fig. 4). All measurements were performed at room temperature.

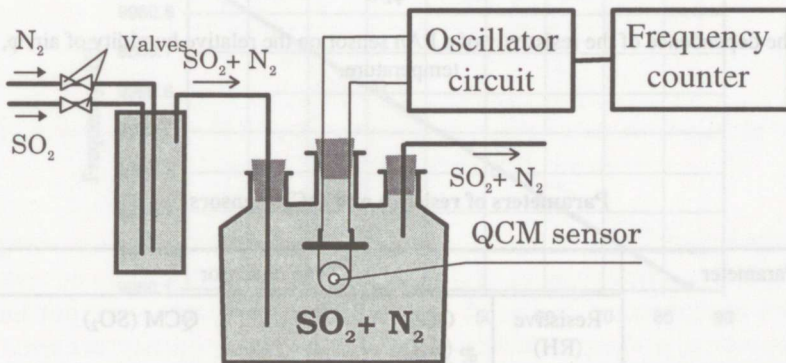


Fig. 4. SO₂ and SO₂ + N₂ QCM sensor monitoring system.

RESULTS AND DISCUSSION

The typical dependence of the resistivity change of the resistive sensors based on PAN doped with H_2SO_4 at room temperature on RH is presented in Fig. 5. The resistivity shows a drastic change in the RH range from 0 up to 20%, after which a saturated area follows, possibly due to the completion of the nitrogen hydration process in the polymer chain. The significant change in the resistivity (about 2 orders of magnitude) in practically dry atmosphere means that the possible working region of these resistive sensors corresponds to the conditions of a number of industrial organic synthesis processes. The short response time (the time necessary for reaching 90% of the final resistivity change at the given RH change) of the resistivity of the sensors in this region, caused above all by the fast change in the humidity, enables the use of these sensors as elements of alarm systems (Table 2). Also, the remarkable change in the measured resistivity makes it possible to execute simple electronic and automatic control.

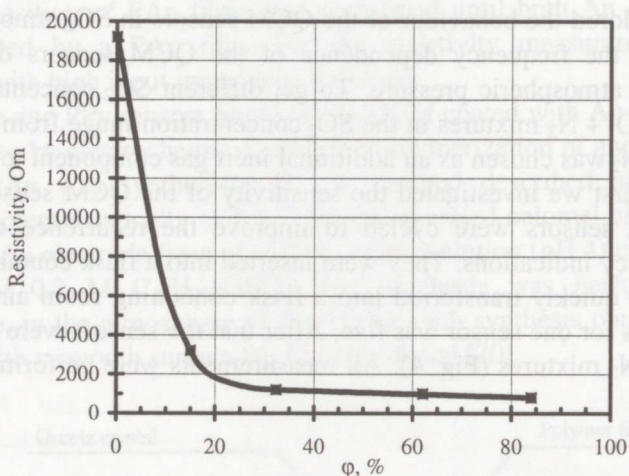


Fig. 5. The dependence of the resistivity of a PAN sensor on the relative humidity of air, ϕ , at room temperature.

Table 2

Parameters of resistive and QCM sensors

Parameter	Type of sensor		
	Resistive (RH)	QCM (RH)	QCM (SO_2) ⁻
Working range	0–20%	0–84%	0–100 vol. %
Response time, 90%	10–20 s	≤ 5 s	≤ 30 s ($N_2 \rightarrow SO_2$) ≤ 5 s ($SO_2 \rightarrow N_2$)
Stabilization time, 95%	30 min	2 min	2 min ≤ 20 s

However, the devices made have some disadvantages: a narrow working range (from 0 to 20% RH), and a long stabilization time (about 30 min is necessary for reaching 95% of the final resistivity change at the given RH change) of sensor indication when RH decreases. In spite of these disadvantages, this technology for the preparation of thin film PAn sensors is more efficiently controllable for making humidity sensors for relatively dry air conditions than the tablet form PAn sensors investigated by Taka [14].

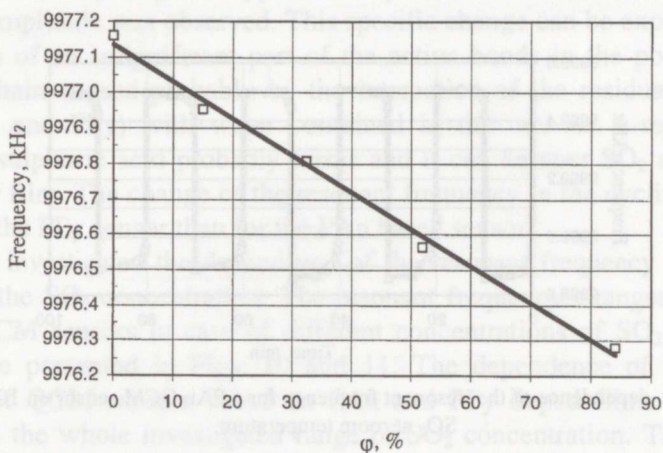


Fig. 6. The dependence of the resonant frequency for a PAn QCM sensor on the relative humidity of air, ϕ , at room temperature.

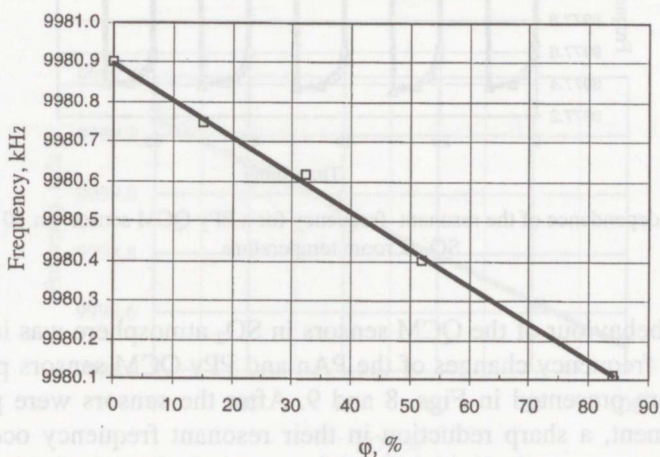


Fig. 7. The dependence of the resonant frequency for a PPy QCM sensor on the relative humidity of air, ϕ , at room temperature.

The dependence of the resonant frequency of the QCM sensors coated with PAn and PPy films on RH of air is presented in Figs. 6 and 7. These dependences are linear in the whole investigated RH range (0–84%) in contrast to the dependence of the resistivity versus RH. Also, the stabilization time of the resonant frequency against the resistivity stabilization time is much less and the response time of the QCM sensors is also very short (≤ 5 s) in the whole investigated RH range (Table 2). However, the QCM sensors require more complex measuring apparatus and have less mechanical durability than the resistive sensors.

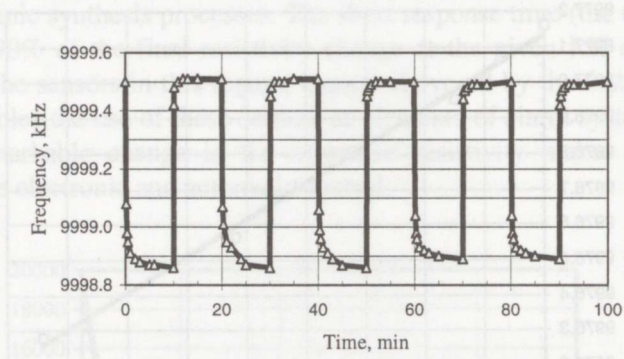


Fig. 8. Cycling dependence of the resonant frequency for a PAn QCM sensor on 10 min pulses of SO_2 at room temperature.

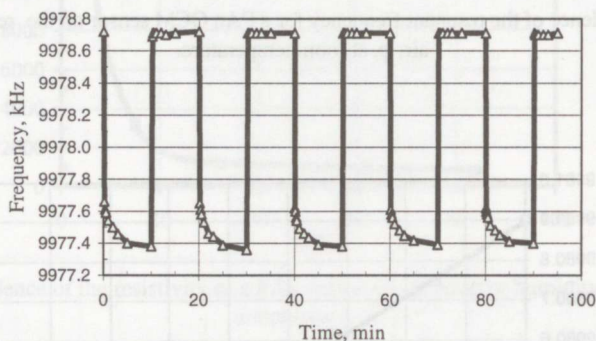


Fig. 9. Cycling dependence of the resonant frequency for a PPy QCM sensor on 10 min pulses of SO_2 at room temperature.

Also, the behaviour of the QCM sensors in SO_2 atmosphere was investigated. The resonant frequency changes of the PAn and PPy QCM sensors put into SO_2 atmosphere are presented in Figs. 8 and 9. After the sensors were put into the SO_2 environment, a sharp reduction in their resonant frequency occurred. The resonant frequency practically stabilized for a period of nearly 2 min. In the SO_2 environment a $\leq 1\%$ deviation from the average resonant frequency cycling amplitude (the difference between the initial and final resonant frequency values

of the cycle) occurred. When the sensors were moved from the SO_2 environment into the air, the resonant frequency rose rapidly close to its initial value and a similar small deviation occurred though it was less than 0.5%. The resonant frequency stabilized for a period of less than 20 s. Therefore, we had different stabilization times for the processes of adsorption and desorption of SO_2 , that is the SO_2 desorption from the polymer films proceeded faster than the SO_2 adsorption.

The “ageing” of the sensors was also investigated. For this purpose cycling was used. After cycling an approximately 2–6% decrease in the resonant frequency amplitude was observed. This specific change can be explained by the deactivation of an insignificant part of the active bonds in the polymers (PAN and PPy) chain caused probably by the interaction of the residual SO_2 in the films (PAN and PPy) with water contained in the air. As a result of such interaction sulphuric acid probably forms and it can hamper SO_2 adsorption to the polymer film. The change of the resonant frequency in the cycling process is smaller for the PPy sensor than for the PAN based sensor.

We also investigated the dependence of the resonant frequency of the QCM sensors on the SO_2 concentration. The resonant frequency changes of the PAN and PPy QCM sensors in case of different concentrations of SO_2 in $\text{SO}_2 + \text{N}_2$ mixtures are presented in Figs. 10 and 11. The dependence of the resonant frequency of QCM sensors based on PAN and PPy doped films has a linear character in the whole investigated range of SO_2 concentration. Therefore, the obtained result gives us a possibility to apply the QCM sensors also for industrial and environmental monitoring of SO_2 . The short response time and the remarkable change in the resonant frequency values compared with air makes it possible to use this sensor device for simple electronic control and also as an element of alarm systems.

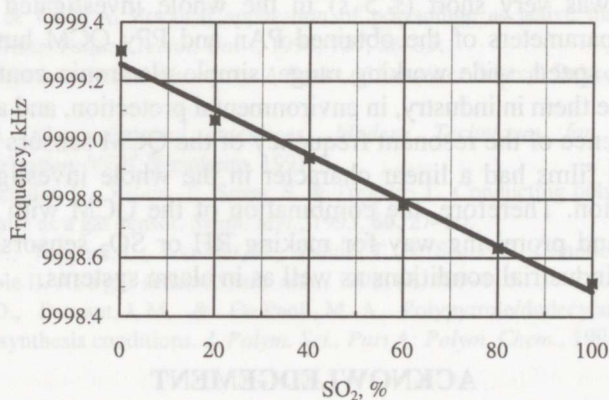


Fig. 10. The dependence of the resonant frequency for a PAN QCM sensor on the concentration of SO_2 .

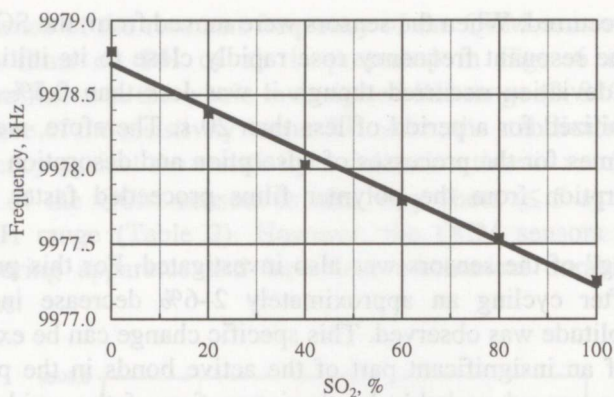


Fig. 11. The dependence of the resonant frequency for a PPy QCM sensor on the concentration of SO₂.

CONCLUSIONS

The maximum resistivity change (about 2 orders of magnitude) for resistive PAn sensors occurred in the range of RH from 0 up to 20%. Therefore, the possible working region of these resistive sensors corresponds, for example, to the conditions of a number of industrial organic synthesis processes. The short resistivity response time of the sensors in this region caused by the fast change in the humidity enables to use these sensors as elements of alarm systems. The change in the resistivity by 2 orders of magnitude makes it possible to use these sensors in simple electronic and automatic control devices.

The dependence of the PAn and PPy QCM sensors on the RH of air had a linear character in the whole investigated range of RH in contrast to the dependence of the resistivity versus RH. Also, the stabilization time of the resonant frequency against the resistivity stabilization time was much less and the response time of the QCM sensors was very short (≤ 5 s) in the whole investigated range of RH (0–84%). The parameters of the obtained PAn and PPy QCM humidity sensors (relatively high speed, wide working range, simple electronic control) give us a possibility to use them in industry, in environmental protection, and at home.

The dependence of the resonant frequency of the QCM sensors based on PAn and PPy doped films had a linear character in the whole investigated range of SO₂ concentration. Therefore, the combination of the QCM with PAn and PPy opens a new, and promising way for making RH or SO₂ sensors applicable in laboratory and industrial conditions as well as in alarm systems.

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Key words: electrodynamic theory, homopolypyrrole derivative, photoconductor, polymer, silicon cells.

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JUHTIVATE POLÜMEERIDE KASUTAMINE KESKKONNATUNDLIKE SENSORITENA

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On uuritud võimalusi kasutada elektrokeemiliselt sünteesitud polüaniliini ja polüpürrooli keemiliste keskkonnatundlike sensorite materjalina. Ühtlasi on selgitatud juhtivate polümeeride toimet koos piesoelektriliste kvartskristallidega. Polüaniliini baasil valmistatud niiskustundlike sensorite elektrijuhtivuse märgatav muutus ilmnes keskkonna suhtelise niiskuse vahemikus 0–20%. Polüaniliini ja polüpürrooliga kaetud piesoelektriliste kvartskristallide resonantssageduse muutus keskkonna suhtelise niiskuse vahemikus 0–85% oli lineaarne. Piesoelektriliste kvartskristallide baasil valmistatud sensorid olid tundlikud ka SO₂ kontsentratsiooni suhtes. Juhtivate polümeeride kasutamine koos piesoelektriliste kvartskristallidega laiendab oluliselt nende rakendusala.

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