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Research Paper

Analysis of the Saw System with the PANI + Nafion Sensing Structure for Detection of Low Concentration Carbon Monoxide

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The paper presents a measuring system based on two resonators with a SAW acoustic surface wave. One of the resonators contains a sensor structure consisting of a Nafion layer with a PANI polyaniline nanolayer deposited on it. The sensor structure was tested for carbon monoxide, with a very low concentration (5, 10, 15, 20 ppm) in the atmosphere of synthetic air. The structure sensitivity was tested for two different PANI thicknesses: (100 and 180 nm). The tests were carried out for two different temperatures: 308 K and 315 K. The investigations shows that the measuring system used with the acoustic surface wave together with the proposed sensing layers is sensitive to the presence of low concentration carbon monoxide molecules in the atmosphere of synthetic air.

Keywords: Surface Acoustic Wave sensors; carbon monoxide detection; poisonous CO.

1. Introduction

Carbon monoxide (CO) poisoning is the most common human accidental gas poisoning. It is caused by inhalation of atmospheric air containing carbon monoxide. It is the most common cause of fatal gas poisoning in many countries. In Poland, according to the State Fire Service statistics, in the period from September 2012 to March 2013, 91 people died as a result of carbon monoxide poisoning, and more than two thousand people were injured (KGPSP, 2014; CDC&P, 2019). Every year in Poland several dozen people die of carbon monoxide poisoning (in the United States, over 400 people die each year for this reason). Carbon monoxide is formed when the combustion of coal or other fuel occurs in insufficient oxygen in the atmosphere. This can happen during a fire, as a result of using malfunctioning heating devices, when reducing coal at a temperature of several hundred degrees with steam. In industrial conditions, it may occur when coke burns in the deficiency of air. Natural sources of carbon monoxide are volcanic eruptions and natural vegetation fires, primarily forest fires (in small amounts CO is also produced in living organisms, where it has anti-inflammatory effects).

The toxic effect of carbon monoxide results from its high affinity for hemoglobin contained in blood erythrocytes which is approximately up to 300-times higher than the affinity of oxygen to hemoglobin at normal atmospheric pressure (Omaye, 2002; Schreter, 2007). In the human body it forms a connection called carboxyhemoglobin (CO + Hb → COHb), which is more durable than oxyhemoglobin (the combination of oxygen with hemoglobin), which is used to transport oxygen from the lungs to tissues. In the human body CO causes tissue hypoxia, which in many cases leads to death. Inhaling air with 1500 ppm CO (0.15% CO in air) causes death after just two hours. At higher concentrations, on the order of 3000ppm (approx. 0.30%), death can occur after 20–30 minutes of being in such an atmosphere. While lower concentrations of CO, with a relatively short inhalation of 20–30 minutes, cause headaches and falling into a coma. These concentrations also lead to death after prolonged (several hours) human contact with such an atmosphere. Higher concentrations, above 1500 ppm (over

0.15%), whose first symptoms of intoxication are severe headache and vomiting, almost always lead to death. Carbon monoxide CO, even at low concentrations of about 10–20 ppm, has the ability to accumulate in the body and can often be dangerous to human health and life. High concentration detection methods (above 1000 ppm) are known and are in frequent practical use (Buckley *et al.*, 2005; Senczuk, 2002). The problem is the detection of low concentrations of CO in the air atmosphere. In this work, an experimental attempt was made to determine whether low CO concentrations in the air atmosphere of the order of 10–20 ppm can be detected by SAW acoustic surfacewave methods. SAW-based detectors have already been developed earlier for several other gases, and are described in the literature on the problem (Jakubik *et al.*, 2005; 2008; Kawalec *et al.*, 2008; Matsunaga *et al.*, 2001; 2003; Jasek *et al.*, 2011; Bielecki *et al.*, 2012).

2. Research stand

In the research, a measuring stand with resonators on acoustic surface waves SAW with a positive feedback loop was used. The system consists of two identical resonators. One of the resonators is isolated from the influence of the external atmosphere. The second resonator is exposed to an external gas environment. Changes in the chemical composition of the atmosphere change the resonance frequency of this resonator. At the output of the resonators, their high frequency signals are electronically mixed. The frequency difference from both acoustical tracks is the measure of changes in the test atmosphere. The measuring system was described in detail in earlier publications (Urbanczyk, 2011; Urbanczyk, Pustelny, 2013). The resonators were made on a substrate with LiNbO3 crystals by the photolithography method. Both resonators had different frequencies in the same atmosphere (in synthetic air or in the atmosphere of nitrogen). The frequency of the resonator without the sensor structure was 43.60 MHz, while that of the resonator with the sensing structure was lower from several dozen to even one hundred kHz (as a result of its mass loading by the sensing structure). The schematic diagram of the system is shown in Fig. 1 (Urbanczyk, 2011).

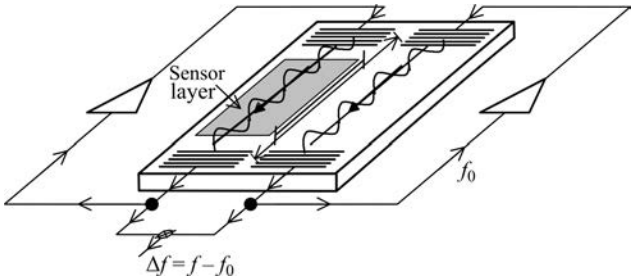

Fig. 1. The idea of the measuring system.

3. Preparation of the sensing layers

According to the analysis of the literature on application of polyaniline and own research, PANI nanolayers have many valuable physical properties useful in various fields of science. These materials are used in medical and biological applications, e.g. for the detection of chemical substances such as selected metal cations and lactic acid as well as biological samples including cancer cells. Polyaniline nanolayers can be used to develop a sensor that detects lactic acid in a range of physiological concentrations reporting different types of diseases (Hejczyk *et al.*, 2016).

In the investigations as mentioned above, the bilayer sensing structures of Nafion+Polyaniline were examined by means of the acoustoelectric method. The frequency mixing process was carried out using a Keithley electrometer due to the high resistances of the resonators in the reference and measuring paths. The main purpose of the Nafion application was the possibilities of controlled protonation of the second layer based on polyaniline to increase its electrical conductivity (Hejczyk, 2013). Nafion (thickness of approx. 300 nm) and polyaniline (for the layers thickness: 100, and 180 nm) were used as sensing structures. A thin layer of nafion was deposited on the surface of $LiNbO_3$ waveguide by the whirling method at speed of 7500 rpm. Thin layers of nafion were annealed at 40°C for 2 hours and then for 15 minutes at 120°C to harden. Polyaniline layers of the thicknesses of 100 nm and 180 nm were made in a vacuum evaporation process. The whole process was carried out in the residual atmosphere of argon (Ar), in connection with the oxidation of the polymer during the time of its application, which affected the sensing properties of the layers.

To achieve the desired quality of atmosphere in the vacuum chamber, the chamber was rinsed three times with argon. Then, in order to evaporate the water vapour trapped in the PANI, the structure was annealed at 200°C for 10 minutes. The polyaniline application process was made at a temperature of 350–400°C. To obtain the desired thickness, the sublimation process lasted 45 minutes.

4. Experiment with the use of Nafion-Polyaniline in the SAW system

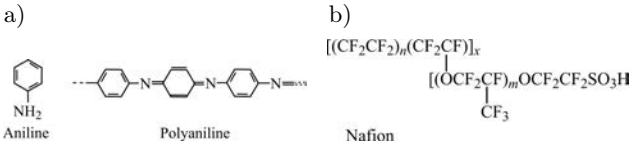

Fig. 2. The chemical structure: a) Polyaniline (PANI), b) Nafion (Huang *et al.*, 2005).

Figure 3 shows a polyaniline (PANI) layer applied by vacuum vapour deposition. The image was ob-

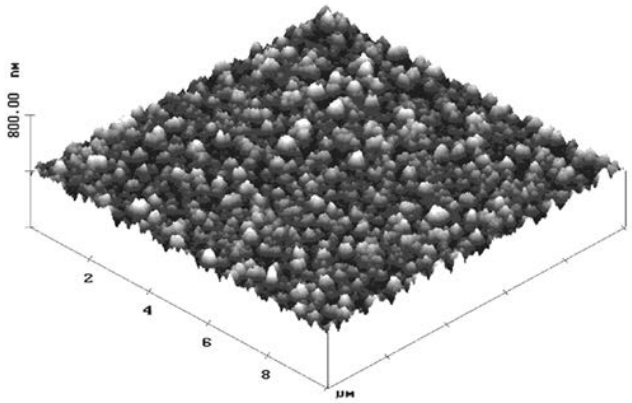

Fig. 3. Image of the surface topography of the thin PANI layer obtained by the AFM NTEGRA-SPECTRA Scanning Electron Microscope FEI 550.

tained with the use of atomic force microscope AFM NTEGRA-SPECTRA type NT-MDT Europa BV Eidhoven (the Netherland).

Figures 4 and 5 show the experimental results for the PANI layers (with thicknesses: 10 nm and 180 nm) for low concentrations of carbon monoxide: 5–20 ppm in the synthetic air at the temperature approx. 34–35°C.

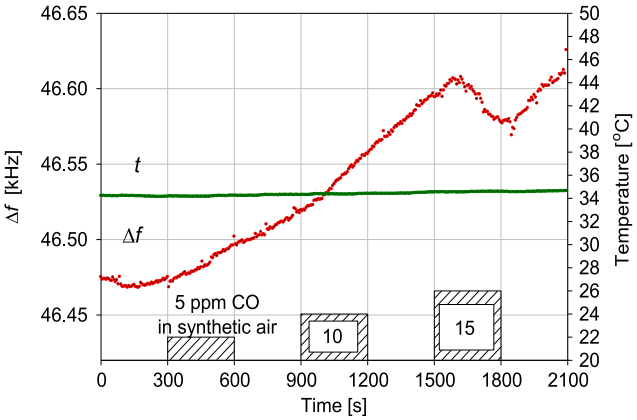

Fig. 4. Response (Δf) of the sensor layer PANI (100 nm) and Nafion to CO gas (5, 10, 15 ppm), T = 34° C.

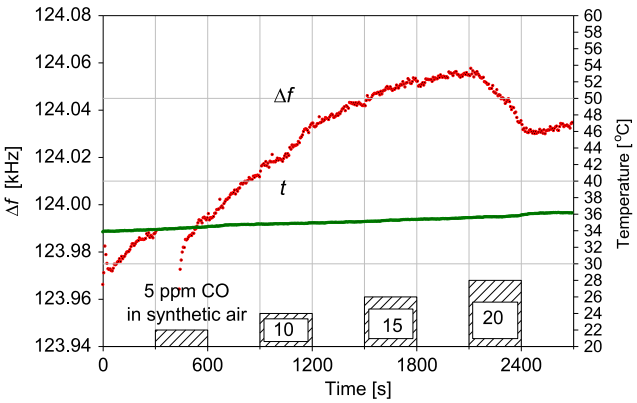

Fig. 5. Response (Δf) of the sensor layer PANI (180 nm) and Nafion to CO gas (5, 10, 15, 20 ppm), T = 35° C.

Figure 4 shows the response of the sensing structure consisting of Polyaniline (100 nm) and Nafion to the CO gas (concentration 5, 10, 15 ppm) in the synthetic air at the temperature 34°C. Figure 5 presents the response of the sensing structure consisting of Polyaniline (180 nm) and Nafion to the CO gas (5, 10, 15, 20 ppm) in the synthetic air at the temperature 35°C. On this basis we could determine a lot of structural dependencies which, in the future, can help to construct a prototype sensor system for applications in detection of a very low concentration of carbon monoxide.

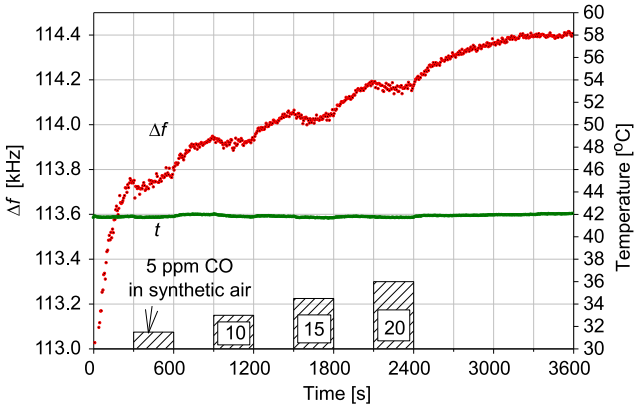

Fig. 6. Response (Δf) of the sensor layer PANI (180 nm) and Nafion to CO gas (5, 10, 15, 20 ppm), T = 42° C.

It should be emphasized that the frequency changes, caused by the interaction of the sensing structure with an atmosphere containing CO, were at the level of tens and hundreds of Hz different (smaller) from the frequency when there was no carbon monoxide in the atmosphere. For modern metrology, measurement of frequency of one hundred kHz with the accuracy of ±1 Hz is not a problem. Based on the previously developed theoretical model of the acoustoelectric phenomenon in the layered structure (Hejczyk, 2013), a numerical analysis of the impact of polyaniline layer thickness on the magnitude of the effect of resonant frequency changes in the structure was carried out. The changes Δf were related to the maximum change $\Delta f_{\max}$. The analysis also took into account the impact of changes in the CO concentration in the synthetic air on changes in the resonance frequency. The influence of the CO concentration on the magnitude of the frequency changes was also analyzed.

The results obtained are presented in a quasi three-dimensional graph in Fig. 7.

Figure 8 shows the relative changes in the frequency difference Δf for the three different concentrations (5, 10, 15 ppm) of carbon monoxide in the air. The numerical analysis clearly suggests that the best sensitivity to CO in the synthetic air has the sensing structure with the polyaniline thickness of about 100 nm.

The sensitivity of sensing structures to external gas atmospheres depends on the temperature of the struc-

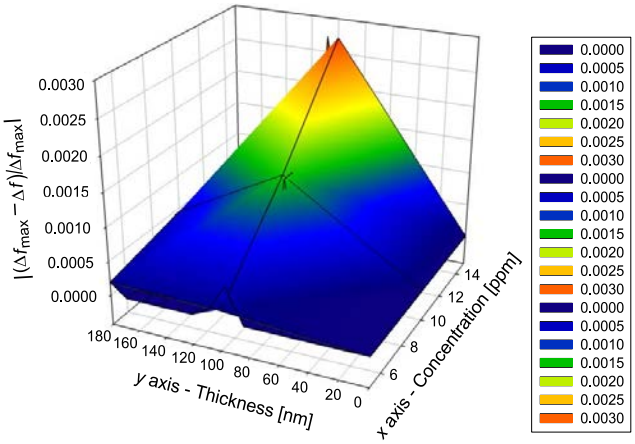

Fig. 7. Holistic three-dimensional representation of the results $(|\Delta f_{\max} - \Delta f)/\Delta f_{\max}|$ showing the presence of the layer of optimum thickness for temperature of approx. 35°C.

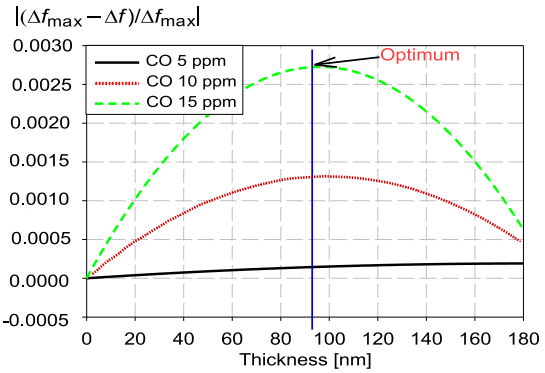

Fig. 8. Collective representation of the results $(\Delta f_{\max} - \Delta f)/\Delta f_{\max}$.

ture. The problem of the structure temperature is also important in the aspect of "detoxifying" its electrical properties after measurements.

Our previous research (Urbanczyk, 2011; Hejczyk, 2013; Hejczyk *et al.*, 2016) shows that the detoxification is much more effective at elevated temperatures. On the other hand, however, the elevated temperature affects the mechanical degradation of the structure and causes irreversible changes in its physicochemical properties. This problem is particularly important when the sensing layers are made of organic semiconductors. Polyaniline and Nafion are organic semiconductors. In order not to destroy the examined structures, the measurements were made at relatively low temperatures: 35°C (308 K) and 42°C (315 K).

The frequency changes of the SAW system under the influence of the atmosphere containing CO are presented in Table 1.

The ΔF values given in Table 1 should be understood as the difference in frequency between the measured differential frequency Δf_s at the beginning of the measurement cycle in the atmosphere containing CO

Table 1. Frequency changes of the SAW system under the influence of the atmosphere containing CO.

Thickness PANI [nm]/ temp. [°C]	ΔF [Hz]				
	0 ppm	5 ppm	10 ppm	15 ppm	20 ppm
100/35	–	–	10	20	35
100/42	–	10	20	35	50
180/35	–	–	–	5	10
180/42	–	5	7	10	15

and the frequency Δf_e after the end of the cycle, i.e. after starting the flow of synthetic air without carbon monoxide CO.

5. Conclusions

The sensing structures, consisting of Polyaniline (PANI) of different thickness, approx. 100 nm or 180 nm, and Nafion of approx. 300 nm thickness, were prepared for investigations. The main purpose of the research was to explain the interaction of carbon monoxide with the sensing structures in the atmosphere of dry synthetic air for a period of 0–2500 s. The frequency differences between the measuring and reference paths in the SAW system were measured. The influence of the temperature on the structure of Nafion and Polyaniline at T = 35°C and T = 42°C was investigated. The measurable effects (changes of Δf) were already observed at low CO concentrations, above 10 ppm in synthetic air (see Table 1).

It can be seen in Figs. 4, 5, and 6 that during the measurements the differential frequency Δf increased. As mentioned earlier, there was no additional layer in the reference track. On this track, the gas acted directly on the surface of the $LiNbO_3$ crystal. As our current and previous studies show, $LiNbO_3$ is insensitive to the effects of the gas environment (Pustelny, Pustelny, 2009; Jasek *et al.*, 2012; Hejczyk *et al.*, 2015). During the measurements, the frequency of the reference resonator was constant with the accuracy of approx. 2 Hz. The reference resonator frequency slightly changed when the temperature of the $LiNbO_3$ waveguides changed. The frequency Δf (being the difference between the frequencies of the reference and measuring resonators) changed during the whole measuring cycle due to the changes in the resonance frequency in the measuring resonator. The frequency Δf, as shown by the characteristics (Figs 4, 5, 6), also increased without the presence of carbon monoxide in the atmosphere. During the flow, the synthetic air molecules (20% O_2 and 80% N_2) settled on the rough sensor surface (Fig. 3). This caused a mass load of this surface and, as a result, changes in the resonance frequency of the measuring resonator (Δf increased). The longer the measurement lasted, the more observ-

able the process was. This physical (in some sense also physicochemical) loading of the surface of the measuring structure blocked the access of CO molecules to the surface when this gas was already in the synthetic air. Even slight heating of the sensing structure from 35°C (308 K) to 42°C (315 K) already caused the visible effect of the presence of CO on the value of Δf. The interaction of CO molecules with PANI is primarily of electrical nature. CO is an oxidizing gas – CO molecules attach electrons from the PANI structure. Polyaniline is a p-type semiconductor. The binding of PANI electrons to CO molecules results in an increase in the electrical resistance of the structure (the difference between the concentration of holes and electrons increases). This is manifested by a decrease in the frequency of the measuring resonator and, as a result, a decrease in Δf relative to the situation without CO particles in the atmosphere. In the measurements, the sensing structure was tested for the presence of very low concentrations of CO (5, 10, 15, 20 ppm) in the synthetic air. These concentrations are so low that for 5 and 10 ppm CO in the synthetic air, the presence of CO in the Δf signal was often not observed. It can be said that in these cases the interaction of CO with the structure was "obscured" by mass actions of molecules of the synthetic air (the molecular masses of O_2, N_2, and CO are similar). The presence of water vapour particles in the gas also influences the mass load of the sensing surface. In the presented experiments, the synthetic air was passed through a moisture absorber, which limited the influence of moisture on the measurement results. An increase in the temperature of the sensor structure to a level of approx. 60°C (over 330 K) should significantly improve the sensitivity of the structure to the presence of CO. However, it should be taken into account that the mechanical properties (and in result also the electrical properties) of the structure at higher temperatures may be significantly impaired. As described in Sec. 1, the problem of detecting such low concentrations of CO is very important in the aspect of human health and should be solved. The authors hope that the above research will set the direction for future works.

Acknowledgements

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