Investigation of electrochemical sensors with thin film nanocomposite Pt/C electrodes obtained by magnetron sputtering

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Abstract. The electrochemical gas sensors with the film nanocomposite electrodes are produced and tested in several gas atmospheres. The experimental results demonstrate that a-C/Pt has high sensitivity and stability for continuous monitoring of carbon monoxide (CO) and hydrogen sulfide (H₂S) gases compared to main counterparts are mass-produced.

1. Introduction

In connection with environmental pollution, the need for real-time air monitoring is constantly growing. For these purposes, the different monitoring systems are used which include electrochemical [1], semiconductor [2], catalytic [3] and IR sensors [4].

The world trend aimed at solving problems of air monitoring over large areas associated with leaks of toxic gases has been the development of sensory networks of various sizes that collect, analyze and make decisions on the management of executive devices to prevent emergencies and alert appropriate services when exceeding the maximum permissible concentration (MPC) of toxic gases.

Depending on the way data is transferred from the sensors to the data reception devices, wire and wireless sensor networks are allocated [5]. The drawback of wired systems is their dependence on power supply systems, which limits the use of wire-based monitoring systems for air composition, in particular, in places with no network power supply. Overcoming of existing limitations is possible due to the creation of autonomous wireless systems for continuous monitoring of toxic gases that provide air composition measurements on the territory of industrial enterprises.

To create autonomous wireless monitoring systems, in addition to low-power electronic components and energy efficient algorithms [6], it is required to use gas sensors with minimal power consumption. From the whole variety of gas sensors, minimal energy consumption and, at the same time, sufficient sensitivity and selectivity have only electrochemical sensors. The wide use of electrochemical sensors in gas analyzers is due to their ease of maintenance, price and a wide range of measured components.

In the electrochemical sensor, the detectable component reacts with the sensitive layer directly on the working electrode. Therefore, the working electrode must simultaneously perform several functions that ensure the operation of sensors: to have the ability to pass gas, play the role of a catalyst, have high electrical conductivity, and prevent the liquid electrolyte from flowing out.

The electrochemical sensor electrode in the general case is a gas permeable membrane with a catalytically active layer deposited on it (Fig. 1). The active layer can be applied by using well-known
deposition techniques such as screen printing [7], chemical and electrochemical deposition [8], ultrasonic spraying [9] and laser technics [10].

Recently, the technology of magnetron deposition of thin-film nanocomposite catalysts based on platinum and amorphous carbon (graphite) has been developed to create working electrode of electrochemical sensor, which improves the reproducibility of electrode parameters [11]. Amorphous carbon is a highly inert material with good stability in many acids, solvents and electrolytes and has a high electrical conductivity. The co-sputtering of graphite and platinum provides the increasing platinum surface and its porosity. Note that platinum and graphite do not participate in the oxidation-reduction process, but are only carriers of atomic oxygen.

Figure 1. Scheme of the electrochemical sensor.

2. Experimental

Thin a-C/Pt films of the composite were produced on a "Elato 600-R" (Izovak) unit equipped with a DC magnetron and a rotation system for the substrate holder. The deposition of the films was carried out in an argon atmosphere at a pressure of ~ 10^{-1} Pa. Spray mode: U = 500V, I = 200mA, t = 20 min. Substrates for the application of the catalyst were Teflon FM-400 (PTFE) with a porosity of 50% and a pore diameter of 1 µm without any additional preparation (Fig. 2a). Photos of the working and auxiliary electrodes are shown in Fig. 2b and 2c. The composition of a-C/Pt catalytic layers was investigated by EDX spectra (Fig. 3). The developed thin film electrodes are embedded in the sensor nodes with a liquid electrolyte and tested in the presence of CO and H₂S. We evaluate the sensor performance in terms of sensitivity, selectivity and response.

Figure 2. Teflon surface (a) and magnetron sputtering electrodes: (b) working, (c) reference and auxiliary.
Table 1 demonstrates the sensor sensitivity (response) in the presence of two gases CO and H\textsubscript{2}S in the environment. The sensors improve the results of commercial sensors by Nemoto (NAP-505 for CO and Ne4 for H\textsubscript{2}S) while guaranteeing low background current which is lower than 1%.

The evaluation of the electrochemical sensor cross sensitivity to different acid gases is highly important when considering the long-term operation of the sensor. The results of this evaluation are presented in Table 2. As a matter of fact, H\textsubscript{2}S sensor has no sensitivity to other gases listed in the column ‘Tested Gas’ in Table 2. In contrast, Nemoto’s NE4 sensor for H\textsubscript{2}S has significant response to SO\textsubscript{2} and NO\textsubscript{2}. As for the CO sensor fabricated in this work, it has negligible sensitivity (at the level of an error rate) to H\textsubscript{2}S and NO\textsubscript{2}.

Comparison of the characteristics – sensitivity (K), lower background currents (I\textsubscript{0}), response times (t\textsubscript{09}), temperature dependence of background current (T\textsubscript{w}) and detection limits for gases (C\textsubscript{min}) are presented in Fig.4. It is seen that developed electrochemical sensors have better characteristics.

![Figure 3. EDX spectra and calculated values of Pt and C.](image)

**Table 1. Sensitivity of electrochemical sensors.**

| Gas      | Sensitivity of electrochemical cell | Gas      | Sensitivity of electrochemical cell |
|----------|-------------------------------------|----------|-------------------------------------|
|          | Background current, µA | Sensitivity, µA |          | Background current, µA | Sensitivity, µA |
| CO       | 0.05 | 48.6 (100 ppm) | H\textsubscript{2}S | 0.01 | 30.1 (30 ppm) |
| H\textsubscript{2}S | 0.01 | 30.1 (30 ppm) |

**Table 2. Cross sensitivity of carbon monoxide and hydrogen sulfide sensors**

| Tested Gas         | Concentration (ppm) | Sensors’ readings (ppm) |
|--------------------|----------------------|-------------------------|
|                    | CO       | H\textsubscript{2}S   |
| Chlorine (Cl)      | 100      | 0                       |
| Carbon monoxide (CO) | 100    | 100                     |
| Hydrogen sulfide (H\textsubscript{2}S) | 30     | 0.5                     |
| Nitrogen dioxide (NO\textsubscript{2}) | 30     | 0.3                     |
| Hydrogen chloride (HCl) | 100    | 0                       |
| Sulfur dioxide (SO\textsubscript{2}) | 25     | 0                       |
| Formaldehyde (CH\textsubscript{2}O) | 10     | 0                       |
| Ethylene oxide (C\textsubscript{2}H\textsubscript{4}O) | 100    | 0                       |
| Ammonia (NH\textsubscript{3}) | 200    | 0                       |
3. Conclusions

It was shown that the developed electrochemical sensors with Pt/C electrodes have greater sensitivity, lower background currents, comparable response times and detection limits for gases. To better understand the relationship between the structure of a-C/Pt catalyst layers and their electrochemical properties, it is planned to use the in-situ X-ray monitoring method [12].

![Figure 4. Comparison of the characteristics of the developed sensors (columns on the right) in comparison with the sensors of the main manufacturers: Alphasense (Great Britain), City Technology (Great Britain), Drager (Germany), Nemoto (Japan); MST (Germany).](image)

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